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IGNITION OF WOOD BY FLAME RADIATION

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Ameer Nasser Koohyar

To

My wife Maryam and our children,

Babak, Hooman and Shirin

ABSTRACT

A new experimental method for investigation of ignition phenomena of combustible solids was developed. In this method, the specimens were heated by direct radiation from free burning, buoyant, diffusion flames from liquid pools. Provisions were made so that the surface temperature and weight of the specimens were continuously measured and recorded.

In the experimental phase of present study, slabs of five different species of wood were tested for pilot and spontaneous ignition. The experiments were carried out for various irradiance levels under the conditions of both one-sided and two-sided (symmetrical) heating. Measurements were made for surface temperature, weight loss and ignition time for various levels of irradiance. The thermal properties of the samples were determined experimentally.

The results of experiments showed that: (a) a constant surface temperature criterion for ignition is not correct, and (b) a criterion of the minimum evolution of volatiles from surface is not adequate.

The ignition data are correlated with two sets of dimensionless groups derived from the solutions of mathematical models of inert and opaque solids. One set of

dimensionless groups is derived from consideration of constant irradiance and Newtonian cooling at the surface, the other considers constant irradiance and no heat loss.

It was shown that the assumption of Newtonian cooling is not correct. The data were correlated using the dimensionless irradiance modulus, $HL/\Delta T_s K$, and the dimensionless Fourier modulus, $\alpha t/L^2$. It was further shown that the ignition process of wood by flame radiation can be described by a mathematical model of inert and opaque solid with the surface boundary condition

$$-K \frac{\partial T}{\partial x} = \kappa H$$

where K is thermal conductivity, $\partial T/\partial x$ is the temperature gradient at the surface, κ is a constant and H is the irradiance at the surface.

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IGNITION OF WOOD BY FLAME RADIATION

CHAPTER I

INTRODUCTION

The study of ignition phenomena is a fundamental aspect of fire research. In order to be able to control and alter the fire performance characteristics of a material, it is necessary to have a knowledge of what constitutes ignition, what the mechanisms and the criteria of combustion and ignition are, and what relationship material properties and imposed external conditions have with regard to ignition phenomena. The ignition and combustion of natural and synthetic materials involve complex combinations of physical and chemical processes. The overall process of ignition of solids includes a series of solid-phase decomposition or pyrolysis reactions, a series of gas-phase pyrolysis and oxidation reactions, and some solid-gas phase oxidation reactions. A basic understanding of these ignition and combustion processes and quantitative data for ignition temperature, surface flammability, rate of charring or decomposition, and heat penetration through the solid are needed before a fire spread problem can be solved. For

example, the results of the experiments at the National Bureau of Standards (42)* following a \$2,609,000 loss in an Army Warehouse disclosed a phenomenon of self-ignition that could not be predicted with the results of any fire spread test carried out in the field. Therefore, basic studies of pyrolysis and ignition of organic solids under different conditions, especially the conditions which are most likely to be present prior and during the course of an actual fire, are essential to fire research and the development of the fire retardants.

When wood or cellulosic materials are heated by any means, their temperature rises until a certain point at which the material starts to disintegrate. This process is termed thermal decomposition or pyrolysis. If the rate of heating is slow, material will continue to decompose to some gaseous products and charcoal. In this case the process is referred to as charring. If air contacts the charcoal which is at high enough temperature oxidation or burning of charcoal will occur and surface glows. This condition is known as glowing ignition. At a relatively higher rate of heating the gaseous products of pyrolysis may be ignited by a small flame or spark. The flame of ignited gases then flashes over the hot surface of the material. This form of ignition is known as pilot ignition and it is of great practical importance. Volatiles may be ignited by

*References are given by numbers in parentheses which are listed in Appendix E.

the source of heat itself or by any other source. The spread of fire from one burning building or timber stack to another can be mentioned as an example of this type of ignition. Information concerning critical irradiance (an irradiance below which ignition will not occur) for pilot ignition is very useful for safe separation of distances between buildings. Still at relatively higher rate of heating volatile products of pyrolysis evolve with sufficient rate and concentration that after mixing with air can ignite spontaneously or without any extraneous source. This type of ignition is known as spontaneous ignition. In the literature the pilot and spontaneous ignitions in which flame appears at the surface of the wood have been frequently referred to as kindling, flaming, or flaming ignition. 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 called sustained ignition.

The ignition studies have been carried out by different investigators and under different heating conditions. One of the methods used for heating the sample is by thermal radiation which is a portion of electromagnetic spectrum lying in the range of wave lengths from 0.1 to 100 microns (For further information on thermal radiation the reader is referred to Appendix C). All cellulosic substances including wood transmit significant quantities of radiant energy into the material. Throughout the literature and in the present study the property of transmitting some portion of

the thermal radiation into the material is referred to as "diathermancy." The materials of this type are called diathermanous or semi-transparent materials. If all of the thermal radiation energy is absorbed at the surface, the material is said to be opaque.

Despite the fact that the behavior of combustible solids under different heating conditions has been the subject of many studies over the past two centuries, attempts to express ignition criteria in terms of temperature or some other unique property have failed. The results of different studies usually do not agree with each other. The major reasons for the diversity of the results are the use of different definitions for ignition and the use of different experimental methods and conditions. Since much of the heat transfer from well-developed fires and most of the energy released from atomic detonations is in the form of thermal radiation, the majority of recent experiments has employed thermal radiation sources such as gas-fired panels, tungsten filament lamps, carbon arcs, and solar furnaces. Practically all previous experiments, including those that have employed radiation sources, have been conducted under conditions which are artificial representations of flame-target situations. While organic materials are diathermanous for pulses of short (infrared) wavelengths (about 0.8 - 2.0 microns), the effect of diathermancy, especially for wood, is negligible for the case of irradiation by flames whose spectral distribution extends farther into

the infrared region (20, 24, 68) and for which surface charring usually precedes ignition. Therefore, in designing a new experimental apparatus, a unique feature of this present study was to produce ignition by a radiant source which at least simulated direct flame radiation.

The quantitative analysis of the ignition of combustible solids is not easy, and a completely general mathematical treatment of ignition phenomena is not presently possible. The difficulties mostly arise because:

1. A single mathematical model cannot be chosen for all combustibles such as woods or plastics. While the gaseous products of decomposition of wood are pushed outward through the pores and are mixed with air to form a combustible mixture, the behavior of thermoplastics is characterized by the appearance of bubbles and swelling of the materials until they are ignited with an explosion or burst of flame (50).

2. Although most of the previous studies concentrated on the quantitative analysis of cellulosic materials, a complete and exact solution has not yet been developed because of the complexity of ignition process. The theory of steady-state reactions requires the solution of ordinary differential equations which, except for isothermal reactions, are nonlinear because the reaction rate depends on the Arrhenius factor " $\exp. (-E/RT)$," where E is the activation energy, R is the gas constant and T is the absolute temperature. Ignition, however, is a transient process leading from one state, that of no reaction, to another, that of self-

sustaining combustion. Therefore, exact ignition theory involves the solution of nonlinear partial differential equations. An exact analytical solution is not expected, and approximate analytical treatments are difficult mainly because the physical and chemical properties as well as the nonlinear terms in the mathematical model are functions of both position and time. Consideration of other factors involved, such as the effect of diathermancy, convective energy transfer by means of gaseous products moving through the sample, the phase and dimensional changes due to charring, the migration of moisture within the sample, and the changes in boundary conditions due to the variation in surface properties only add to the complexity of the problem. Therefore the prospect of quantitative treatment becomes even more remote.

Several simplified models, to be discussed in the next chapter, have been treated by some investigators. These treatments have only considered a one-dimensional model in which the convective energy transfer arising from bulk flow of volatiles has been omitted, and in some cases the effects of diathermancy and/or chemical heating have been neglected.

The experimental and theoretical treatment of two- or three-dimensional models, which are very important in predicting the behavior of kindling fuels, have been totally ignored. Although the literature is voluminous, much of the work deals with the ignition of cellulosic materials by high intensity thermal radiation. The concentrated interest in

this particular area has been prompted by concern for civil defense against nuclear weapons.

As it will be noticed in the next chapter, all investigators have attempted to express the ignition criteria in terms of either the rate of weight loss or some characteristic temperature, or both. Most of the recent studies speculate that a constant surface temperature could be used as a criterion of ignition. Neither the rate of weight loss nor the surface temperature criterion has been confirmed by direct experimental measurements.

In this work a new method for the study of ignition processes of solid materials has been devised. The experimental apparatus has different features from those reported in the literature. This method differs from others because heat is supplied by radiation from two parallel sheets of free burning, buoyant, diffusion flames without radiating panels such as those used in gas-fired panels and furnaces. Another aspect of this method is the provision for the continuous measurement of sample weight and surface temperature as functions of time. The rate of weight loss is then found from the slope of the weight loss curve. Experimental apparatus and weighing system are described in Chapter III. The irradiance and surface temperature measurements are explained in Appendices A and C respectively. The equipment can be modified to change the sample from one-dimensional to two-dimensional configuration and to change from wood to other target materials such as cloth, plastics, and rubber.

Nearly 300 ignition tests were made using five types of wood and the resulting data are tabulated in Appendix D and discussed in Chapter IV.

In order to avoid confusion the reader is cautioned that in reviewing the previous work, especially in the early part of the Chapter II, the definitions and terminology used belong to the individual investigator cited. The diversity of terminology and definitions is due both to the investigator's taste in words and to the experimental method. A standardized terminology which is consistent with the discussion of this chapter and later discussion of the present study is given in a separate section titled "Terminology" in Chapter II. The nomenclature used in the discussion of mathematical treatments is consistent throughout this thesis. A comprehensive list of nomenclature is given in Appendix F.

CHAPTER II

REVIEW OF PREVIOUS WORK

Several concepts of ignition and numerous methods of finding the ignition criteria have been presented in the literature. In order to discuss the ignition process it is first necessary to define what chain of events leads to ignition and at what point in that chain ignition occurs. In this chapter the most important topics of the ignition process are reviewed systematically. It should be emphasized that the definitions and terminology used by different investigators to whom references are made depend on the appropriate experimental method. A standardized terminology which is used in this study will be given in a subsequent section titled "Terminology."

Ignition Phenomena

After making a comprehensive literature survey and classifying the definitions and methods used prior to 1934, Brown (9) concluded that if a combustible material is heated gradually from a low temperature in the presence of sufficient air, a very slow reaction between the material and the oxygen occurs. The reaction becomes faster at higher

temperatures. This reaction is termed combustion, and the attending release of heat tends to raise the temperature of the combustible material which further increases the rate of reaction. On the other hand heat is lost to the surroundings by radiation, conduction, and convection. At some temperature the rate of reaction between the combustible and the oxygen is sufficiently rapid so that the resulting rate of heat production exceeds that of heat loss. When the temperature of the material rises faster than the rate due to the external heating alone, the reaction accelerates and rapid self-heating follows. This process continues until visible evidence of ignition such as glow or flame occurs.

Brown makes a point that ignition is a process requiring time rather than being an event in time; in other words ignition does not imply a discontinuity between the rate of the reaction and temperature. He further emphasizes that ignition cannot be considered synonymous with the appearance of glow or flame, as sometimes held, since these phenomena cannot occur unless the ignition process is first carried out.

Based on the above concept, Brown defines the ignition temperature as being the temperature in the center of the combustible material at which the rate of heat developed by the reactions inducing ignition just exceeds the rate at which heat is dissipated by all causes under the given conditions. The ignition point defined by Brown is, therefore, identified as the inflection point on the temperature-time curve.

Mitchell (42) has shown that a stack of wood preheated to a certain temperature will not always cool off because of its low thermal conductivity. Instead, the temperature may rise within the pile due to exothermic decomposition at the center of the stack so that self-ignition results.

Gardon (20) studying the "temperature attained in wood exposed to high intensity thermal radiation," states that at sufficiently high temperature wood is pyrolyzed in two steps; the first being an endothermic decomposition and the second an exothermic decomposition. It is likely that the gaseous products of the reactions, which are generated in a relatively thin zone near the irradiated surface, escape from the wood before the attainment of chemical equilibrium, especially in the case of rapid heatings. Combustion, which is an exothermic process, occurs at the wood-air interface with a resulting uncertainty as to what fraction of the evolved heat is retained in the wood.

The mechanism of ignition of cellulosic materials is best understood from the following discussion which is based on the comprehensive literature surveys of Martin (37), Browne (10), Schaffer (47) and Lipska (31) on the pyrolysis of cellulosic and synthetic materials. They concluded that with the exception of charcoal and some punky materials, solid fuels do not burn directly. The combustion of solids involves two separate and distinct processes; the decomposition of the solid into simpler volatile products, followed

by a gas phase oxidation of these products usually at some distance from the surface of the solid. Unless the sum of the heat contributed to the solid by the gas phase reaction, exothermic pyrolysis of the solid, and outside heating is at least as great as the heat consumed in the endothermic pyrolysis of the solid plus heat loss to surroundings, the solid will not continue to burn.

When an organic solid is heated above a certain temperature, the molecules begin to shed molecular fragments, and the solid rearranges and condenses into a form which is more stable at that temperature. These molecular fragments escape the solid in their original form, or in combination with one another, and mix with the surrounding air where they may or may not react with the oxygen of the air. If this process continues at a high enough rate, flaming ignition results.

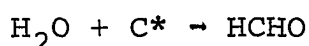
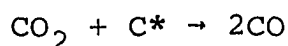
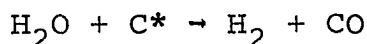
The chain of events leading to ignition and combustion of wood may be understood by studying the pyrolysis of wood in the absence or presence of oxygen. When wood is irradiated at the surface, because of its relatively low thermal conductivity and high specific heat, zones develop parallel to the heat absorbing surface. The first zone formed is denoted as Zone A which is a layer of wood near its surface having a temperature under 200°C, which becomes dehydrated and evolves water vapor and traces of carbon dioxide, formic and acetic acids, and glyoxal. The

wood loses weight, but the gaseous products are not ignitable. Because wood may eventually char at temperatures as low as 95°C (10,36), oxidation reactions in the gas phase may occur that are exothermic and, if the heat is conserved, may lead to self-heating and self-ignition. Sound wood, however, does not ignite within this zone.

Upon further irradiation, the temperature of the material rises. In the range of 200-280°C, zone B is formed while zone A is moved inward. The rate of pyrolysis in zone B is still slow; gaseous products leaving the surface of the solid are the combined gases from zone A, plus the products of zone B, consisting of water vapor, carbon dioxide, formic and acetic acids, glyoxal, and a little carbon monoxide. During this time the wood chars slowly. The total products of pyrolysis are not readily ignitable, but upon mixing with the surrounding air exothermic oxidations may occur. The exothermic temperature in the gas phase has been reported to be as low as 150°C and as high as 260°C depending on the experimental conditions.

As zones A and B move inward, zone C forms near the surface in the range of 280-500°C. The pyrolysis products of this zone are less oxygenated. The evolved products of overall pyrolysis at this time, are mainly carbon monoxide, methane, formaldehyde, formic and acetic acids, methanol, and later hydrogen. These products, plus some water vapor and carbon dioxide, evolve forcibly enough to carry with them droplets of highly inflammable tars that appear as smoke.

The residue of zone C is then charcoal. The pyrolysis products of zones A and B passing through zone C enter secondary reactions which are believed to be catalyzed by the active charcoal formed at the temperature of zone C. The secondary pyrolysis of tars is said to be strongly exothermic. When water vapor and carbon dioxide of zones A and B pass through the hot region of zone C, which is extremely rich in carbon (both as free carbon and carbon-rich cyclic compound), they enter into combination reactions as follows:



where * denotes the active reactant.

As the overall gaseous products diffuse outward from the surface of zone C, they can be ignited readily by a pilot flame, in which case they burn with a luminous diffusion flame at a considerable distance from surface. Self-sustaining diffusion flames from organic fuels burn at 1100°C or somewhat more (10). One-half to two-thirds of the heat of combustion of wood is liberated by flaming in the gas phase, the balance in glowing combustion of charcoal. External conditions such as fuel geometry and the velocity of the air and its direction determine the contribution of the fraction of this heat to the spread of combustion. As long as the gases pour forth rapidly enough to blanket the wood surface to the exclusion of oxygen,

the charcoal formed cannot burn and is left to accumulate. Since charcoal has only one-third to one-half the thermal conductivity of wood, the layer of charcoal retards the penetration of heat and delays the attainment of the exothermal point in the wood underneath. Thus after the first vigorous flaming of wood, there is often a diminution of flaming until sufficient heat has passed through the insulating layer of charcoal to pyrolyze deeper portions of the wood.

However, flaming ignition of the gas phase may not occur in the absence of a pilot until the pyrolysis in zone C is nearly complete and the emission of the gases slows sufficiently to allow air to make contact with the charcoal. Charcoal is an excellent absorber of radiant heat and has a lower spontaneous ignition temperature (without pilot) than any of the major products of pyrolysis. The spontaneous ignition for mixtures in air, between the limits of flammability, is reported as low as 355°C for pine tar and as high as 539 to 750°C for methane; for charcoal it is reported to be as low as 150 to 250°C. Even at 100°C the combustion of charcoal with oxygen generates 2.7 cal per cc of oxygen reacting (10). Therefore, if the flaming ignition does not occur at the surface of zone C, as soon as air makes contact with the surface the charcoal will glow.

As the surface temperature reaches 500°C and above, zone D is formed and zones A, B and C move inward. Zone D, composed of charcoal, becomes the bed for more vigorous secondary reactions of outward diffusing gaseous products

and tars. The resulting products of the secondary reactions of zone D are highly combustible; in contact with air they can be ignited spontaneously. At 500°C (incipient red heat) the charcoal of the surface layer glows and is consumed. Above 1000°C (yellowish-red heat) carbon is consumed at the surface as the reaction zones penetrate into the wood. The luminous diffusion flames give way, as the reactions of primary wood pyrolysis become exhausted, to the nonluminous diffusion flames of burning carbon monoxide and hydrogen. Finally the remaining charcoal merely glows with little or no flame.

The above mechanism of thermal decomposition of a solid, followed by gas-phase oxidation reactions, has been proved experimentally. The high speed photography of Simms (52, 53) also showed that when the wood samples were ignited, flame first appeared in the volatile stream where the laminar flow became turbulent and then flashed down the surface.

However, it should be pointed out that the above mechanism of zone development merely illustrates an ideal situation. Although it helps to visualize ignition phenomena, it should not be taken as a general rule for every condition. It must be emphasized that the arbitrary division into zones, described above, is according to approximate temperature intervals in the solid rather than sharp, visual zones. (For example, in the present work, the cross sections of a number of irradiated wood samples were examined. In

most cases the charring was continuous and no sharp boundary between charred and uncharred layers was observed.) It should also be mentioned that the char zone mechanism will not apply to very high rates of heating as evidenced by the flash pyrolysis of cellulosic material (30).

The mechanism of thermal decomposition and the composition of the products are different for the two extreme cases of very low and very high thermal radiation. For very slow heating the sample is eventually charred without flaming. The rate of evolution of gases is so low that when they mix with air, the mixture concentration is below the flammable limit. Simms (52) reports that below a certain intensity, ignition of the volatiles did not occur although specimens were observed to glow.

Martin and Ramstad (39) discuss the results of other investigations. They state that contrary to normal processes which precede and accompany the ignition resulting from slow heating, intensely irradiated cellulose undergoes no discernible charring up to about the time of ignition. It subsequently decomposes rapidly and almost completely to volatile substances, leaving only a trace of solid residue. This type of rapid thermal decomposition has been termed "flash pyrolysis."

The experimental work of Lincoln (30) deals with the analysis of the products of flash pyrolysis of solid fuels exposed to pulses of high intensity radiation for

periods of the order of one millisecond or less. The analysis was carried out in vacuo or in an inert atmosphere by means of gas chromatography and mass spectrometry. Lincoln confirmed the dependence of the product composition on the rate of heating. For example, he found that 2-mil sheets of black cellulose were almost completely vaporized by a total radiant heat exposure as low as 2 cal/cm^2 incident on both surfaces. The irradiance used by Lincoln in these experiments was on the order of $3000 \text{ cal/cm}^2 \text{ sec}$ (peak value) over a period of $1/2$ millisecond.

To summarize, the results of the discussion of this section reveals that:

1. Ignition of wood involves two separate and distinct processes: (a) the thermal decomposition of a solid phase into volatile products and charcoal and, (b) gas phase oxidation reactions of volatiles near the surface.

2. Flaming ignition is identified as visible phenomena in the gas phase near the surface of the solid. Glowing ignition is identified as visible phenomena at the surface of the solid which is the result of direct oxidation of charcoal.

Terminology

Unfortunately, the terminology used in the literature on ignition is not standardized. In this section some examples of the variety of definitions are discussed first, and then the terminology used in this work is given. These

differences in definitions will point out the major reasons for the apparent diversity of the results of various ignition studies.

Brown (9) grouped some of the terms used prior to his investigation. Then, based on his own criterion of ignition, as discussed in previous section, he defined the ignition temperature or ignition point to be the temperature in the center of the combustible at which the rate of heat developed by the reactions inducing ignition just exceeded the rate at which heat was dissipated by all causes under the given conditions.

Delmont and Azam (16) ignited plastics by contacting them with a mass of fused inorganic compound of known temperature. They defined the ignition temperature as the temperature at which the plastic, when placed momentarily in contact with the surface of a mass of a fused inorganic compound, spontaneously burst into flame.

Bamford, Crank and Malan (5) studied the behavior of wood exposed to direct flame and to radiation from an electric heater. In the case of direct contact with flame they determined the minimum time for which the sample continued to burn completely to charcoal after external heating ceased. They termed this burning as "spontaneous." In the case of irradiation of the surface by an electric heater they found that when the surface is exposed to radiation of sufficient intensity, there comes a time at which any small flame held in contact with the surface for 1 or 2 seconds will initiate flames which will spread over the whole heated

area, provided the intensity of incident radiation is maintained. For a given intensity, in the limiting case when ignition of this type was just possible, the surface layer of the wood was said to be "critically hot."

Setchkin (50), studying the ignition characteristics of plastic, defined ignition as "a self perpetuating exothermic reaction that is initiated at the temperature of the incipient oxidation, and that increases the temperature of the reactants above the initial air temperature (the samples were placed in an atmosphere of preheated air) until an explosion, flame or sustained glow occurs." He then defined two ignition points as follows: The "flash temperature" was defined as the initial temperature of the air passing around the specimen, at which a sufficient amount of combustible gas is developed so that it can be ignited by an external heat source such as a flame, spark, or hot surface. The "self-ignition temperature" was defined as the initial air temperature at which, in the absence of an ignition source, ignition occurs of itself, as indicated by an explosion, flame, or sustained glow.

Schoenborn and Weaver (48, 49, 67) measured the temperature of plastic samples with thermocouples at different depths, at the time of surface flaming, and called them "apparent ignition temperatures." Extrapolating these temperatures to the surface they found the ignition point of plastics. In other words they considered the surface

temperature at the time of flaming to be the ignition temperature, which they determined by an extrapolation technique.

These citations are only a few examples of the lack of consistent definitions. Each of these definitions is based on different criteria for ignition, specific to the method of investigation. They result in different values for ignition temperatures of solid material. Therefore, in order to avoid misunderstanding and confusion the quotation of any characteristic property of a material should be accompanied by an explanation of the method by which it was determined if it is not standardized.

More recent articles have tacitly agreed upon the following definitions of the terms under the prescribed conditions. This terminology has been used throughout the present study.

Glowing Ignition

In this type of ignition no flaming is observed and the solid starts glowing, normally from a corner, or edge, or a cracked portion of the sample.

Pilot Ignition

At a certain temperature the volatiles evolved from material form a mixture with the surrounding air that can be ignited by a pilot flame or spark. This temperature has also been called the condition of potential ignitibility. The pilot of this type of ignition

is placed in the volatile gas stream.

Pilot Ignition Temperature

The surface temperature of the solid sample at the moment when flaming ignition by a pilot occurs is called the pilot ignition temperature. The pilot consists of a small flame located near the surface. (In this study the pilot flame was produced by propane and air as shown in Figure III-6.)

Spontaneous Ignition

At a high heating rate, the temperature of the solid reaches a point such that a sufficient amount of volatiles are evolved and the mixture of these volatiles and the surrounding air is ignited spontaneously. This condition is also referred to as spontaneous flaming ignition or as self-ignition. The occurrence of spontaneous ignition has been said to be independent of material thickness (13).

Spontaneous Ignition Temperature

The surface temperature of the solid sample at the moment when spontaneous ignition occurs is called the spontaneous ignition temperature.

Sustained Flaming Ignition

If the solid material continues to burn completely after removal of the external heating source, sustained flaming ignition or sustained ignition is said to have

oddured. This condition must necessarily be preceded by either pilot or spontaneous ignition. Whether a material under a given heating condition, which normally causes either pilot or spontaneous ignition, undergoes sustained flaming ignition or not depends on the thickness of the sample. In addition to a high surface temperature, a high equilibrium temperature within the material is required for sustained flaming ignition. This condition is also referred to as sustained, persistent or continued burning or flaming. The condition in which the flaming is not sustained is referred to as transient flaming.

Surface Ignition

Surface ignition is similar to pilot ignition except that the pilot is placed in contact with the surface of the solid instead of in the volatile gas stream.

Necessary Conditions and Criteria for Ignition

In order to define the criteria for ignition, it is necessary to review briefly the experimental and mathematical studies made by previous investigators. Each of the mathematical treatments of the ignition process has been made with several different simplifying assumptions. For this reason, a general case and its assumptions will be presented first so that the reader can better evaluate the effect of the further simplifications made by various investigators. It should be mentioned that because of the

complexity of the problem all of the treatments have been confined to one-dimensional models.

The preliminary assumptions made for deriving a reasonably general equation defining the process of thermal damage to cellulosic material are:

1. The solid material is porous and the transfer of heat and volatile products is one-dimensional.
2. The gaseous products escape with negligible pressure drop.
3. The vapor temperature at any depth can be approximated as the solid temperature at that depth.
4. The process is diffusion controlled. In other words, it is controlled by diffusion of heat and not by rate of reaction.
5. An overall first order reaction with a constant heat of reaction for the weight loss is applicable.
6. The material is isotropic and its properties are independent of temperature.
7. The intensity of the radiation is constant and uniform over the entire surface boundaries.
8. Average constant values can be used for optical properties of the sample.
9. Lambert's law for semi-transparent material is applicable.
10. Some modified physical properties can be used to offset the effect of moisture content.

11. The dimensions of the solid remain constant.

Assumption 1 is valid for materials manufactured from cellulose. However, it has been noticed that the volatile products resulting from the decomposition of irradiated natural wood samples normally evolve from one or several cracks which are not uniformly distributed over the surface. The assumption of one-dimensional mass transfer in these models may therefore be questionable. The amount of energy transfer by gaseous products is relatively small and therefore assumptions 2 and 3 are considered to be fair. Experimental results (10, 13, 37, 45) show that Assumption 4 may be considered valid. Assumption 5, as discussed later in a section concerning the reaction kinetics, has been shown to be valid by experimental work. Assumption 6, especially in the case of wood, is defenseless. The properties of wood across the grain are different from those along the grain. The properties of wood and charcoal are also different. However, the thermal diffusivity of wood and charcoal are approximately the same (45). In the case of the one-dimensional model the properties along the heat transfer path are reasonably constant provided that the sample is free from checks, knots, and cross grain structures. Without assumption 6, analysis of ignition problems is extremely difficult; with it, simplified models can be used. Assumption 7 depends on the experimental conditions, and assumptions

8, 9 and 10 may be considered valid if some suitable values for the optical and physical properties are used. Assumption 11 is usually valid prior to ignition, but expansion and/or shrinkage are common during pyrolysis and following ignition.

On the basis of these assumptions the energy balance for a one-dimensional, diathermanous, porous solid undergoing thermal decomposition is

$$K \frac{\partial^2 T}{\partial x^2} + \gamma H e^{-\gamma x} - m c_g \frac{\partial T}{\partial x} = \rho c \frac{\partial T}{\partial t} + Q \frac{\partial \omega}{\partial t} \quad (\text{II-1})$$

$$- \frac{\partial \omega}{\partial t} = f \omega e^{-E/RT} \quad (\text{II-2})$$

where K = thermal conductivity

γ = Lambert's law attenuation factor

H = incident flux at the surface (surface absorptance assumed to be unity)

m = the rate of weight loss = $\partial \omega / \partial t$

c_g = average heat capacity of volatile products

ρ = density

c = heat capacity of solid

Q = overall heat of decomposition reaction

ω = the weight loss

E = activation energy

R = gas constant

T = absolute temperature

t = time

The nomenclature used above is consistent with this study. New variables are defined as they appear later. A comprehensive listing of nomenclature is given in Appendix F.

Consideration of every aspect of the ignition process greatly complicates the analytical treatment of the problem. Even after all the above simplifying assumptions are made, Equations II-1 and II-2 are too complicated to be solved analytically. Several investigators have attempted to discuss the ignition process of combustible solids mathematically with further simplifications. In this section some of the most important mathematical and experimental approaches made to formulate the criteria of ignition and thermal damage to organic solids will be reviewed briefly.

Brown (9) took the ignition point to be the point of inflection on the temperature-time curve. This temperature is much less than the ignition temperature defined in section II-2. He also listed certain requirements that must be met in order for ignition to occur. They are:

1. A combustible must be present.
2. A source of oxygen, such as air, must be available within certain concentrations relative to the combustible.
3. Heat must be evolved as the net result of the reaction or reactions, producing active combustion.
4. The reaction must proceed more or less rapidly over a certain temperature range.

5. The reaction must be accelerated by a rise in temperature.

6. A supply of energy, sufficient to raise the temperature of the reacting substances to the point where the reaction becomes autogeneous, is necessary.

Lawrence (28) reviewed the above conditions critically. Condition 6 does not seem to be general and would be required only for the cases of spontaneous ignition. Statement 4 is vague and misleading. Probably by the word rapid, Brown meant rapid enough that the rate of heat gain from external sources and chemical reactions exceeds all losses. The heating of the samples in Brown's experimental apparatus was accomplished by convection. Under this condition there was no possibility of heat dissipation.

By the term reaction Brown refers to the heterogeneous combustion reaction of solid and oxygen. The criterion of a temperature inflection point is not acceptable as a general definition of an ignition point because that is the point at which the self-heating from exothermic pyrolysis plus the external heat balances the cooling effects of endothermic pyrolysis and the heat loss to the surroundings. If the source of energy is removed immediately after the inflection point, pyrolysis may not continue. It is also noticed that Brown's concept of ignition is not based on gas phase reactions. However, the other conditions listed are, in general, correct.

In his experiments, Brown exposed the sample to a continuously rising temperature environment in a muffle furnace. The ignition temperature was assumed to be the central temperature of the sample at an inflection point in the temperature-time curve. These temperatures were listed for different materials. They ranged from 172°C for hay and tobacco to 314°C for cellulose acetate. For wood, Brown's ignition temperatures range from 192°C for western red cedar to 220°C for longleaf pine.

In his review of the literature, Martin (37) gave general qualitative statements for the necessary and sufficient conditions for the ignition of the fuel gas and air mixtures which apply to gas phase reactions in ignition processes. These conditions were stated as: (a) the gaseous fuel must have a high chemical potential by virtue of its chemical composition and/or its kinetic energy and, (b) the relative concentration of fuel and oxygen must lie between the two flammability limits. Each of these conditions commonly exists at different levels above the decomposing solid, but until they occur simultaneously at the same location, ignition will not occur. If the oxygen concentration is less than its lower limit, the generated heat dissipates faster than it is released and the reactive species decay via collision. If the concentration of oxygen is greater than its upper limit, the frequency of the reactive collision is not sufficient to give rise to ignition. If the oxygen concentration is

within the flammable limits the temperature will rise high enough so that the mixture ignites.

Although the above conditions have to be fulfilled for the ignition of a solid to occur, they do not quantitatively give the desired answer to the problem of finding the criteria of ignition. For example, it might be more practical to ascribe the flammable limits to a certain rate of evolution of volatiles from the material.

Bamford et al. (5) simplified their one-dimensional slab model to the case of an opaque solid and neglected the energy transfer due to mass transfer through the sample. With these assumptions, Equations II-1 and II-2 become

$$K \frac{\partial^2 T}{\partial x^2} - Q \frac{\partial \omega}{\partial t} = \rho c \frac{\partial T}{\partial t} \quad (\text{II-3})$$

$$- \frac{\partial \omega}{\partial t} = f \omega e^{-E/RT} \quad (\text{II-2})$$

Since heating of the slab was accomplished by contacting luminous gas flames on both sides, the system was symmetrical and only half of the slab may be considered. The initial and boundary conditions that apply to equations II-2 and II-3 in this case become:

$$@ t = 0; 0 < x < L; T = T_0; \omega = \omega_0 \quad (\text{II-4})$$

$$t > 0; x = 0; -K \frac{\partial T}{\partial x} = f(T_s) \quad (\text{II-5})$$

$$x = L; \frac{\partial T}{\partial x} = 0 \quad (\text{II-6})$$

In Equations II-4 through II-6, zero and L for the values of x refer to the surface and middle of the slab respectively. The subscripts o and s denote the initial value and surface condition respectively. The function $f(T_s)$ is described by combining the radiative and convective heat transfer between the surface and contacting flame as follows:

$$f(T_s) = h_c(T_f - T_s) + \sigma(\epsilon T_f^4 - T_s^4) \quad (\text{II-7})$$

where h_c = surface convective heat transfer coefficient

T_f = flame temperature

T_s = surface temperature

σ = Stefan-Boltzman constant

ϵ = flame emittance

In Equation II-7 black body radiation has been assumed for wood.

To solve Equations II-2 and II-3 with conditions II-4 through II-7 and express ω and T as functions of x and t , Bamford et al. (5) transformed the equations into dimensionless forms and then solved them by finite difference methods. In order to evaluate solutions of Equations II-2 and II-3 it was necessary to assign numerical values to all constants and to function $f(T_s)$. Since the work of Bamford

et al. has been widely referred to in literature, it is worthy to mention their method for estimating the numerical constants. The thermal properties of wood and charcoal were assumed to be the same. The initial amount of volatile, ω_o , was obtained by direct weighing of the wood sample before and after pyrolysis in the absence of oxygen. The heat of decomposition Q was estimated from the sudden rise in central temperature which occurred when the center of the sample was decomposing. Assuming that this sudden rise of temperature ΔT was due to the heat of decomposition and that no heat was conducted away, Q was calculated from heat balance $\rho c \Delta T = Q \omega_o$. In other words a constant value of Q which was based on evidence of exothermic reactions was assumed for the entire range of the decomposition process. This value, therefore, does not account for any endothermic pyrolysis or heat loss. Since the details of the decomposition reactions of wood were not known, a single reaction with constant activation energy E and frequency factor f was assumed. The values of E and f were then found by a number of trial solutions of Equations II-2 and II-3 such that the calculated central temperature curve agreed closely with experimental measurements. As for the heat transfer at the surface, the values of $f(T_s)$ in Equation II-7 were found for two different conditions. Measurement was made for $T_s = 300^\circ\text{K}$ by substituting a blackened tin cube containing water for the wood sample

and measuring the rise in temperature of the water when the flame was in contact with vertical face of the cube. Assuming the final uniform temperature of wood being in contact with flame to be about 800°K , they took $f(800^{\circ}\text{K}) = 0$. Having two values of $f(T_s)$, i.e., $f(300^{\circ}\text{K})$ and $f(800^{\circ}\text{K})$ they calculated h_c and ϵ of Equation II-7 and therefore $f(T_s)$ became a known function of surface temperature. The reported constants that Bamford et al. have used are:

c = specific heat,	$0.55 \text{ cal/gm } ^{\circ}\text{C}$
ρ = density,	0.60 gm/cm^3
K = thermal conductivity,	$2.7 \times 10^{-4} \text{ cal/cm}^2 \text{ sec } ^{\circ}\text{C/cm}$
E = activation energy,	$33,160 \text{ cal/gm mole}$
f = frequency factor,	$5.3 \times 10^8 \text{ sec}^{-1}$
Q = heat of decomposition,	86 cal/gm
ω_0 = the initial weight of volatiles	0.375 gm/cm^3

The calculated temperature at the center of the slab showed good agreement with a thermocouple measurement for a 2-cm thick sheet of wood (the name of the wood species is mentioned as "deal"). For a 4-cm thick sample, calculated values were about 80°C lower than the measured values. From interpretation of their calculated results for weight loss, they reported that a minimum rate of evolution of gases of $2.5 \times 10^{-4} \text{ gm cm}^{-2} \text{ sec}^{-1}$ is necessary for a sample to burn with flame. It was also calculated that the temperature of the pyrolysis zone ranged from 300 to 450°C .

The criterion of the rate of evolution of gases from the surface as stated by Bamford et al. (5) was only calculated for sustained flaming under conditions where the heating source contacted the sample. The required rate of evolution of gases prior to ignition for different cases of piloted and spontaneous ignition are not known.

Subsequently, Lawrence (28), in his study of spontaneous ignition of wood and plastic, stated the necessary conditions for ignition to occur as: (a) the rate of evolution of combustible gases during the thermal decomposition should exceed a certain minimum value and (b) the kindling (ignition) temperature of the combustible gas should be reached or exceeded. He assumed the rate of evolution to be $5.0 \times 10^{-4} \text{ gm/cm}^2\text{sec}$, twice the figure reported by Bamford et al. (5). He also assumed the kindling temperature to be 500°C . He justified these figures by noting that the assumed rate of evolution of volatiles was on the safe side for wood and approximately correct for plastic. The kindling temperature was chosen on the basis of Setchkin's (50) reported ignition temperatures of plastic, which were in the region of $430\text{--}500^\circ\text{C}$. Lawrence then considered two cases: (a) opaque materials with a chemical reaction term similar to that proposed by Bamford et al. (5) and (b) modification of Equation II-3 by adding a term $\gamma\text{He}^{-\gamma x}$, for diathermancy. This second equation was

$$K \frac{\partial^2 T}{\partial x^2} + \gamma\text{He}^{-\gamma x} = \rho c \frac{\partial T}{\partial t} + Q \frac{\partial \omega}{\partial t} \quad (\text{II-8})$$

where γ = Lambert's law attenuation constant
 and H = incident flux at the surface

In both cases the equations were solved numerically. For the purpose of calculation, a third assumption was made. When the surface temperature reached the kindling temperature (500°C), ignition was assumed to have occurred, provided that the assumed minimum gas rate had been attained. On this basis, Lawrence found that the calculated rate of evolution always exceeded the pre-assumed value before the kindling temperature of 500°C was reached. He thus concluded that the rate of production of volatiles reported by Bamford et al. (5) was never a critical factor. Lawrence also found that the effect of exothermic decomposition was negligible for an activation energy of 35,000 cal/gm mole. However, a reduction from 35,000 to 25,000 cal/gm mole caused the thermal effect of decomposition to become important.

Because the rate of decomposition reactions of organic materials depends directly upon the rate of absorbed energy and the temperature of the material, several investigators have tried to express ignition criteria in terms of the required energy or surface temperature. Fons (17) solved the equation of heat conduction in an inert cylinder of radius R , and initial temperature T_0 , which was inserted into several atmospheres of constant temperature T_a ranging from 450 to 700°C . The equation to be used is

$$K \left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right] = \rho c \frac{\partial T}{\partial t} \quad (\text{II-9})$$

where r is the radial distance from the center of the cylinder. The boundary conditions are:

$$@ t > 0; r = R; \frac{\partial T}{\partial r} = - \frac{h}{K} (T_a - T) \quad (\text{II-10})$$

$$t \rightarrow \infty; 0 \leq r \leq R; T = T_a \quad (\text{II-11})$$

From the analytical solution of the above equations he tabulated the values of dimensionless temperature for certain ranges of other dimensionless parameters. By measuring the temperature at two different depths in the wood sample at the time of flaming ignition and by using his table, he estimated the surface temperature at the ignition point. With this method he found the ignition point of ponderosa pine to be around 340°C . From the results of experiments he mentioned that the material may spontaneously ignite if parts of it are at 425°C or higher. If part of the wood has been reduced to charcoal, he stated that it can glow at about 230°C .

Lawson and Simms (29) studied the heating rate required for ignition of wood and noticed that lowering the intensity of radiation increases the ignition time; i.e., it takes longer until the requirement for ignition is satisfied. However, they found that there is a minimum heat flux that can lead the process to ignition. They correlated the radiation heat flux and time for the two cases of pilot and spontaneous ignition as follows:

$$(H - H_p)t^{2/3} = 0.025 \times 10^6 (K\rho c + 68 \times 10^{-6}) \quad (\text{II-12})$$

$$(H - H_s)t^{4/5} = 0.05 \times 10^6 (K\rho c + 35 \times 10^{-6}) \quad (\text{II-13})$$

where H = incident radiation flux, $\text{cal/cm}^2 \text{ sec}$

H_p, H_s = critical irradiance of pilot and spontaneous
ignition respectively, $\text{cal/cm}^2 \text{ sec}$

K = thermal conductivity, $\text{cal/cm}^2 \text{ sec}^\circ\text{C/cm}$

ρ = density, gm/cm^3

c = specific heat, $\text{cal/gm}^\circ\text{C}$.

Values of H_p and H_s correspond to ignition at infinite exposure time and have been found to be about 0.35 and 0.6 $\text{cal/cm}^2 \text{ sec}$, respectively. If the exposure time is not reasonably short, ignition may not occur at all because with prolonged heating the amount of volatiles may be exhausted before ignition can occur. Therefore the equations apply only to a level of irradiation somewhat above the critical values.

Buschman (12), using the same type of correlation for his data on pilot ignition of wood, found that the constants of Equation II-12 are not the same for all materials and therefore Equation II-2 and II-3 cannot be generalized.

Lawson and Simms (62), in continuation of their earlier study (29), suggested that wood ignites when the surface reaches a fixed temperature rather than when it has received a fixed quantity of energy. They estimated

the spontaneous ignition temperature to be 350-450°C for different species of wood and 600°C for fiber insulating board. The level of irradiance for their experiments was between 0.5 and 2.0 cal/cm²sec.

Simms (51, 52, 53, 54, 55, 56) later did a semi-quantitative analysis by considering Equations II-1 and II-2 and compared the outcome with the experimental results. He neglected the effect of mass convection through the solid and included the general case of a radiation pulse which has a peak flux of H'_p at the time t_p so that

$$H = \lambda H'_p (t/t_p) \quad (\text{II-14})$$

where λ is a shape function which is unity for a constant intensity. Equation II-1 and II-2 are combined to yield

$$K \frac{\partial^2 T}{\partial x^2} + \gamma H'_p \lambda (t/t_p) e^{-\gamma x} = \rho c \frac{\partial T}{\partial t} - Q f \omega e^{-E/RT} \quad (\text{II-15})$$

The initial condition is given as $T = T_0$ and $\omega = \omega_0$ and the boundary conditions are described by Newtonian cooling, $h(T - T_0)$. By introducing the following dimensionless groups,

$$\xi = x/L ; \text{ Dimensionless distance}$$

$$\tau = ft ; \text{ Dimensionless time}$$

$$\Phi = TR/E; \text{ Dimensionless temperature}$$

Equation II-15 becomes

$$(\alpha/fl^2) \frac{\partial^2 \Phi}{\partial \xi^2} + \lambda \left(\frac{\tau}{ft_p} \right) \left(\frac{\gamma H_p' R}{E \rho c f} \right) e^{-\gamma L \xi} = \frac{\partial \Phi}{\partial \tau} + \frac{QR \omega_o}{E \rho c} \frac{\partial (\omega/\omega_o)}{\partial \tau} \quad (\text{II-16})$$

where

$$- \frac{\partial (\omega/\omega_o)}{\partial \tau} = \left(\frac{\omega}{\omega_o} \right) e^{-1/\Phi} \quad (\text{II-17})$$

The initial conditions for all ξ then become $\Phi = \Phi_o = RT_o/E$ and $\omega/\omega_o = 1$. The boundary conditions become

$$@ \tau > 0; \xi = 0 \text{ or } 1; \pm \frac{\partial \Phi}{\partial \xi} = \frac{hL}{K} (\Phi - \Phi_o) \quad (\text{II-18})$$

From these equations it follows that the solution will be in the form

$$\frac{RT}{E} = F_1 \left[\frac{RT_o}{E}, \gamma L, \frac{hL}{K}, \frac{\alpha}{fl^2}, \frac{x}{L}, ft, \frac{QR \omega_o}{E \rho c}, \frac{\gamma H_p' R}{E \rho c f}, ft_p \right] \quad (\text{II-19})$$

and

$$\frac{\omega}{\omega_o} = F_2 \left[\frac{RT}{E}, ft \right] \quad (\text{II-20})$$

Useful simplifications are made by neglecting one or more terms. For example, if the effect of diathermancy is neglected, the terms containing γ are omitted from the above equations. However, any groups that can be formed out of the excluded terms which do not contain γ must be retained. The same result would be obtained by reverting to and

modifying the original differential equation and boundary conditions. In the following paragraphs some important cases as well as the significance of some of the dimensionless groups are discussed.

In the case of opaque materials the terms γL and $\gamma H'_p R/E\rho c f$ are excluded, but $H'_p R/E\rho c f L$, their ratio, is retained. Combining this ratio with the group $f t_p$ the energy modulus $H'_p t_p R/E\rho c L$ is formed and Equation II-19 reduces to:

$$\frac{RT}{E} = F_3 \left[\frac{RT_0}{E}, \frac{hL}{K}, \frac{\alpha}{fL^2}, \frac{x}{L}, ft, \frac{QR\omega_0}{E\rho c}, \frac{H'_p t_p R}{E\rho c L}, ft_p \right] \quad (\text{II-21})$$

If the material is inert, all terms containing Q , E , R , and f must be deleted from Equation II-19, and it is the temperature rise, $(T - T_0)$, not the absolute value of T , which is the relevant parameter. The result for the case of an inert, diathermanous material in terms of the energy modulus $H'_p t_p/\rho c L(T - T_0)$, becomes

$$\frac{H'_p t_p}{\rho c L(T - T_0)} = F_4 \left[\frac{hL}{K}, \frac{x}{L}, \frac{\alpha t}{L^2}, \frac{\gamma K}{h}, \frac{\alpha t_p}{L^2} \right] \quad (\text{II-22})$$

For an opaque, inert material it becomes

$$\frac{H'_p t_p}{\rho c L(T - T_0)} = F_5 \left[\frac{hL}{K}, \frac{x}{L}, \frac{\alpha t}{L^2}, \frac{\alpha t_p}{L^2} \right] \quad (\text{II-23})$$

Equation II-23 may be further simplified by referring to two cases of thick and thin materials. All dimensionless groups may be regarded as the ratio of two terms, each of which usually has a physical meaning attached to it. The two important groups considered here are $\alpha t/L^2$, the Fourier number or dimensionless time variable, and hL/K , the Biot number. The Fourier number may be written as

$$\frac{(K/L) \Delta T t}{\rho c L \Delta T} = \frac{\text{rate of conduction of heat away from surface}}{\text{rate of retention of heat}}$$

The Fourier number is a measure of the age of the process. When $\alpha t/L^2$ is small, the conducted heat will not have penetrated far, and the material is effectively of infinite depth [see also references (13), (20) and (68)]. When $\alpha t/L^2$ is large, the rate of retention of heat is relatively small and the material is approaching conditions where conductivity is no longer a relevant factor since the material is effectively thin.

The Biot number, hL/K , may be considered to be the ratio of surface to internal resistance to heat flow. For the case of the semi-infinite solid, the thickness of the specimen is not a factor in heat transfer modeling. Eliminating L from the Fourier and Biot numbers by combining the two yields the parameter $h^2 t / K \rho c$. Therefore, the solution of Equation II-19 for the case of semi-infinite, opaque and inert solid becomes

$$\frac{H'_p t_p}{\rho c (\alpha t_p)^{1/2} (T - T_o)} = F_6 \left[\frac{hx}{K}, \frac{t}{t_p}, \frac{h^2 t}{K \rho c} \right] \quad (\text{II-24})$$

For a constant pulse of radiation, t/t_p will be unity, and may be neglected. The surface condition ($x = 0$) for this case is expressed by

$$\frac{Ht}{\rho c (\alpha t)^{1/2} \Delta T_s} = F_7 \left[\frac{h^2 t}{K \rho c} \right] \quad (\text{II-25})$$

The analytical solution of Equation II-16 corresponding to the case of Equation II-25 was given by Simms (51) as

$$\frac{Ht}{\rho c (\alpha t)^{1/2} \Delta T_s} = \frac{\beta}{1 - \exp \beta^2 \cdot \operatorname{erfc} \beta} \quad (\text{II-26})$$

where $\beta = [h^2 t / K \rho c]^{1/2}$. β is called the cooling modulus and ΔT_s is the surface temperature rise. If $h^2 t / K \rho c$ is small, the surface heat losses may also be neglected. The energy modulus therefore would be constant.

When the Fourier number is large enough for a quasi-steady state to exist, thermal conductivity must not appear in the groups containing time. By eliminating K from the product of the Fourier number and the Biot number, the resulting parameter becomes $ht / \rho c L$ and the solution to the case of an infinite slab of opaque and inert solid for a constant flux becomes

$$\frac{Ht}{\rho c L \Delta T_m} = F_8 \left[\frac{ht}{\rho c L} \right] \quad (\text{II-27})$$

where ΔT_m is the mean temperature rise of the slab. If the effect of cooling is negligible, the cooling modulus ($ht/\rho c L$) is also omitted. The analytical solution of Equation II-16 corresponding to the case of Equation II-27 was given by Simms (51) as

$$\frac{Ht}{\rho c L \Delta T_m} = \frac{2 \, ht/\rho c L}{1 - \exp(-2ht/\rho c L)} \quad (\text{II-28})$$

Simms (51, 54) then plotted the energy modulus against the cooling modulus, $h\sqrt{t}/\sqrt{K\rho c}$, and applied a constant ignition temperature, T_s , such that the theoretical curve of Equation II-26 gave the best fit through the experimental data (within about 30 percent). The characteristic ignition temperature or surface temperature rise at ignition was found to be $\Delta T_s = 525^\circ\text{C}$ for the case of spontaneous ignition of thick or semi-infinite samples of wood. The heating sources used in Simms experiments were a gas-fired panel, a tungsten lamp and a carbon arc. The reported experimental conditions (51) were:

Materials: Oak, Fiberboard, Cedar and Mahogany.	
Range of irradiances	1.2 - 14 cal/cm ² sec
Range of densities	0.25 - 0.70 gm/cm ³
Range of ignition times	2 - 30 seconds

In the case of thin slabs with linear temperature gradients, a mean temperature rise, $\Delta T_m = 525^\circ\text{C}$ used in Equation II-28 gave the best fit through the experimental data (within about 30 percent). The reported experimental conditions (51) were:

Materials: Cotton, Filter paper, Denim, Drill and Gabardine

Range of irradiances	1 - 14 cal/cm ² sec
Range of thicknesses	0.02 - 0.065 cm
Range of ignition times	1 - 20 seconds

Simms then concluded that a fixed temperature criterion for the attainment of ignition is valid. The same procedure was applied to the case of pilot ignition (55). The required temperature depended on the position of the pilot in the gaseous stream and ranged from 300 to 410°C. In these experiments only thick samples of wood (1.9 cm thick for all specimens except fibre board which was 1.25 cm) were used. The densities ranged from 0.24 to 0.72 gm/cm³ and the irradiances ranged from 0.25 to 1.5 cal/cm²sec.

Buschman (12), using his data and the solution of the conduction equation for opaque, inert solids, calculated the pilot ignition temperature. The tabulated results show a relatively constant value for surface temperature of each species of wood at ignition. The irradiance level varied in the interval of 0.342 to 0.890 cal/cm²sec. The reported ignition temperatures varied for different kinds of wood

ranging from 298°C for tempered hard board to 391°C for Balsa.

Gardon (20) and Butler et al. (13) consider the case of an infinite slab of thickness L and give the solution for a one-dimensional, inert, opaque solid. The differential equation and boundary conditions are:

$$\alpha \frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t} \quad (\text{II-29})$$

At the initial condition for all x, $T = T_0$. The boundary conditions have been given as:

$$t > 0; x = 0; -K \frac{\partial T}{\partial x} = H \quad (\text{II-30})$$

$$t > 0; x = L; \frac{\partial T}{\partial x} = 0 \quad (\text{II-31})$$

The solution in terms of dimensionless parameters was given as

$$\frac{\rho c L \Delta T}{H t} = 1 + \frac{1}{F} \left[\frac{1}{2} \left(1 - \frac{x}{L} \right)^2 - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 \pi^2 F} \cos \frac{n \pi x}{L} \right] \quad (\text{II-32})$$

where $\frac{H t}{\rho c L \Delta T}$ = dimensionless energy modulus,
 $= \frac{H L}{K \Delta T} \cdot \frac{\alpha t}{L^2}$

$\frac{H L}{K \Delta T}$ = irradiance modulus

$F = \frac{\alpha t}{L^2}$ = Fourier number or dimensionless time modulus

and $\frac{x}{L}$ = dimensionless depth modulus.

Butler et al. (13), cross plotting from Gardon (20), noticed that dimensionless groups plotted as energy versus time with depth as a parameter show an essentially isothermal profile for $\sqrt{F} > 3.0$ if the thermal properties and the irradiance are constant. At $x = 0$ Equation II-32 reduces to an expression for surface temperature rise

$$\frac{\Delta T_s \sqrt{K\rho c}}{H\sqrt{E}} = \sqrt{F} + \frac{1}{\sqrt{F}} \left[\frac{1}{3} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 \pi^2 F} \right] \quad (\text{II-33})$$

where the left side of the equation is the dimensionless temperature rise. Plots of Equation II-33 and the surface temperature rise of semi-infinite solid show that for $\sqrt{F} < 0.6$ a slab heated on one side can be considered a semi-infinite solid. Based on Equation II-33 for $\sqrt{F} < 0.7$, Butler et al. (13) estimated the surface temperature of cellulosic material for the case of spontaneous ignition to be in the range of 700 to 800°C.

Martin and Ramstad (39) measured the temperature of blackened α -cellulose, exposed to high intensity radiation (5 to 16 cal/cm²sec), at different depths at the moment of spontaneous ignition and extrapolated these temperatures to the surface. The results of these experiments, although not very reliable because of the extrapolation technique, showed a range of spontaneous ignition temperature from 600

to 900°C. They recalled the results of the investigation by Lawson and Simms (62) which showed spontaneous ignition temperatures on the order of 350 to 450°C for irradiances between 0.5 and 2.0 cal/cm²sec. They also reported some low spontaneous ignition temperatures from other investigators, in the range of 250 to 350°C, who had generally used an irradiance level smaller than that used by Lawson and Simms (62). They then suggested that the spontaneous ignition temperature depended on the radiation heating rate.

Williams (68) neglected the chemical reaction term and derived the one-dimensional heat conduction equation for diathermanous solids as

$$K \frac{\partial^2 T}{\partial x^2} + \gamma H e^{-\gamma x} = c\rho \frac{\partial T}{\partial t} \quad (\text{II-34})$$

Three cases were considered, as follows:

Case I - Heat flow in semi-infinite solid with no heat losses from irradiated surface. The initial and boundary conditions are:

$$@ t = 0; \text{ for all values of } x; T = T_0 \quad (\text{II-35})$$

$$t > 0; x = 0; \partial T / \partial x = 0 \quad (\text{II-36})$$

$$x \rightarrow \infty; \partial T / \partial x = 0 \quad (\text{II-37})$$

Williams solved this case by Laplace transform. The result is given in two alternative forms

$$\begin{aligned} \frac{\Delta TK \gamma}{H} &= 2\chi \operatorname{ierfc} \left(\frac{\Psi}{2} \right) - e^{-\varphi} \left[1 - e^{\chi^2} \right] \\ &- \frac{1}{2} e^{\chi^2} \left[e^{-\varphi} \operatorname{erfc} \left(\frac{\Psi}{2} - \chi \right) - e^{\varphi} \operatorname{erfc} \left(\frac{\Psi}{2} + \chi \right) \right] \end{aligned} \quad (\text{II-38a})$$

or

$$\begin{aligned} \frac{\Delta TK}{Hx} &= \frac{2}{\Psi} \operatorname{ierfc} \left(\frac{\Psi}{2} \right) - \frac{1}{\varphi} e^{-\varphi} \left[1 - e^{\chi^2} \right] \\ &- \frac{1}{2\varphi} e^{\chi^2} \left[e^{-\varphi} \operatorname{erfc} \left(\frac{\Psi}{2} - \chi \right) - e^{\varphi} \operatorname{erfc} \left(\frac{\Psi}{2} + \chi \right) \right] \end{aligned} \quad (\text{II-38b})$$

where $\chi = \varphi/\Psi = \gamma\sqrt{\alpha t}$

$$\varphi = \gamma x$$

$$\Psi = x/\sqrt{\alpha t}$$

$$\operatorname{erfc} x = (1 - \operatorname{erf} x)$$

and $\operatorname{ierfc} x = \int_0^x \operatorname{erfc} x$

Either Equation II-38a or II-38b can also be written in the functional form

$$\frac{\Delta T \sqrt{K \rho c}}{H \sqrt{t}} = f \left[x/(2\sqrt{\alpha t}), \gamma\sqrt{\alpha t} \right] \quad (\text{II-39})$$

It can be shown that, for a large absorption coefficient, γ , the Equation II-38a or II-38b reduces to the solution for the opaque solid as

$$\Delta T = T - T_o = \frac{2H\sqrt{\alpha t}}{K} \text{ierfc} \left[\frac{x}{2\sqrt{\alpha t}} \right] \quad (\text{II-40})$$

Case II - Surface temperature in semi-infinite solids allowing for first power losses from the irradiated surface. The appropriate surface boundary condition (Equation II-36) was modified to:

$$t > 0; x = 0; \frac{\partial \Delta T}{\partial x} = - \frac{h}{K} \Delta T_s \quad (\text{II-41})$$

The solution for this case was given in an integral form. Dealing only with the variation in the surface temperature, the solution was approximated, for the condition of $h/K\gamma < 1$, to

$$\begin{aligned} \frac{\Delta T_s K\gamma}{H} = & \left[\frac{\Delta T_s K\gamma}{H} \right]_{h=0} - \frac{h}{K\gamma} (0.7522\chi^3 - 1.057\chi^4 + 0.3009\chi^5) \\ & + \left(\frac{h}{K\gamma} \right)^2 (\chi^4 - 0.6361\chi^5) - \left(\frac{h}{K\gamma} \right)^3 (0.6018\chi^5) \end{aligned} \quad (\text{II-42})$$

where $\chi = \gamma\sqrt{\alpha t}$ and $\left[\frac{\Delta T_s K\gamma}{H} \right]_{h=0}$ is given by Equation II-38a at $x = 0$.

Case III - Heat flow in semi-infinite diathermanous solids allowing for linear decrease in the reflectivity of the irradiated surface with time. If the surface reflectivity at any time is represented by r_t , the flux of unreflected radiation, H_s , may be given by

$$H_s = (1 - r_t)H \quad (\text{II-43})$$

Where H is the incident radiation flux. Expressed mathematically, this condition becomes

$$(H_s)_t = H'_s (1 + \zeta t) \quad (\text{II-44})$$

where H'_s is the initial incident flux of unreflected radiation at the surface and ζ is a constant. In this case Equation II-34 becomes

$$\alpha \frac{\partial^2 \Delta T}{\partial x^2} + \frac{H'_s \gamma e^{-\gamma x}}{\rho c} (1 + \zeta t) = \frac{\partial \Delta T}{\partial t} \quad (\text{II-45})$$

with the initial and boundary conditions:

$$@ t = 0; \text{ for all } x; \Delta T = 0 \quad (\text{II-46})$$

$$t > 0; x = 0; \frac{\partial \Delta T}{\partial x} = 0 \quad (\text{II-47})$$

$$x \rightarrow \infty; \frac{\partial \Delta T}{\partial x} = 0 \quad (\text{II-48})$$

The solution to this case was also found in an integral form. Considering only the surface temperature, the solution in dimensionless form was approximated by

$$\frac{\Delta T_s K \gamma}{H'_s} = \left[1 + \frac{\zeta}{\alpha \gamma^2} \right] \left[\frac{\Delta T_s K \gamma}{H'_s} \right]_{\zeta=0} - \frac{\zeta}{\alpha \gamma^2} \left[\chi^2 - \frac{4\chi^3}{3\sqrt{\pi}} \right] \quad (\text{II-49})$$

where again $\chi = \gamma\sqrt{\alpha t}$ and $\left[\frac{\Delta T_s K \gamma}{H'_s} \right]_{\zeta=0}$ is given by Equation II-38a.

The solution to Case I was plotted for dimensionless temperature versus dimensionless time-position combination $\left[\frac{\alpha t}{x^2} \text{ or } \frac{x}{2\sqrt{\alpha t}} \right]$ with a factor including the extinction coefficient as a parameter (20, 24, 68). It was shown that the temperature behavior approached that of opaque solids (i.e., γx or $\gamma\sqrt{\alpha t}$ equal to ∞) with increasing γx or $\gamma\sqrt{\alpha t}$. It is therefore concluded that at sufficiently large values of the time or depth, the effect of diathermancy becomes negligible.

The above analysis strictly applies only to cases involving monochromatic radiation. It may, however, be extended to cover cases where various portions of the incident flux are characterized by different γ 's. In such situations, one merely computes the temperature rise at any depth and time produced by each fraction of the incident flux acting independently and sums them arithmetically. Mathematically, the total flux at any depth x can be expressed by

$$H_x = H \sum_{i=1}^{\infty} F_i e^{\gamma_i x} \quad (\text{II-50})$$

where F_i represents the fraction of the total incident flux H characterized by the absorption coefficient γ_i . The total solution is then given by

$$\left[\frac{(\Delta T)K}{Hx} \right]_{\text{total}} = \sum_{i=1}^{\infty} F_i f\left(\frac{\alpha t}{x^2}, \gamma_i x\right) \quad (\text{II-51})$$

where $f\left(\frac{\alpha t}{x^2}, \gamma_i x\right)$ refers to the solution for $(\Delta T)K/Hx$ as represented in Case I by Equation II-38b.

Gardon (20) shows that the above presented treatment of diathermanous, semi-infinite solids is applicable to scattering materials also, provided that γ is taken as

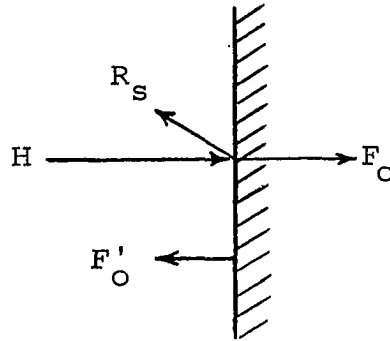
$$\gamma = \sqrt{(\gamma_A + \gamma_s)^2 - \gamma_s^2} \quad (\text{II-52})$$

where γ_A and γ_s are the coefficients of absorption and scatter which are found by measurement of the transmittance and reflectance of a thin slab and H_s is taken as the net flux entering the solid, i.e.,

$$\begin{aligned} H_s &= F_o - F_o' \\ &= H - (R_s + F_o') \end{aligned} \quad (\text{II-53})$$

As illustrated in the following sketch F_o refers to the amount

entering, F'_O refers to the amount reflected due to internal scatter and R_s is the amount of incident energy reflected at the surface



The results of computations (24, 28, 68) show that, for short exposure times, wood specimens can be treated as semi-infinite solids, and convective and radiative losses from the surface are relatively minor.

Boehringer and Spindler (6) also gave the solution of the semi-infinite, diathermanous, and inert solid considered by Williams (68) as mentioned under Case I, but modified for aerodynamic heat rate and corrected for wall temperature and emissivity. The modified surface boundary condition is given by:

$$-K\left(\frac{\partial T}{\partial x}\right)_{x=0} = N = \text{constant} \quad (\text{II-54})$$

After transforming the solution of Boehringer and Spindler into a dimensionless form in order to compare with Williams' solution, it becomes:

$$\begin{aligned}
\frac{(\Delta T)K}{-Hx} = & \left(1 + \frac{N}{H}\right) \left[\frac{2\psi}{\sqrt{\pi}} e^{-1/4\psi^2} - \operatorname{erfc} (1/2\psi) \right] - \frac{1}{\phi} e^{-\phi} (1 - e^{\psi^2\phi^2}) \\
& - \frac{e^{\psi^2\phi^2}}{2\phi} \left\{ e^{-\phi} \operatorname{erfc} \left[\frac{1}{2\psi} - \psi\phi \right] - e^{\phi} \operatorname{erfc} \left[\frac{1}{2\psi} + \psi\phi \right] \right\}
\end{aligned}
\tag{II-55}$$

where $\phi = \gamma x$ and $\psi = \sqrt{\alpha t/x^2}$. It is noticed that only the first term in Equation II-55 is different from the solution of Williams given by Equation II-38b.

Williams (68), working on damage initiation in organic materials by thermal radiation, also made a quantitative study on the conditions requisite for the inception of internal charring in irradiated wood specimens. Two criteria for the occurrence of such damage were evaluated, one being the achievement of a specified temperature at a given locality, and the other, the attainment at that same locality of a definite value for the "punishment integral," P , defined by the relation

$$P = \int_0^t e^{-E/RT} dt \tag{II-56}$$

Within experimental precision, either criterion was found to be an adequate basis for correlating the depth of char data within the limits of his radiation intensities, which ranged up to $3.5 \text{ cal/cm}^2\text{sec}$. The punishment integral was based on the assumption of a first order reaction mechanism for wood

pyrolysis. Because this integral was extremely difficult to use, Williams chose the criterion of fixed temperature in his study and found an adequate correlation between his measured and predicted depth of charring, for short times. He neglected the heat losses from the surface and correlated the energy modulus $Ht/\rho c d \Delta T$ and Fourier number $\alpha t/d^2$ where d is the depth of char. A value of 500°C was used for the characteristic temperature rise, ΔT , to give the best fit to the data (within $\pm 25\%$). Data on the depth of char obtained at the Naval Materials Laboratory (NML) were also superimposed on the same correlation chart. The NML data were in the same range of accuracy but with a $\Delta T = 400^\circ\text{C}$. The reason for the discrepancy in temperatures was claimed to be the effect of differences in definition of char depth as well as possible error in the values of surface absorptance. These data also proved that the effect of diathermancy was negligible.

In his correlation analysis of charring of wood Sauer (45) argued that " . . . the imposition of a charring temperature does not conform to our present knowledge of the mechanism of charring which indicates that thermal decomposition is a time-dependent as well as temperature-dependent phenomenon. This deficiency in analysis is exemplified by the necessity of using different charring temperatures for each set of data analyzed." Sauer then postulated that charring, at any depth, occurs when the ratio of the density to original density falls to a given value. He assumed the density change to follow a

similar pattern as the weight loss, namely the first order reaction formula. Based on a mathematical model of semi-infinite solid with neither heat losses nor chemical reactions, he derived two sets of dimensionless groups, one for a rate controlled process and the other for a diffusion controlled process. Attempts at correlating the depth of char and weight loss data of other investigators revealed the process to be diffusion controlled. In other words, the rate of reaction, compared to the rate of diffusion of heat, is sufficiently rapid that it may be considered to occur instantaneously. The irradiance levels used in these data ranged from 2.5 to 25 cal/cm²sec, and the data for 2.5 cal/cm²sec correlated the most poorly. The deviation of data points from the expected trend at lower irradiance (longer exposure time) was explained in terms of surface heat losses that could not be ignored at long exposure time. The dimensionless groups used by Sauer for depth of char were the energy modulus $H\sqrt{t}/T_0\sqrt{K\rho c}$ (which is the same as $Ht/T_0\rho c\sqrt{\alpha t}$) and char depth modulus Hd/KT_0 . Simms (54) suggested $Ht/\rho c(\alpha t)^{1/2}\Delta T$ and hd/K , which would take care of the surface losses, would be more appropriate parameters to use for correlating the data. In his analysis, Sauer (45) correlated the data for a constant value E/RT_0 . His correlation, therefore, is actually based on a constant temperature criterion for the damage process (T_0 was assumed to be 300°K).

Gray and Harper (21) proposed another approach for the mathematical solution of the ignition problem. First they approximated the non-linear term of chemical decomposition. They then attempted to solve the problem analytically. Two forms of approximation were chosen:

1. Exponential approximation where the argument of the exponential term is expanded in Taylor's series in $(T - T_0)$ and higher order terms are neglected, resulting in

$$E/RT \approx E/RT_0 - (T - T_0) E/RT_0^2$$

Hence $\exp(-E/RT) \approx \exp(-E/RT_0) \exp(y)$ (II-57)

where $y = (T - T_0) E/RT_0^2$

2. Quadratic approximation where $\exp(y)$ is replaced by a quadratic expression

$$\exp(-E/RT) \approx \exp(-E/RT_0) [a + by + cy^2] \quad (\text{II-58})$$

where a , b and c are constants. These authors proposed further approximations by neglecting the spatial temperature variation, which is valid for thin materials.

Schaffer (46) discussed the problem by considering phase changes. He showed that the temperatures at the base of the char zone were constant for a number of species and that the rate at which the char temperature was attained

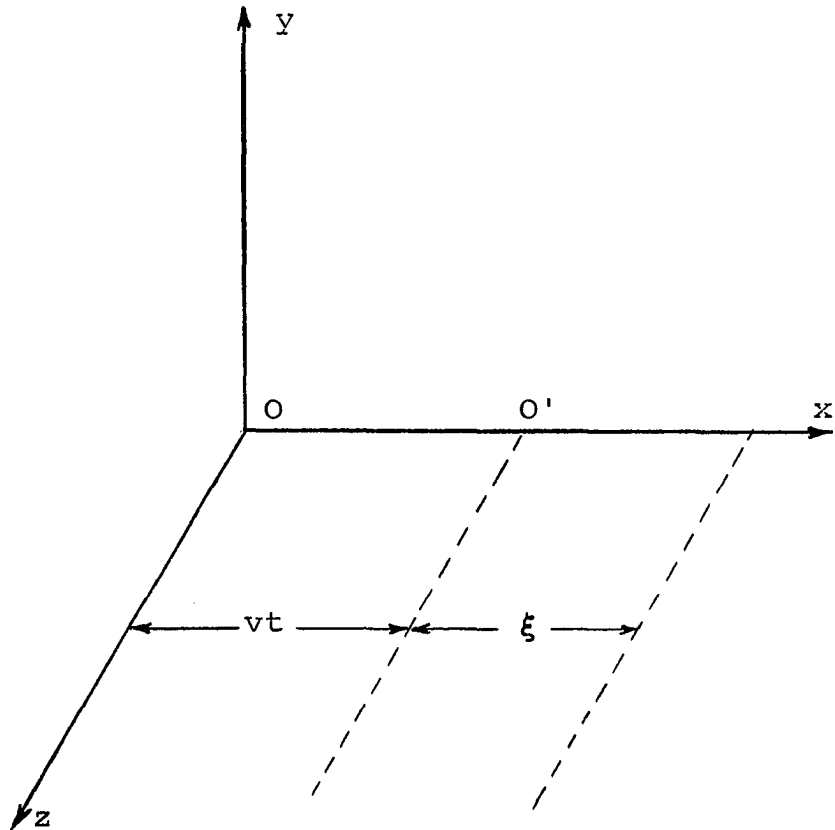
through the sample was normally constant. The equation of heat transfer in an inert material in a general form is:

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (\text{II-59})$$

Assuming that heat, at the rate q'' , is supplied by a point source, moving along the x -axis with a constant velocity v , then one can write

$$x = vt + \xi \quad (\text{II-60})$$

where at the point source $\xi = 0$ and $x = vt$



Substitution of Equation II-60 into Equation II-59 yields

$$\frac{\partial^2 T}{\partial \xi^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} = - \frac{v}{\alpha} \frac{\partial T}{\partial \xi} \quad (\text{II-61})$$

The solution to this equation can be represented by

$$\Delta T = T - T_0 = e^{-\frac{v}{2\alpha} \xi} \Phi(\xi, y, z) \quad (\text{II-62})$$

where Φ is a function of the geometry of the solid. Substituting T from Equation II-62 into Equation II-61 gives

$$\frac{\partial^2 \Phi}{\partial \xi^2} + \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial^2 \Phi}{\partial z^2} - \left(\frac{v}{2\alpha}\right)^2 \Phi = 0 \quad (\text{II-63})$$

Now taking the char zone base as a plane source which advances at a constant temperature along the x -axis

$$\frac{\partial \Delta T}{\partial y} = 0; \quad \frac{\partial \Delta T}{\partial z} = 0$$

and Equation II-63 reduces to

$$\frac{\partial^2 \Phi}{\partial \xi^2} - \left(\frac{v}{2\alpha}\right)^2 \Phi = 0 \quad (\text{II-64})$$

The boundary conditions are:

$$\xi \rightarrow \pm \infty; \quad \Delta T = 0 \quad \text{or} \quad \frac{\partial \Delta T}{\partial \xi} = 0 \quad (\text{II-65})$$

$$\xi = 0; -K \frac{\partial \Delta T}{\partial \xi} = q'' \quad (\text{II-66})$$

The general solution to the Equation II-64 is

$$\Phi = A e^{-\frac{v}{2\alpha} \xi} + B e^{\frac{v}{2\alpha} \xi}$$

or

$$\Delta T = T - T_0 = A e^{-\frac{v}{\alpha} \xi} + B \quad (\text{II-67})$$

where A and B are constants. Applying the boundary conditions II-65 and II-66 one obtains

$$\xi = 0; A = q''/\rho c v \quad (\text{II-68})$$

For $\xi < 0$; Since $\frac{d\Delta T}{d\xi} = 0$ for $\xi \rightarrow -\infty$ then $A = 0$ and in this region

$$\Delta T = B \quad (\text{II-69})$$

for $\xi > 0$; as $\Delta T = 0$ for $\xi \rightarrow \infty$ then $B = 0$ and in this range

$$\Delta T = A e^{-\frac{v}{\alpha} \xi} \quad (\text{II-70})$$

At $\xi = 0$, Equations II-69 and II-70 must lead to the same value

$$A_{\xi=0} \geq 0 = B_{\xi=0} \leq 0$$

and from Equation II-68

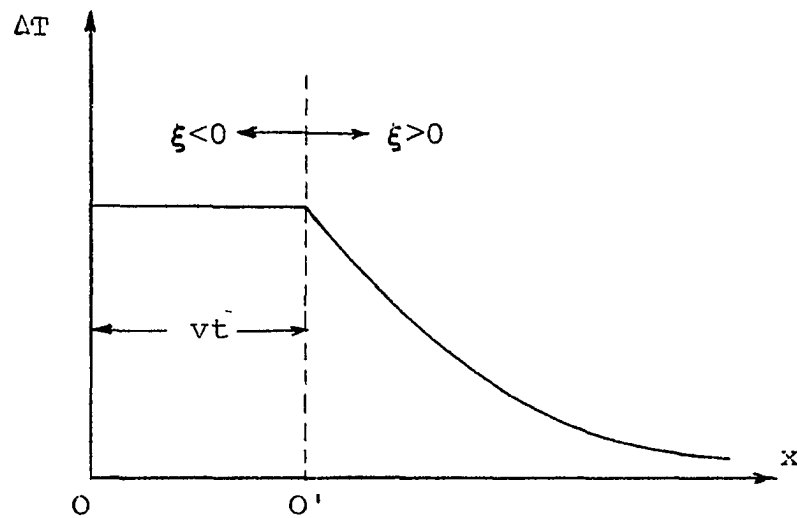
$$B = q''/\rho cv \quad (\text{II-71})$$

Finally from Equations II-69 and II-71

$$\xi \leq 0; \Delta T = q''/\rho cv = \Delta T_{\max} \quad (\text{II-72})$$

$$\xi \geq 0; \Delta T = q''/\rho cv e^{-\frac{v}{\alpha} \xi} = \Delta T_{\max} e^{-\frac{v}{\alpha} \xi} \quad (\text{II-73})$$

The graphical representation of the preceding equations at any time (t) is illustrated below. At $\xi = 0$ a discontinuity in heat flow occurs where all heat flows in the positive direction of ξ and none flows in the opposite direction.



It has been found experimentally that the char zone base temperature for Douglas fir, red oak, white oak, and southern pine, is about 288°C and that the char zone base penetrates (for Douglas fir) at a rate of 1.54 inches per hour.

Another contribution to quantitative analysis is the work done at the Southwest Research Institute (59, 64, 65, 66). In the initial step of the mathematical treatment, using the approach proposed by Bamford et al. (5), Squire and Foster (59) developed a computer program for numerical solution of the ignition of wood under conditions of symmetrical heating. Weatherford (64) later expanded this program to include conditions corresponding to one-sided heating.

Weatherford and Sheppard (65) introduced the concept of a "thermal feedback wave" being propagated from the surface of symmetry to the heating surface. They correlated the time required for this wave to reach the surface with surface temperature and Biot number. The result showed that the criterion of fixed temperature was not adequate to describe ignition and that the criterion of specified fuel-generation-rate proposed by Bamford et al. (5) for the sustained ignition was not correct.

Based on the results of experiments on non-symmetrical and symmetrical heating, Weatherford, Sheppard and Valtierra (66) suggested that a fixed fuel-generation-rate criterion must be satisfied in order to achieve sustained piloted ignition in the presence of a heat source. Because of the scatter in their data, which was believed to be caused by the effect of substantial influence of physical and thermal properties, they concluded that a more quantitative

definition of fixed fuel-generation-rate as an ignition criterion was not feasible.

The discussions throughout this section referred to only a few of the most pertinent articles on the subject of ignition. Emphasis was given to the areas in which attempts were made to formulate a generalized criterion for ignition. As the reader has already realized, and to the best of writer's knowledge, no such generalized ignition criterion has yet been proved to satisfy the data obtained under different experimental conditions. There are a number of references that in one way or another contribute toward a better understanding of the ignition problem, but discussion of all of them is beyond the scope of this section. Further discussion of points pertinent to the present work will be made in the chapter concerning the presentation and analysis of the results.

Reaction Kinetics

The composition and the yield of gases, vapors, tars, and char, and the relative proportion of flammable and non-flammable gases that are produced will vary widely according to the conditions of temperature, pressure, time, geometry, and environment under which pyrolysis of an organic material occurs in the presence of retardants or combustion catalysts.

As mentioned previously in this chapter, slow heating (either in the presence or absence of air) of

cellulosic material produces much charcoal, little tar, and less flammable gases but much water and carbon dioxide. Rapid heating, on the other hand, tends to produce little charcoal, much tar, and highly flammable gases that are rich in hydrogen, carbon monoxide and hydrocarbons (37). In slow heating decomposition proceeds in an orderly manner in which there is stepwise formation of increasingly stable molecules, richer in carbon and converging toward the hexagonal structure of graphite carbon (10). In very rapid heating, macromolecules may be literally torn into volatile fragments with little possibility of orderly arrangements (31).

The rate of evolution of gaseous products is also dependent on the rate of heating. Relatively slower heating leads to a slower pyrolysis. To demonstrate the apparent change in reaction mechanism, Martin (37) and others (10, 31, 47) qualitatively discussed two possible competing reaction mechanisms. The discussion was based on thermochemical data and the assumption that the solid residue was carbon (graphite). The two hypothetical reaction mechanisms were illustrated as shown in Table II-1. This scheme shows that reaction (a) produces charcoal and oxygenated gases and releases energy whereas reaction (b) yields little or no carbon, mostly hydrogenated gases and absorbs energy (requires higher rate of heating). The role of highly reactive free radicals is not known

TABLE II-1
HYPOTHETICAL COMPETING REACTION MECHANISMS
IN PYROLYSIS OF WOODS

	Volatile Products*	Heat of Formation ΔH_f (cal/mg)
{ Cellulose } ($\Delta H_f = -1.0$ to - 1.5 cal/mg)	(a) — Carbon + ($\Delta H_f = 0$)	H ₂ O -3.2 CO ₂ -2.14 RCOOH -1.9 CO -0.93 RCHO -0.9 CH ₂ CO -0.36
	Slow heating Fast heating (b)	ROH -1.3 CH ₄ -1.0 C ₂ H ₆ -0.66 H ₂ 0 C ₂ H ₄ +0.45 C ₂ H ₂ +2.1 Free Radicals: CH, CH ₂ , CH ₃ , CHO, 2 to 10 C ₂

*Listed in order of decreasing oxygenation

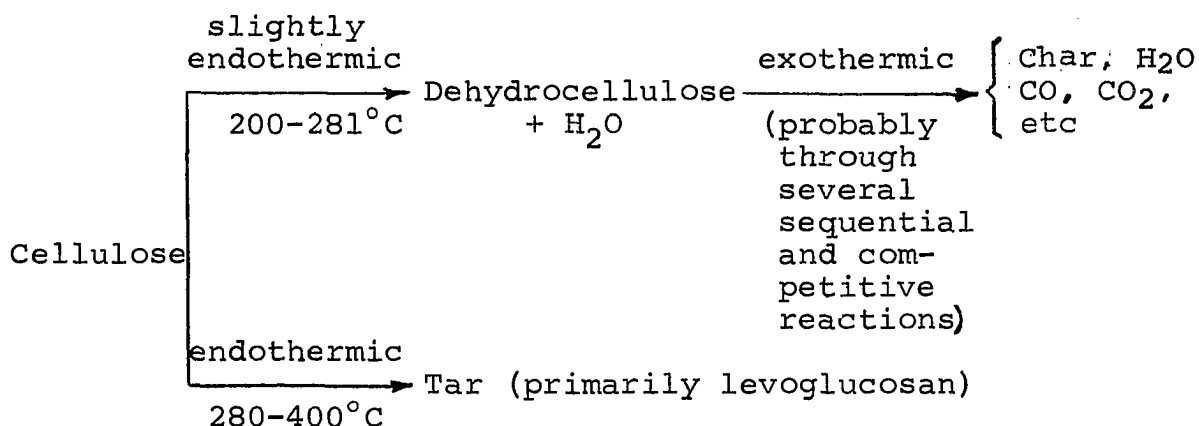
clearly, but it seems rather likely that they may exist in significant concentrations in the vapors away from the surface of the pyrolyzing cellulose where they mix with air.

According to Table II-1, heat is generated as a result of primary pyrolysis. However, since the rate of primary pyrolysis is slow, the amount of generated heat is

not appreciable and is lost mostly through conduction and convection. The experimental study of Mitchell (42) showed that when a stack of wood fiberboard was kept in a constant temperature oven, self heating and charring developed in the center of the stack. The self heating of the stack caused the center of the blocks to glow when they were unstacked. The ambient temperature at which these tests were carried out varied inversely with the size of the samples. In other words, the larger the sample the lower the ambient temperature required for ignition. For example his data show that for an ambient temperature of 260°F (127°C), the temperature rise above ambient, due to self-heating at the center of the stacks, was 30°F (17°C) for four-inch thick samples as compared to 80°F (44°C) for eight-inch thick samples. The reason for this behavior is the preservation of heat in the center of the stack. The low conductivity of wood prevents the generated heat of exothermic pyrolysis from being conducted away. The heat loss from the center of the stack to the surroundings is easier for the smaller size samples than the larger size. Mitchell (42) confirmed the effect of heat preservation by separate experiments on freshly crushed coal in an ambient temperature of 90°C. After the temperature of the sample, due to self-heating, had slightly passed 90°C, he raised the ambient temperature in appropriate intervals to keep it under, but close to, the temperature of the edges of the specimen. With this

procedure he prevented undue heat losses to the surroundings. The self-heating in this experiment was relatively more pronounced at the center of the sample. The result of Mitchell's study showed that self-heating in large samples of wood fiberboard was accomplished in an ambient temperature of even as low as 66°C. This study, therefore, confirms that slow pyrolysis is exothermic.

Kilzer and Broido (27), speculating on the nature of cellulose pyrolysis in the temperature range of 200 to 400°C suggest two competitive endothermic processes which depend on the rate of heating. One process is postulated to be an unzipping reaction producing 1, 4-anhydro- α -D-glucopyranose which rearranges to give levoglucosan. The other reaction is a dehydration which produces H₂O and dehydrocellulose. The latter is then decomposed, through exothermic processes, to CO₂, CO, further H₂O and char. Kilzer and Broido demonstrated the above mechanism as shown in the following scheme:



The values of heats of formation (ΔH_f) of pyrolysis products listed in Table II-1 further reveal that the pyrolysis of wood, if carried out at a higher rate of heating, tends toward an endothermic process. Butler et al. (13) referring to the work of Martin (37) point out that " . . . there is some reason to believe the temperature dependence of cellulose degradation to be anti-Arrhenius and the process more endoenergetic at higher temperatures."

However, it should be noted that, contrary to the result of above discussion, several investigators have said the primary pyrolysis (below about 280°C) of wood or cellulosic material to be endothermic; the process then changes to exothermic at higher temperatures. Martin (37) and Browne (10) in the discussion of zone development in irradiated wood mention that below 280°C the reactions are endothermic but between 280-500°C (zone C) the reactions become exothermic. The products of zone C contain large quantities of flammable gases. In these same references Martin (37) and Browne (10) introduced the schemes of Table II-1. The reason for contradictions in the endothermal and exothermal phenomena in different investigations is possibly due to the experimental conditions and/or some catalytic effects. For example, Arseneau (4) studied the pyrolysis of balsam fir and several components of wood by Differential Thermal Analysis (DTA). The

heating rate was programmed for 5.8°C per minute. The wood sample was treated to become free of extractives (extractives, constituting about five percent of wood, are comprised of substances such as fats, fatty acids, resin acids, resins, waxes, gums, starches and many others). The thermograms of DTA showed that pyrolysis of wood and cellulose when heated in air was endothermic up to about 280°C; then the reactions became exothermic which reached their peak around 330°C. Arseneau then refers to another investigator whose work showed that cellulose was characterized by an endotherm at 340°C when heated in nitrogen. Lipska and Parker (32) studying the pyrolysis of α -cellulose in nitrogen atmosphere show that oxygen contamination increased the rate of pyrolysis rapidly. Alvares (2, 3) found that the oxygen concentration at the surface of cellulosic fuel affected the surface temperature rise which he believed to be the reason for the change in pyrolysis. When oxygen concentration at the surface was reduced, the surface temperature and time for ignition were increased. (The reasoning of Alvares in relating the variation in ignition temperature to the change in pyrolysis in this case is questionable. The mechanism of gas phase reaction is also affected by oxygen concentration. The required condition for the ignition of the gaseous products may have been delayed by reduction in oxygen at the surface.) However, the data of Alvares show that the pyrolysis prior to ignition was endothermic.

The overall rate and order of the pyrolysis reaction of cellulosic materials have also been studied by numerous investigators (5, 7, 8, 10, 22, 30, 32, 36, 37, 40, 43, 45, 47, 60, 69). Wright and Hayward (69) studied the kinetics of the pyrolysis of western red cedar and western hemlock by introducing the cubes or disks of samples to an atmosphere of nitrogen at 500, 700 and 900°C. The result of experiments showed that for the cubic pieces the reaction was approximately of the one-half order; for the disks it was of zero order. The reaction rate constant was shown to be directly proportional to temperature and specific surface (surface area per unit weight); the proportionality constant was the same for both species of wood. It was also shown that the rate of propagation of reaction zone along the grain is faster than that across the grain.

Lipska and Parker (32) studied the pyrolysis of α -cellulose in an isothermal atmosphere of nitrogen at temperatures ranging from 250 to 298°C. They found three distinct stages of pyrolysis in the following sequence: (a) a rapid pyrolysis, mostly dehydration, (b) a range in which pyrolysis is zero order, and (c) a region in which pyrolysis is first order leaving char deposit. The weight loss in initial pyrolysis was about two percent for 250°C and increased with temperature to 6.5 percent for 298°C. The transition from zero order to first order occurred when 50 percent of the original weight was lost.

With reference to all prior investigations Martin (37) and Sauer (45) discuss the concept of thermal decomposition as a kinetic reaction, and they conclude that first order reaction kinetics satisfactorily correlate the weight loss data. The expression for the first order reaction mechanism is:

$$-\frac{d\omega}{dt} = k \omega = f e^{-E/RT} \omega \quad (\text{II-2})$$

where k is reaction rate constant and ω is loss in weight of volatiles. It is emphasized that ω in these expressions is not the amount of cellulose unreacted or uncharred at any time.

Values of activation energies and frequency factors have been estimated by several investigators (5, 7, 8, 22, 32, 37, 45, 60). The rate of heat evolution data due to exothermic reactions has also been reported (5, 7, 8). However, these data are not comparable since they are only for a certain range of temperature and heating condition. The effect of chemical heating with respect to values of E was studied by Lawrence and was discussed previously. Generally the values of heat of reaction Q , activation energy E and frequency factor f vary with temperature as well as reaction mechanism. Each of these constants may be considered to be a combination of appropriate values of different elementary, consecutive, and competitive reactions.

Martin (37) has tabulated the values of activation energy and frequency factor of cellulosic materials for different temperature limits. These values range from 25.0 kcal/gm mole and $1.9 \times 10^9 \text{sec}^{-1}$ for temperature limits of 110-220°C to 32.1 kcal/gm mole and $1.3 \times 10^{12} \text{sec}^{-1}$ for 165-265°C for E and f respectively. Although the temperature ranges are not significantly different, the tabulated data show a distinct trend of increasing magnitude in both the activation energy and the frequency factor with increasing temperature. Lipska and Parker (32) found the value of E to be 42 kcal/gm mole for α -cellulose in the temperature range of 250-300°C. Butler et al. (13) mention that appropriate thermochemical data for ignition of cellulosic material are either very scanty or nonexistent. Practically nothing is known of heats of reactions.

It has been shown (10, 13, 37, 45) that if the rate of reaction compared to the rate of diffusion of heat into the solid is sufficiently rapid, the reaction rate may be considered to occur instantaneously without introducing serious error. Therefore, the process is considered to be diffusion controlled rather than rate controlled.

The application of a first order reaction expression in the mathematical development of thermal ignition was discussed in a previous section which was concerned with the mathematical treatment. At this point it is appropriate to discuss very briefly the factors and the mechanisms involved

in the process leading to ignition in the gaseous phase.

Martin (37) analyzes the mechanism and the kinetics of the gas phase reaction and explains that except for the case of very high heating rates ($> 20 \text{ cal/cm}^2\text{sec}$) where ignition occurs almost instantaneously, the first gases leaving the surface of the cellulosic material are incombustible and after expanding outward provide a nonoxidizing blanket on the surface. As the products of pyrolysis diffuse out, they push this blanketing layer ahead. In the process of expanding to atmospheric pressure they cool, and the concentration of the unstable species diminishes. Then the boundary layer begins to diffuse with air. The pattern of gaseous flow then assumes a quasi-steady state, with a region near the solid of expanding combustibles followed by a region of diffuse mixing. Finally at a distance from the sample a nearly uniform mixture of combustible gases and air is formed. The above mentioned mechanisms of gas phase behavior seem to be applicable only to the case of pyrolysis of uniformly made cellulose material in still air and with a rate of heating of much smaller than $20 \text{ cal/cm}^2\text{sec}$. (For example, at an irradiance level of about $0.8 \text{ cal/cm}^2\text{sec}$ in the present study, gaseous products were observed to jet out of the wood samples from several cracked spots.) Some of the factors affecting the mixing are: (a) the rate of evolution of gases, (b) the motion and direction of the air over the solid, and (c) the geometry and attitude of the surface of

the sample. Conditions (a) and (b) are also discussed by Simms (55). At low rates of heating, when the evolution of gases was small, the maximum thickness of the boundary layer at the top of a 5-cm sample was calculated to be 2.5 cm. Experimental results showed that when the pilot and sample were separated by 2 cm, the sample did not ignite. At higher rates of heating ($> 3 \text{ cal/cm}^2\text{sec}$) the volatiles issued as a jet and the volatile stream became turbulent, making spontaneous ignition possible.

Upon mixing of the combustible gases with oxygen, exothermic oxidation reactions occur. If the oxygen and gas concentrations are within the flammable limits, the mixture ignites.

The ignition temperature of a gas mixture is a function of time. For example, if a hydrogen-air mixture is heated suddenly to 630°C , it ignites in about half-second (37). At 588°C it ignites only after being kept at that temperature for 5 seconds, while at 572°C a 15 second period is required. This induction period has been termed "the lag on ignition." The lag decreases rapidly with a rise in temperature. However, other factors such as oxygen concentration, pressure, presence of catalyzers and inhibitors affect the ignition temperature. Martin (37) has tabulated the ignition temperature in air of several flammable materials including some of the expected pyrolysis products of cellulose.

In summary, the rate and mechanism of solid phase pyrolysis and gas phase reaction strongly depend on the rate of heating and mixing mechanism of volatiles and air at the surface. At the lower rates of heating the products of pyrolysis are mostly water vapor and CO_2 (oxygenated products) with little combustible gases, some tar which appears as smoke and relatively higher percentage of charcoal. The gaseous products are not readily ignitable. At the higher rates of heating, the products are more hydrogenated and combustible gases and the percentage of charcoal residue is relatively less. Although a first order reaction mechanism for the weight loss has been said to be applicable, the values of appropriate activation energy E , and frequency factor f , which are temperature dependent, have to be found by trial for every experimental condition. The value of heat of reaction, Q , depends on sample temperature and particular stage of pyrolysis. Even if an average value for Q could be applied to every test, this average would not be the same for different experiments which are carried out under different heating rates and experimental conditions. If the rate of weight loss, $\partial w / \partial t$, during an ignition study is measured experimentally, the need for estimation of activation energy and frequency factor (for certain correlations which require only the rate of weight loss) is eliminated. However the value of Q remains to be estimated by some method.

Factors Involved

There are several factors which greatly affect the occurrence and nature of the ignition and consequently the experimental results. These factors may be classified in two categories:

1. Experimental procedure: criterion of ignition, experimental method, nature and size of container, geometry of the sample, ignition atmosphere, rate of air flow, time of exposure, and rate of heating.

2. Properties of the combustible solid: fineness, moisture content, extraneous materials, diathermancy, surface absorptivity, constituents of compounds, physical and chemical properties, and pretreatment of the material.

Brown (9) gives a rather detailed analysis of these factors. He classified and named the experimental methods as (a) constant temperature, (b) compensated temperature rise or adiabatic and (c) rising temperature; each of which is divided into subclasses. In Class (a), the sample is brought into contact with a constant temperature heating medium such as hot air or hot plate. In Class (b), the sample is first heated by a constant heating medium for some time. Upon indication of self-heating by temperature rise, the medium temperature is then increased gradually so as to follow the temperature of the specimen and therefore decrease the amount of heat loss from the specimen to the container. Class (c) is characterized by heating the

specimen with a medium whose temperature is continuously rising until ignition occurs. There is still another method, the ignition of a specimen by thermal radiation, which is not covered by Brown's classification. It is obvious that each of these methods require different definitions and criteria of ignition; furthermore they yield different experimental results.

Effect of Size

The effect of sample size on ignition characteristics has been studied by several investigators. Brown (9) gives an account on the prior work. By his own experiments he finds that his characteristic ignition temperature is affected by the size of the specimen. The plot of ignition temperature versus either rate of air flow or rate of heating passes through a minimum, the position of which is a function of the sample size.

Fons (17) concludes that for furnace temperatures less than 1300°F (704°C) ignition time increases as the size is increased.

The quantitative relation due to the effect of size is not known because a certain volume or weight of the specimen will have different effects depending on the geometry of the sample. It is known, however, that the rate of heat generation due to the exothermic chemical reactions is proportional to the volume, but the rate of heat gain from, or loss to, the surroundings is proportional to the surface area.

The size of materials used in laboratory experiments is different from those exposed to actual building fires or irradiation from incendiary weapons. The area of the material in the laboratory is limited by the required radiation intensity or source temperature. This limitation usually is imposed by the requirement of a described condition such as "uniform flux over the entire surface in a one-dimensional model" with regard to the size of the radiation beam (52, 56). In general, the higher the characteristic temperature of the radiation from a particular source, the smaller the irradiated area.

Simms and co-workers (57) have studied the effect of systematic variation of irradiated area (either by using different specimen sizes or by masking off part of the radiation field) on the time for spontaneous ignition of both thin and thick samples. They found that the effect of area lies presumably in its effects on the stream of volatiles. Later, it was found (55) that in low heating rates, the stream of volatiles at the top of a sample (vertical dimension 5.1 cm) was laminar. In order to obtain turbulence at the top of the specimen, it would need to be at least 25 cm high. It will be recalled that turbulence in the volatile stream encourages ignition.

The correlated data of the Joint Fire Research Organization (52, 57) show that for a specimen of material receiving a given intensity of radiation, the time to ignite

increases as the area of irradiation decreases, particularly for the lower intensities. The increase in time to ignite is greater at low intensities of radiation. Also the minimum intensity (52) at which ignition will occur increases as the irradiated area decreases.

Effect of Air Flow

It was mentioned previously that ignition of solid material occurs in the gas phase. The mechanism of diffusion and mixing of volatiles with surrounding air was also discussed. Obviously the supply of sufficient amount of air is as important to ignition as the production of gaseous products by pyrolysis. Besides the sufficiency, the velocity of air near the heated surface will determine the mechanism of mixing, i.e., by diffusion in laminar flow or by turbulent mixing. On the other hand a very high velocity of air will cool the surface by convection, thus carrying away a large amount of heat generated by exothermic oxidation. The convective losses become more important as the exposure time increases. At some optimum air flow ignition will occur at a minimum temperature or time.

For example, Brown (9) defined the optimum rate for air flow as the minimum in his plot of ignition temperature versus air flow.

For the ignition of solids by radiation, Simms (52, 53) has studied the behavior of the volatile stream by visual observation and high speed photography. He found that at

high rates of heating (above $3 \text{ cal/cm}^2\text{sec}$) with a tungsten lamp source, the flow of volatiles appeared to become turbulent very close to its point of emission from the surface of the heated specimen, and ignition usually followed quickly. At lower rates (below $3 \text{ cal/cm}^2\text{sec}$), the flow was clearly laminar near the heated surface and became turbulent above the sample. High speed photography showed that the flame first appeared in the volatile stream where the laminar flow became turbulent and then flashed down the surface. Using a gas-fired panel, a carbon arc, and a tungsten source to determine the minimum intensity required for ignition, he found that a higher intensity of radiation was required for the case of irradiation with tungsten lamp. The nature of the gas-fired panel and carbon arc was such that they produced convective currents so that the stream of volatiles became turbulent regardless of the rate of heating. By inducing a draft by other means, it was shown that the minimum intensity required from a tungsten lamp became equal to those of a gas fired panel or carbon arc when the volatile stream became turbulent. It was also shown that the absence or presence of external air movement of a velocity on the order of 25 cm/sec did not affect the time required for ignition at those intensities sufficient to cause ignition (53).

Effect of Heating Rate

Aside from the variations in composition of the pyrolysis products produced under different heating rates

the effects of heating rate on ignition time and ignition temperature need to be considered.

Lawson and Simms (29) showed that there is a "critical heat flux" below which wood cannot be ignited. The values for these heat fluxes were reported to be above 0.3 and 0.6 cal/cm²sec for the cases of pilot and spontaneous ignition respectively. These values were found by extrapolation of heat fluxes to infinite time.

Below 0.3 cal/cm²sec wood charred, but flaming ignition was not possible. Above 0.3 cal/cm²sec ignition was possible by a pilot flame or spark, but the time of pilot ignition decreased with increasing intensity of radiation. Above 0.6 cal/cm²sec spontaneous ignition was possible. The time for spontaneous ignition also decreased as the heating rate increased. It should be recalled that neither the pilot nor spontaneous ignition implies sustained flaming after ignition occurs (13, 54). Pilot and spontaneous ignition depend on surface temperature, but sustained flaming depends on the thickness of the material as well. Therefore, when the rate of heating is increased, a level depending on the thickness of material (13) is reached at which ignition is sustained, i.e., the burning will continue after the removal of the external heating source. The reason for this behavior is probably the nature of pyrolysis, which results in greater production of volatiles during pyrolysis. As mentioned before the amount of solid residue is reduced

by increasing the heating rate (10, 13, 30, 37, 40). For very high rates of heating ($> 20 \text{ cal/cm}^2\text{sec}$) it has been found (30, 37) that a cellulose sample can be ignited almost at the instant of exposure and the flame is sustained if the sample is thin. If the thickness is large the low conductive char layer on the surface may protect the layers underneath from surface heating even with the continuation of external heating.

The dependence of ignition time on irradiance level has been found by several investigators at different ranges of intensities. The experimental determination of spontaneous ignition time, t , at various levels of irradiance, H , has revealed that t is inversely proportional to H^2 when the ignition time is sufficiently fast so that heat losses are negligibly small (13, 39, 40). The range of heat flux for these experiments was 5 to $25 \text{ cal/cm}^2\text{sec}$. At lower irradiance levels, the functional relations given by Lawson and Simms (29) and Buschman (12) give the best fit in their experimental data.

The results of different studies have also shown that the ignition temperature increases with an increase in heating rate (13, 39, 52, 53, 54, 65). This dependence has only been correlated with the Biot number by Weatherford and Sheppard (65) in graphical form and needs further investigation.

Effect of Moisture Content

The moisture content of a specimen is known to affect the ignition process by changing the composition of volatiles and by its effect on thermal conductivity. MacLean (34, 35) gives empirical formulas for the thermal conductivity of wood as a function of specific gravity and moisture content, showing that thermal conductivity increases with moisture.

Fons (17) found that ignition time increases with moisture content.

The results of the work of Mitchell et al. (43) showed that the rate of decomposition of sawdust increased with moisture content.

Brown (9) found inconsistent effects of moisture on the characteristic ignition temperatures as reported by prior investigators.

Williams (68) was able to make allowance for alterations in the physical properties due to moisture content in his transient heat flow model. However, his data on the temperature histories prior to local boiling at a depth of approximately 2-3 mm suggested that some of the steam produced in violent vaporization processes near the surface was forced into the interior of the samples, where it condensed and was then revaporized. Migration of moisture in the sample was also studied by MacLean (35).

The effect of moisture on ignition time and critical energy required has been studied quantitatively. Bruce and Downs (11) found the following relation for the ignition of newspaper:

$$Q_c = W^{0.1}(0.0347M + 3.16)$$

where Q_c = critical ignition energy demarking the areas of flaming and charring, cal/cm²

W = atomic weapon yield in Kilotons

M = moisture content of newspaper samples, percent

They also mentioned that the form reported by Sauer for crumpled newspapers and a variety of forest fuels is

$$Q_c = W^{1.25}(AM + B)$$

where A and B are constants.

Thomas, Simms and Law (63) have found that the minimum intensity at which ignition actually occurs increases linearly with moisture content. In their report, the ignition time of moist wood as a function of time and intensity required for dry wood has been correlated. The physical properties of moist wood are also related to the physical properties of dry wood and its moisture content.

Pickard and Wraight (44) have also studied the effect of moisture content up to 150 percent of original dry weight of wood and have correlated the ignition time with thickness of the sample, density of dry wood, moisture

content, latent heat of steam, and the intensity of radiation.

Effect of Prolonged Heating

Since some wood structures are exposed to sunshine or other kinds of moderate heating for prolonged periods of time, it is important to know whether any physical or chemical changes occur during such exposure. Simms and Roberts (58) have studied this effect by preliminary heating for extended periods at temperatures between 120 and 180°C. This temperature region has been shown to be below that at which ignition is possible. The results showed that preheating drove off some of the volatiles, leading to an increase in the minimum intensity required for ignition. The increase in minimum intensity was proportional to the loss in weight. Insofar as the ignition process was concerned, no evidence was found that prolonged heating led to wood being ignited more easily--other than the effects due to drying out the wood. The results therefore suggest that any factor prolonging the period between the surface reaching the temperature at which volatiles are emitted and the surface reaching the temperature at which ignition takes place tends to increase the minimum intensity of radiation required for ignition.

Effect of Diathermancy and Absorptivity

Surface absorptivity plays an important role in the ignition of combustible solids by thermal radiation. Most organic materials reflect some of the incident energy and

also transmit some of it. In the case of opaque materials the absorption of energy is accomplished at the surface, whereas diathermanous materials are partially transparent to radiation which may or may not be in the visible region. Unlike opaque materials, diathermanous materials such as wood absorb radiant energy in depth, accompanied by some scattering.

For mathematical treatment investigators have used Lambert's law to describe the effect of diathermancy. This law gives the monochromatic radiation flux passing through a diathermanous material as:

$$H_x = H_s e^{-\gamma x}$$

where H_x is the monochromatic radiation flux passing a plane at a distance x from the irradiated surface, H_s is the monochromatic radiation flux entering the material and γ is called absorption coefficient, extinction factor or attenuation constant. The value of γ varies with the wavelength of the incident radiation and the computation of total effect should be made, in practice, by adding up the energy absorption at each wavelength. Gardon (20) found that the effects of diathermancy of wood are more pronounced for radiation of wavelengths from about 0.8 to 2.0 microns. He also mentions that the higher reflectance of wood in the interval of 0.8 - 2.0 microns is a manifestation

of the greater diathermancy, which permits more of the internally scattered radiation to reach the irradiated surface once again. Hottel and Williams (24) reported that the maximum diathermancy for polyester plastic occurred between 1.1 and 1.7 microns, and above 1.7 microns the sample was opaque. Wood, however, acted as opaque material in all regions. The reason for this behavior was believed to be due to the high reflectance of wood in the interval of 0.9-2.3 microns which makes the amount of unreflected energy very small and brings any effect of diathermancy within the experimental scatter of the data.

The temperatures attained at or near the irradiated surface of diathermanous materials are lower than those in opaque materials. Therefore, diathermancy reduces the possibility of thermal damage to the material. Martin and Alvares (38) found that the critical irradiance for thin, white, and diathermanous material is greater than $1.0 \text{ cal/cm}^2\text{sec}$, whereas for darker and more opaque materials it approached $0.4 \text{ cal/cm}^2\text{sec}$. On the other hand, scattering materials reflect back some of the incident radiation from the interior of the material and therefore reduce the effect of diathermancy. Gardon (20) proposed the following expression for absorption coefficient, γ , for scattering material

$$\gamma = \sqrt{(\gamma_A + \gamma_s)^2 - \gamma_s^2}$$

where γ_A is the true monochromatic absorption coefficient of a scattering material and γ_s is the scatter coefficient.

Diathermancy also varies with exposure time and the degree of surface charring during the irradiation. As the surface chars the absorption of the unreflected incident energy will be more readily accomplished at the surface so that its penetration into the interior will be decreased. Hottel and Williams (24) show this effect graphically. Therefore, the effect of diathermancy is greater in the case of heating by an intense radiation pulse of short duration. On the other hand diathermancy may be negligible for the case of long exposure time to lower intensities of radiation in which the sample normally ignites after the surface has been charred. When the surface of wood samples approaches 340°C , it becomes black and relatively opaque (37). Most investigators working with high intensity radiation have found it convenient to blacken the sample either by paint or by adding to it a certain amount of carbon black. Butler et al. (13) found that paper made from pulp containing $2\frac{1}{2}$ percent carbon black provided an optimum reduction in the effect of reflection and diathermancy. Simms (54) reported from his communication with Robertson that wood with a blackened surface behaves as an opaque material.

From the above discussion it is concluded that the effect of diathermancy in studying the ignition of wood under flame radiation, as performed in present study, is

negligible. The reasons are: (a) Effect of diathermancy in wood is mainly pronounced in the range of wavelengths of 0.8-2.0 microns. High scatter and reflectance of wood in this wavelength interval, however, offsets the effect of diathermancy (20, 24). In addition, the thermal radiation from flame is extended farther into infrared region for which wood behaves as an opaque material. (b) The exposure time of the experiments carried out in the present study is relatively long and the surface of the samples normally chars before ignition occurs. The effect of surface absorptivity, however, is very important. Gardon (20) and Williams (68) estimated the amount of absorbed energy from a heat balance in a certain period of time. Gardon reported the apparent absorptivities to be in the interval 44-70 percent. Williams, in a sample calculation, reported the corresponding value for birch to be 66 percent. In these calculations the effect of chemical reactions have been ignored, and the heat balances have been calculated by the measured temperature in the sample. Simms (52) found that in heating wood to ignition, absorptivity is dependent on exposure time. He, then, suggested the application of an empirical absorption factor corresponding to different exposure times. This factor is obtained by comparing the intensities of irradiation required to ignite the natural material with those required when the material is artificially blackened by carbon black.

For more comprehensive discussions on the subject of this section, the work of Williams, (68), Hopkins (23), Lawrence (28), Hottel and Williams (24), Sauer (45), Gardon (20), Boehringer and Spindler (6), Alvares (1) and Simms (52, 54) give the most detailed information.

CHAPTER III

EXPERIMENTAL APPARATUS AND PROCEDURE

Although a voluminous literature has been compiled on the ignition of materials in furnaces, by hot gases and radiation sources, such as carbon arcs, radiation panels and solar furnaces, no data on ignition by radiation from flames are available. For this reason and for the purpose of closer simulation to natural fires with their particular spectral distribution, it was desirable to use sheets of flames as the irradiating sources. An ignition cabinet which utilized flame radiation as the heating source was therefore designed and built.

Experimental Apparatus

Figure III-1 shows the front and the left side of the ignition cabinet, and Figure III-2 shows the back and the right side of it. The schematic diagram of Figure III-3 shows a cross section of the front view of the apparatus. A target of test material (A) is supported by a fixed vertical panel of "Fiberfrax" laminated ceramic board (B). Channel burners (C) are mounted on either side, at equal distances from the sample panel. The burners are 2 inches wide and 20 inches long and are made of galvanized steel.



Figure III-1. Front and Left Side View of the Ignition Cabinet.

Preliminary experiments showed that if a flame was brought close to a wall, it leaned toward the wall. The closer it gets the more it elongates and pulls itself up the wall. To counteract this characteristic of the flames, two guide panels of "Fiberfrax" laminated ceramic board (E), each containing a high temperature glass observation window (F), were mounted on the opposite sides of the flames (D) from the sample. Since the guide panels were very close to the flames, "Vicor" glass, which can be used for a maximum working temperature of 1200°C, was used for the observation windows.

In order to alter the irradiance level at the sample position, arrangements were made to readjust the distances between the burners and the target. The burners were supported at both ends on rollers which traveled horizontally in channels mounted on the apparatus framework. By means of gears and a chain and sprocket arrangement, connected to a drive wheel mounted on the left side of the cabinet as seen in Figure III-1, both burners could be moved simultaneously away from or toward the target panel. The guide panels (E) were also mounted on mechanisms similar to the burners and their movements were linked to the burners by means of gears so that they could be moved toward, or away from, the target panel as desired, while maintaining the burners always equidistant from the sample panel (B) and the guide panels (E). To allow these movements, the burners were connected to the fuel tank through flexible tubes.

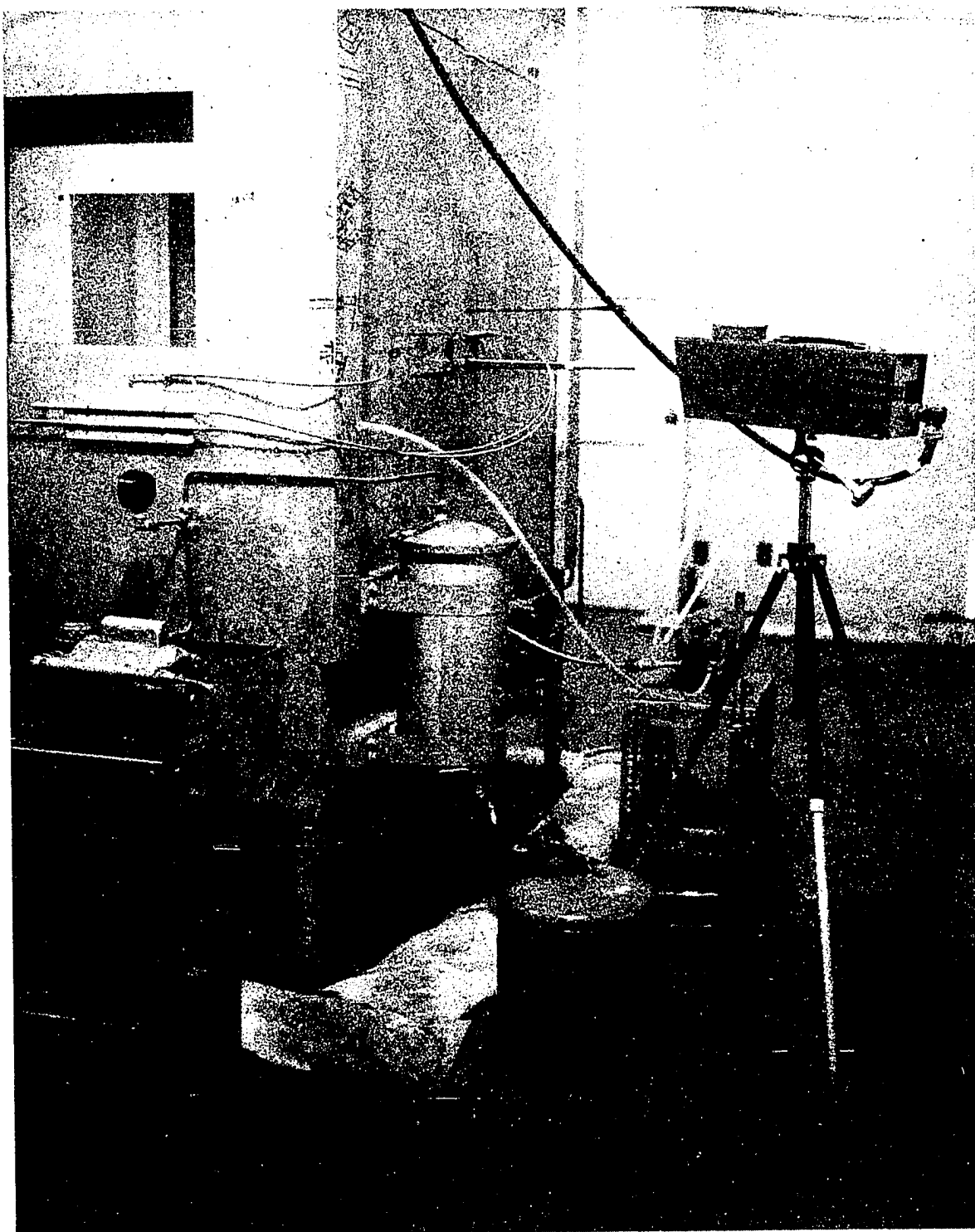


Figure III-2. Back and Right Side View of the Ignition Cabinet.

The Fiberfrax panels (B) and (E) consist of laminations of Fiberfrax papers using an inorganic binder to obtain a rigid structure. Subsequently they were treated with an inorganic binder to increase their strength and surface erosion resistance. These panels as received from the manufacturer, can be used continuously at temperatures up to 2300°F and for intermittent periods at higher temperatures. They exhibit good resistance to thermal shock and provide excellent thermal insulation. They have a density of approximately 50 lb/cu ft and a thermal conductivity of 1.4×10^{-4} cal/cm² sec °C/cm. Fiberfrax board can be die cut, sawed or machined and as seen later it was used to construct the sample holder as well as the sample and guide panels. The guide panels (E) were 2 ft wide and 2 ft high. The sample panel (B) was 2 ft wide and 2½ ft high; all of them were ½ inch thick.

A smooth flow of air upward through the ignition cabinet was necessary to control flame flickering. To provide this smooth flow, as well as removing the smoke and fumes from the ignition cabinet and laboratory, an exhaust fan was mounted in the hood above the cabinet as seen in Figure III-1. This fan also served to pull fresh air into the cabinet. The air velocity required through the cabinet to give steady sheets of flames above the burners was obtained by adjusting the position of a damper in the exhaust line. In order to streamline the air flow, the

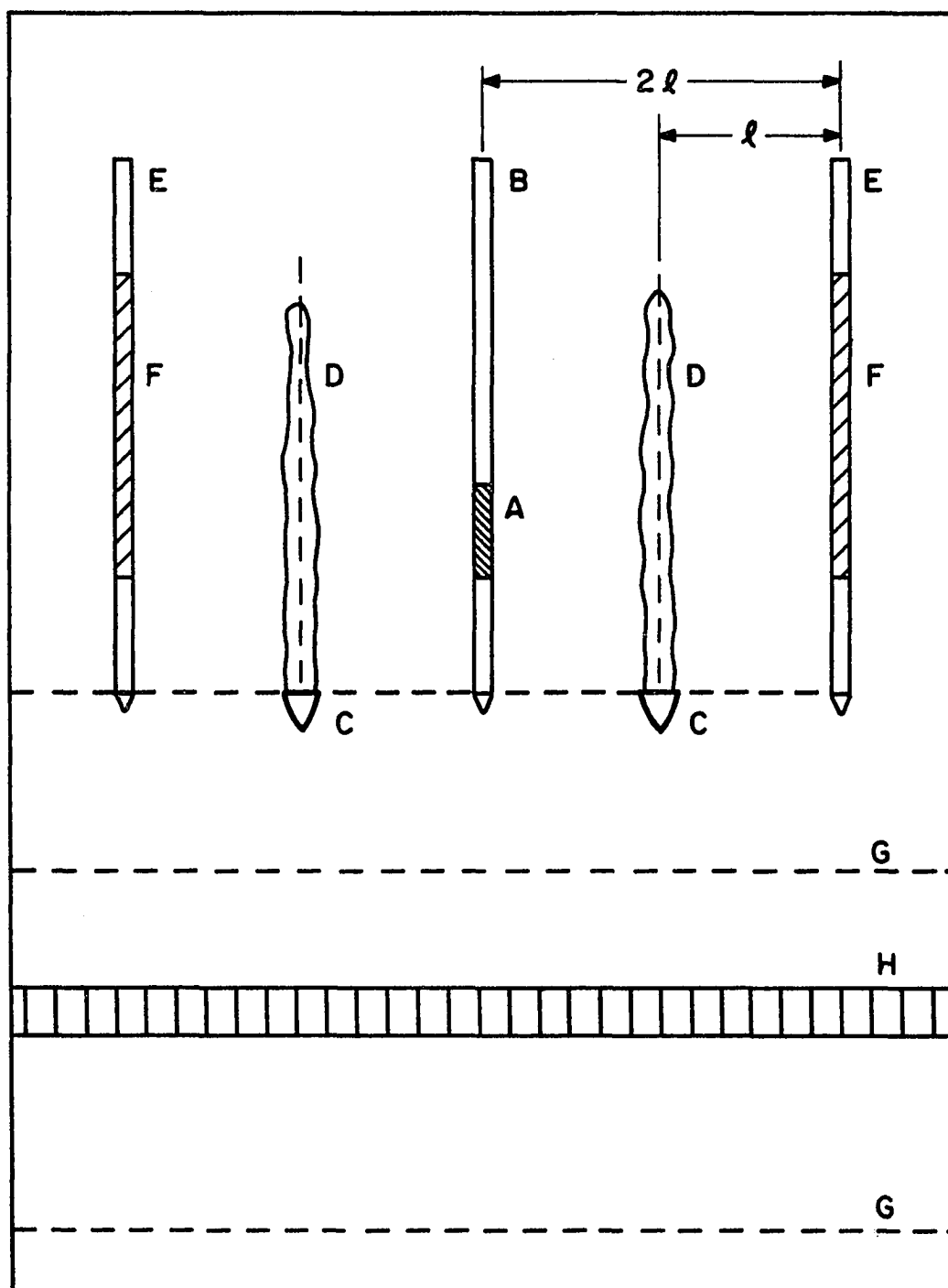


Figure III-3. Schematic Diagram of Ignition Cabinet.

burners and the panels were curved on their undersides. Air supply to the cabinet was from beneath the burners through a specially-designed, metal honeycomb section (H). Two screens (G) were also provided to decrease the turbulence of the air, one below the honeycomb, and one above it.

The cabinet itself was made of galvanized sheet metal and insulated inside. It was 5 ft wide, 3 ft deep and 7 ft high, and was open at the bottom and top. The windows in the cabinet, as shown in Figure III-1 and III-2, are Herculite, tempered plate glass (in front and on both sides) for visual observation and photography. Herculite glass has a thermal endurance of 210°C differential and is safe under a maximum working temperature of 290°C .

A schematic diagram of the fuel system is shown in Figure III-4. The fuel reservoir was made from a 6-inch diameter aluminum pipe with a capacity of about 5 gallons. This reservoir was mounted on the left side of the cabinet (see Figure III-1). The fuel reservoir and burner system work on the principle of a constant head siphon which uses the liquid fuel in the delivery lines as a liquid seal between the burners and the reservoir. The end of the breather tube is positioned at the same level as is desired for the burners. When liquid flows to the burners, and as the level in the burners approaches the breather's level, the head between the burners and the tank balances and the flow stops. The liquid level inside the tank is under a

slight vacuum induced by the removal of the fuel. As the fuel burns, and the level in the burners starts to drop, air is sucked in through the breather tube. As the pressure rises slightly, more fuel flows into the burners.

If a certain irradiance level causes ignition to occur, it is logical to assume that surface flaming after ignition, plus continued external heating from the source, will cause the sample to burn completely. However, in order to determine whether or not sustained ignition has occurred, it is necessary to remove the radiant heat source immediately following ignition. Extinguishment of the flames was accomplished with the aid of the vacuum tank shown in the diagram of Figure III-4. At the instant flaming ignition occurred, a three-way valve was actuated to isolate the fuel reservoir and to suck the fuel from the burners into a vacuum tank. As soon as the three-way valve was turned, two straps of sheet metal, guided by slits provided in the front door of the cabinet, were also slid across the top of the burners. With this method the flames could be extinguished in less than 5 seconds.

The following precautions were taken as safety measures in the fuel system:

1. A piece of screen was installed over the fuel inlet hole in the burners to prevent flash-back to the vacuum tank.

2. The vacuum pump was kept running throughout the test until the burner fires were extinguished. This procedure was followed to keep oxygen out of the fuel exhaust

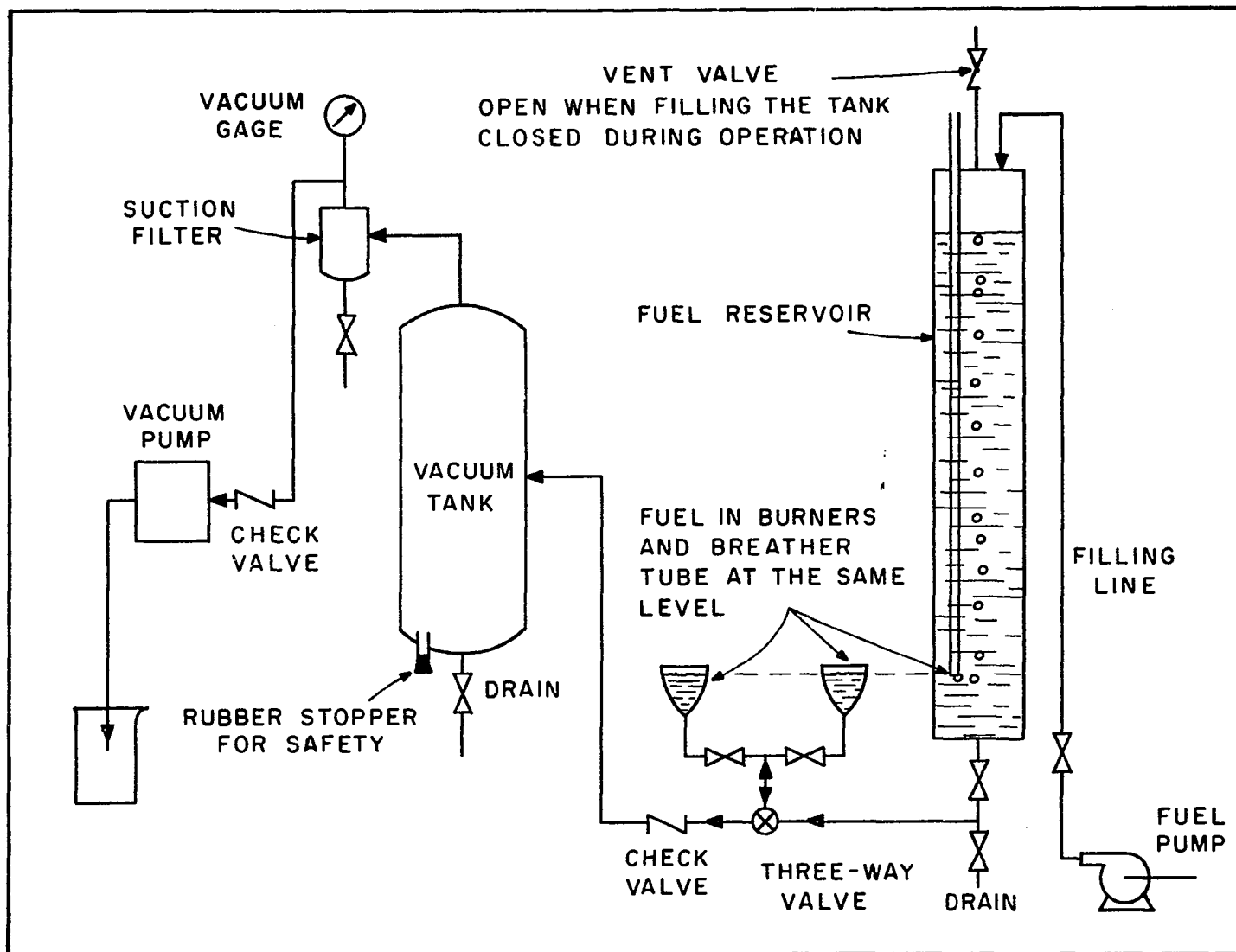


Figure III-4. Schematic Diagram of Fuel Supply and Control System.

system. A vacuum gauge was installed at a conspicuous location to show the vacuum in the tank, which was maintained at 24 inches of mercury throughout each run.

3. Two check valves were used in the system. One of these was installed at the vacuum tank inlet. It was used to prevent a blowback of the hot fuel from the burners in case of an explosion in the tank upon the arrival of the fuel. The second check valve was used at the suction to the vacuum pump to prevent backward flow of air in case the vacuum pump failed.

4. A rubber stopper, lubricated with a little vacuum grease, was held at a hole at the bottom of the vacuum tank and the vacuum pump started. The stopper was pulled in and sealed the tank. The stopper could be blown out by a pressure only a few pounds per square inch above atmospheric and worked as a rupture disk to vent the vacuum tank in case of fire inside the tank.

5. As seen in Figure III-1 the ignition cabinet was surrounded by sand bags to confine the liquid fuel in case of spillage.

6. Fire extinguishers and a fire blanket were kept near the cabinet.

All the valves used in the fuel system, except the inlet to the burners, were brass ball valves with teflon seals. Either burner or both could be used for one-sided heating or two-sided heating respectively.

During the early stages of a fire from a liquid pool, the burning rate and consequently the radiation intensity increases. This increase levels off after some time to a steady state for which the radiation intensity remains approximately constant. In order to expose the sample to square-wave irradiation of known intensity the sample was shielded during the above-mentioned transient period. The schematic diagram of Figure III-5 shows the relative position of the sample and the shield over it. The shields were made of Ferrottype plate used in photography and Fiberfrax, non-laminated insulating board designated as GH. Most of the radiant energy is reflected away. Thus the Fiberfrax board plus the air gaps on both sides of it conduct negligible amounts of heat to the sample during the shielding time. The shields are guided and can be moved forward horizontally to cover the sample or backward to expose the sample. The operation is carried out by means of two choke-wires which are installed on the right side of the cabinet and can be seen in the Figure III-2. The left shield can be seen in the photographs of Figure III-7. In the top picture the shield covers the sample until the flame reaches the steady state condition. In the bottom picture the shield is pulled and the sample is exposed to radiation of constant intensity. More information on the shielding time is given in Appendix A.

Provisions were also made for studying pilot ignition. Small pilot flames were provided by burning a mixture of

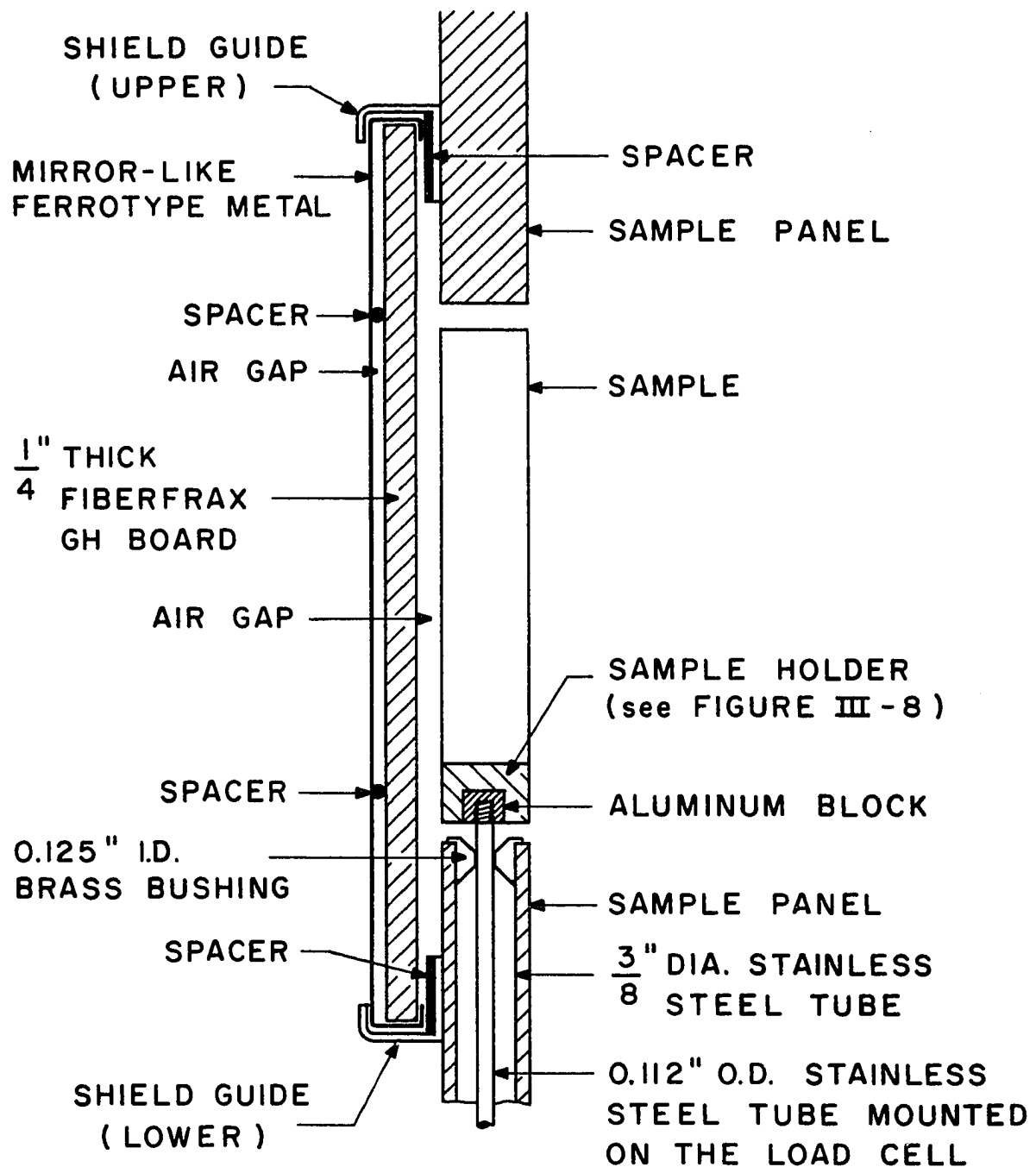


Figure III-5. Schematic Diagram of Left Side Sample Shield (a second shield is located on the right side).

propane and oxygen supplied from bottles. Each pilot was made by inserting a piece of 1/8-inch stainless steel tubing into a 3/8-inch stainless steel tube as shown in Figure III-6. The inner tube is about 2 inches shorter than the outer tube and carries the propane. The oxygen is supplied through the annular region and mixes with the propane before leaving the pilot tip. The pilot tip is made of brass and has a 1/32-inch orifice which can produce a miniature flame torch.

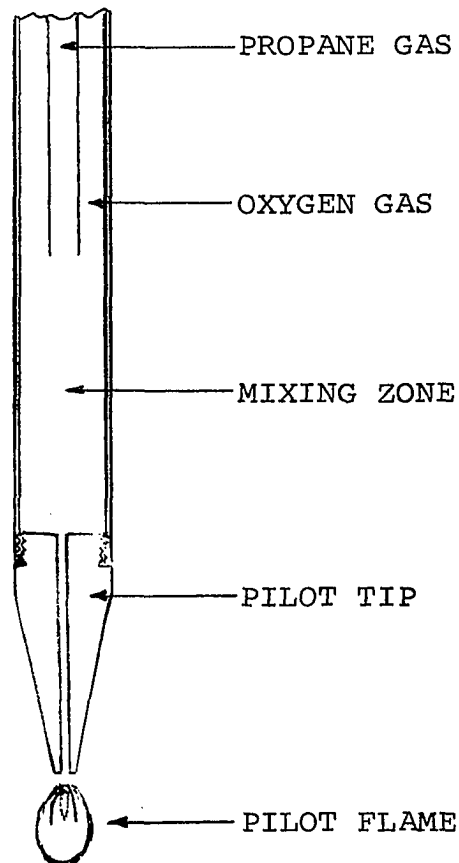


Figure III-6. Schematic Diagram of the Pilot.

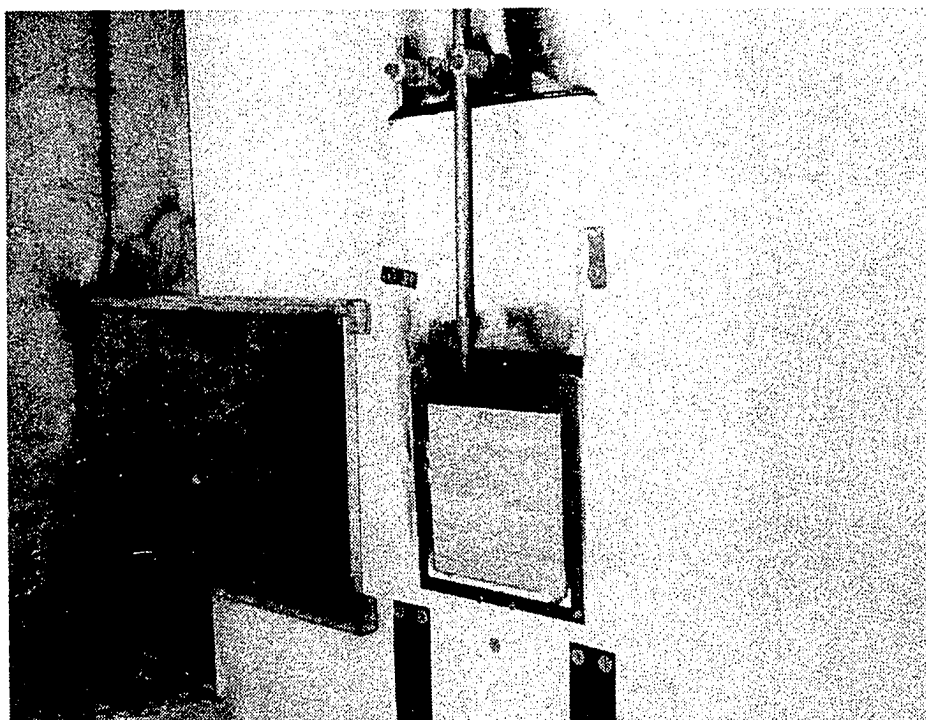
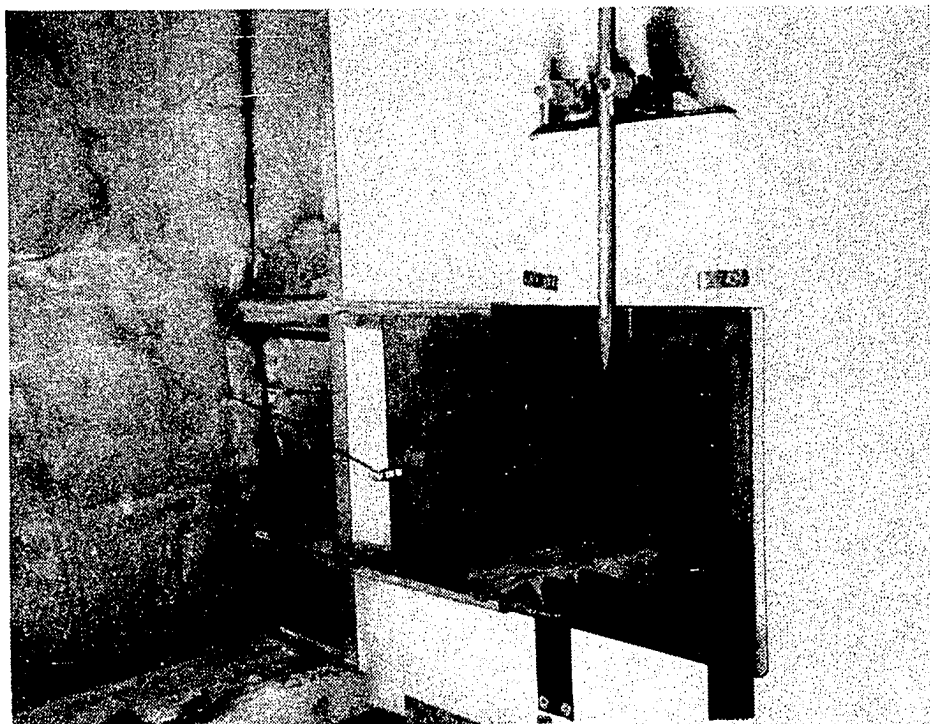


Figure III-7. Left Side Sample Shield.
(Top) Sample is Shielded.
(Bottom) Sample is Exposed to
Radiation.

One of the pilots can be seen on the left in Figure III-7. Provisions were made to adjust the pilot distance from the sample both horizontally and vertically. The pressures on the propane and oxygen bottles were maintained by regulating valves. The gases were carried to the cabinet in two separate 1/4-inch copper tubes containing the check valves in each line to prevent the back flow of either gas to the other bottle. Needle valves were used in each line for final adjustment of the flow before entering the pilot tube. The optimum pilot flame was obtained by setting the supply lines pressure at 12 and 7 psig for the oxygen and propane respectively. These pressures allowed the fine-adjustment, needle valves to be operated in the middle of the open and closed limits. By adjusting these valves small blue flames of the desired size were produced that were not blown off under the air velocity through the cabinet.

Instrumentation

One of the systems built in as a supplementary part of the apparatus was the weighing system. This system was included in the apparatus for continuous weighing of the target materials, which lose some of their weight due to pyrolysis prior to ignition. To detect a small weight loss due to evolution of gases from the sample, the weighing device should be relatively sensitive, which normally restricts the limits of the applied load. In the ignition studies smoke and soot leave deposits on any part of the apparatus above

them. For this reason it seemed most desirable to mount the weighing device beneath the sample, and at the same time, to isolate the sample from the sample panel to exclude the panel from the weighing system. Figure III-8 shows the weighing system which was designed and built to provide for continuous sample weighing.

The sample holder was made of Fiberfrax board, which has a thermal conductivity lower than wood. In order to keep the sample in a vertical position throughout the test and to prevent it from bending, the two side pieces of the sample holder were machined with a rectangular groove in them. Then the side pieces were attached vertically to the base at two ends. Two straps of stainless steel, one on each face, were screwed together, clamping the sample holder firmly in-between. The thickness of the sample holder was $1/2$ inch, the same as the sample panel. Its overall width was five inches and the inside width was four inches. The samples were cut with a tongue on two opposite sides and could be slid into a groove in the sample holder from the top. A photograph of a sample positioned in the sample holder can be seen in Figure III-6.

An aluminum block was mounted in the base of the sample holder and two stainless steel tubes of 0.112 inch outside diameter were screwed to this block to support the sample holder. These tubes passed through two stainless steel tubes of $3/8$ inch outside diameter which were mounted inside the bottom section of the sample panel beneath the

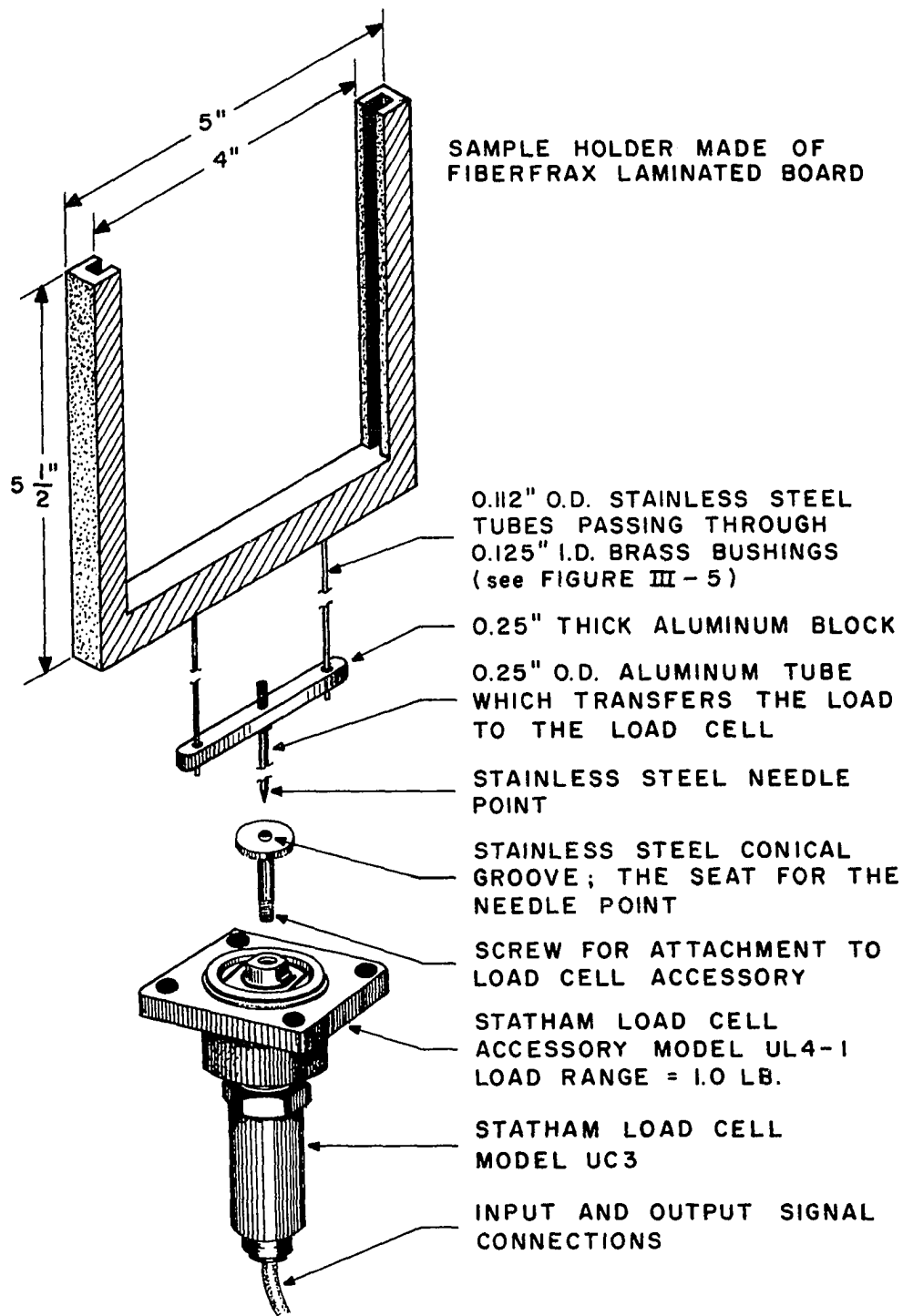


Figure III-8. Three-Dimensional View of Sample Weighing System.

sample holder. For the sake of clarity this part is not shown in the diagram of Figure III-8. Figure III-5 shows the details of the support tubes. A brass bushing of $1/8$ inch inside diameter was fitted in the top section of each of the outer tubes to keep the sample holder centered. The hole in one of the bushings was widened in the direction along the sample to allow for thermal expansion of the aluminum block in the base of the sample holder.

The two small stainless steel tubes transfer the load to a single aluminum tube of $1/4$ inch outside diameter by means of an aluminum strap (see Figure III-8). The two side tubes are above the strap and the single middle tube is located under the strap. The linkage of this strap also provides for vertical adjustment of the sample holder through the middle tube that can be screwed in and out. Horizontal leveling of the sample holder is achieved by adjusting the side tubes.

The load is transferred from the single middle tube to the load cell through a needle point and conical groove which are made of stainless steel. The total weight measured by the load cell is therefore the weight of the sample plus the sample holder and weight transfer system. Effort was made to keep the weight of the sample holder and weight transfer system as low as possible. For this reason aluminum was used wherever possible, and tubes were chosen in place of rods.

The weight of the sample holder was about 100 grams including a piece of Fiberfrax that was slid into the sample holder to cover the top of the sample from irradiation (see Figure III-10). The weight of the accessories added up to 58 grams making a total weight of about 158 grams. The load cell used in this system was a Statham Universal Transducing Cell, model UC3, with a 60 gram force range. A model UL4-1 load cell accessory was added to the load cell to extend the force range to 453 grams, which allows 295 grams for the samples. The weight of the samples ranged from about 50 grams for 1/2 inch thick pine to 155 grams for 3/4 inch thick oak.

The combination of the load cell and its accessory had a reported specification of 0.12 millimeter displacement and an accuracy of better than ± 0.15 percent of full scale. It had continuous resolution and the accuracy was not affected under an operating temperature of -65 to $+250^{\circ}\text{F}$. To protect the weighing device from heat, it was mounted below the honeycomb and was suspended from the sample panel by means of four sheet metal straps. The entire load cell and its cable was wrapped with Permacel reflecting tape to protect it from accidental fuel spillage and fire.

The sample and the rest of the materials supporting it were seated directly on the load cell. The load is transferred by means of two stainless tubes which are supported by brass bushings (see Figure III-5) and linked to a single

tube through a strap (see Figure III-8). Enough clearance was allowed between the bushings and tubes to prevent gripping. The system, however, is seated on only one point (on the load cell) and the stainless tubes touch the bushings by leaning to one side or another. The vertical movement of the weighing system will therefore cause a friction introducing an error in weight measurement. The infinitesimal displacement of the system at any instant and the continuous resolution of the load cell plus a little vibration in the ignition cabinet caused by the vacuum pump prevented any significant error resulting from the tubes touching the bushings. This was found by calibration as discussed below.

The input power to the transducer load cell was supplied by a mercury cell. The output was recorded on a two-channel Honeywell Electronik 19 potentiometric recorder. One channel of this recorder was used for weight measurement, and the other channel was used for the temperature measurement. The input voltage to the load cell was altered, along with zero suppression of the recorder, such that the weight of the weighing system without a sample was recorded as zero. The adjustments were made such that the total span of the recorder was 100, 150 or 200 grams, depending on the weight of the sample. The accuracy of the recorder was ± 0.25 percent of span or 1 microvolt whichever was greater. The speed of recorder pen was reported to be less than 0.5 second for full scale step response. This pen movement was fast enough

to monitor the continuous weight and temperature change of the sample. The weighing system was calibrated by direct application of laboratory weights; its overall accuracy was within ± 0.5 gram.

Another system used in this study was the temperature measuring instrument. Details of the temperature measurement are given in Appendix C. In this section only the instrument and the technique of its application are briefly discussed. The Barnes Engineering Industrial Radiometer Model R-4D1 used in these experiments is an instrument that detects the infrared radiation from a target and thereby permits measurement of the surface temperature if the optical properties of the surface are known. It consists of two separate parts:

(a) The Radiometer Head: contains an optical system for collecting and focusing infrared radiation, a detector which converts this radiation into an electrical signal, a radiation reference source against which the detector is continuously standardized, and a preamplifier. The infrared detector is an optitherm thermistor bolometer having uniform sensitivity from ultra-violet through far infrared. A germanium absorption-edge filter is used to eliminate radiation of wavelengths shorter than 1.8 microns; thus measurements are not affected by reflected visible light but only by infrared radiation emitted or reflected from the target. The focusing on the target is accomplished by a concave

primary and a convex secondary mirror which are first-surface aluminized and hard coated. A focusing control moves the secondary mirror along the optical axis for rapid focusing from two feet to infinity.

(b) The Radiometer Amplifier Unit: consists of a vacuum tube voltmeter, a synchronous rectifier circuit with a feedback amplifier, a reference temperature monitoring circuit, power supplies and means for testing and calibration. The vacuum-tube voltmeter and the synchronous rectifier operate independently so that a meter reading and a recorder output signal are always simultaneously available.

The range of temperature measurement by this instrument is from ambient to 1200°C (normal range) and from ambient to 2200°C (extended range). Either of these ranges can be selected by the appropriate switch. This instrument is sensitive enough to detect temperatures with an accuracy of approximately 2 percent at temperatures above several hundred degrees Centigrade or 2°C for lower temperatures. It has a response time of 10 milliseconds, which is considered to be adequate for the present study.

The output signal of the radiometer was continuously recorded on the Honeywell Electronik 19, potentiometric recorder discussed previously in this section. The recorder was calibrated versus the amplifier vacuum-tube voltmeter by means of an internal calibration device. This calibration was checked frequently to ensure satisfactory performance of

the system (for calculation of temperature from recorded output see Appendix C).

The schematic diagram of figure III-9 shows a plan view of the radiometer-sample configuration for surface temperature measurement. A two-inch diameter viewing window was punched in the back of the cabinet, horizontal to the sample. The lateral position of the window was such that the sample could be seen at a 75° angle from normal to the sample. A sliding door, G, operated by choke wire mechanism, was provided to close off the viewing window until shortly before the sample was exposed to the radiation. The reason for this provision was that at small burner distances, flame was reflected to the radiometer by the sample shield and caused large fluctuation in the recorder output. This sliding door was always opened before the sample shields were pulled back to expose the sample to radiation. A baffle, F, blocked the direct radiation from flame to the radiometer at smaller burner distances.

The radiometer head, H, was mounted on a tripod and focused on the sample, A, from a focal distance of 56 inches. Focusing was accomplished by the optical system described above in connection with the radiometer head. The temperature measured on the face of the sample corresponds to the area as shown by the focusing light. For the adjusted focal distance of these experiments, this area was about $1/8$ square inch and was located about $1\frac{1}{2}$ inches from the top of the

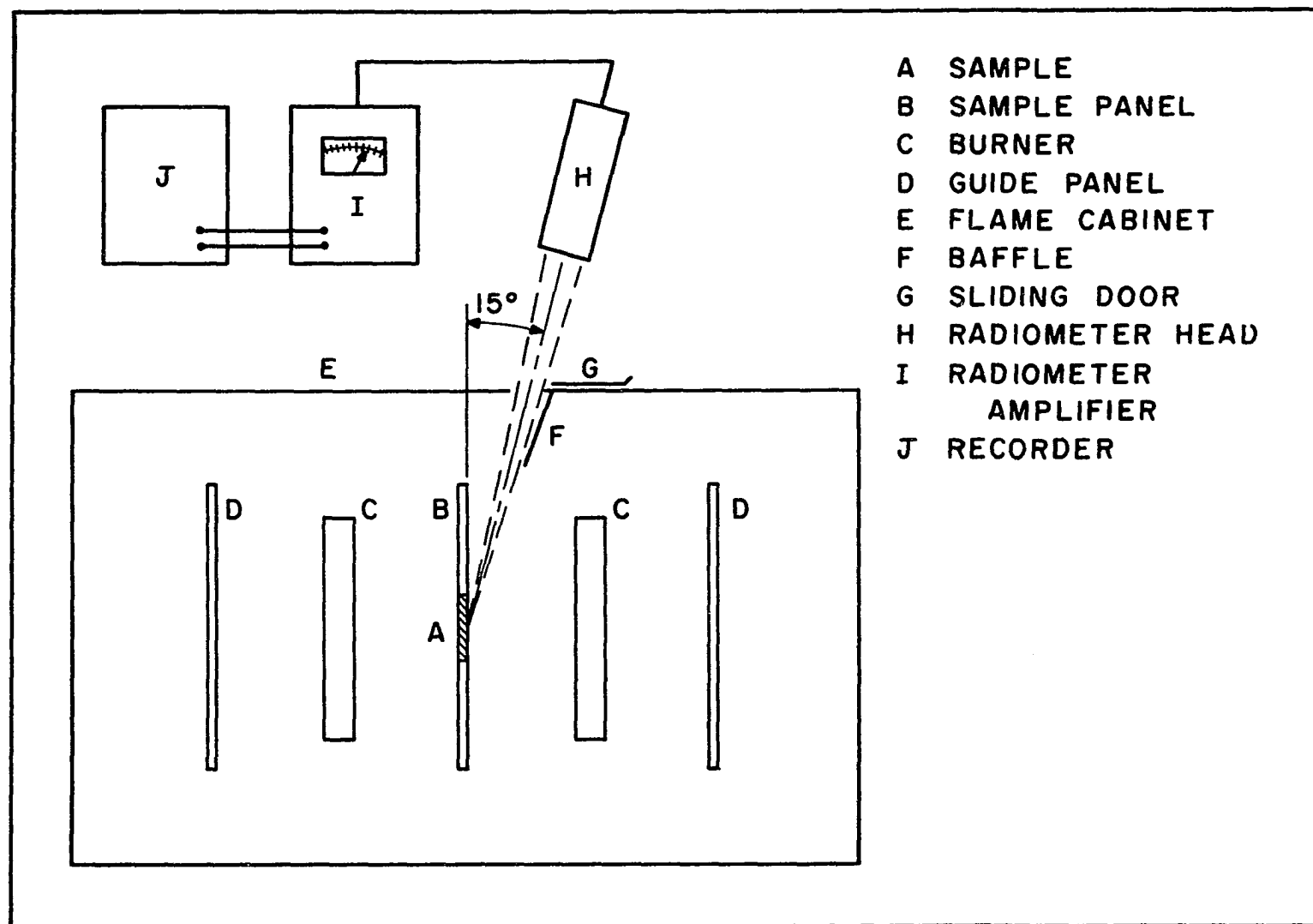


Figure III-9. Schematic Plan View of the Ignition Cabinet Showing the Relative Position of the Radiometer Head with Respect to the Ignition Cabinet.

sample and midway between the sides. The radiometer head and viewing window behind the cabinet can be seen in the photograph of Figure III-2.

The performance of the entire temperature measuring system was checked by means of a Barnes Engineering Model 11-101 Infrared Radiation Reference Standard. The operating limits of this source are from 20°C above ambient to 230°C. The radiometer-window configuration was simulated to the actual angle used in the ignition tests. The reference Standard was set at a known temperature and the radiometer was focused on the reference Standard. The recorded output signal was checked against the calibration curves. The procedure was repeated for several temperatures in the range 30 - 230°C; in all cases the response was within the reported accuracy of the instruments. In the photograph of Figure III-1, some of the instruments can be seen on a bench. From left to right they are: load cell instrument panel, recorder, radiometer amplifier, and infrared radiation reference Standard.

Another instrument used in this study was a Hy-Cal Engineering Asymptotic Rapid Response Calorimeter for irradiance measurement. The ignition cabinet was calibrated for the radiation flux received at the surface of the sample as a function of burner distance. Detailed information concerning this instrument, the procedure, and the results of the calibration are presented in Appendix A.

Experimental Procedure

The experimental technique used in this investigation differed from those used in previous ignition studies. Therefore, some of the difficulties encountered during the work will be discussed along with the experimental procedure.

The present study utilized one-dimensional samples of five species of wood. The samples of each species were cut from the same board in three different thicknesses of 1/2, 5/8 and 3/4 inch. The nominal exposed area of the samples was 3.9 by 3.9 inches. The shape of the samples and the way they fit into sample holder is shown in Figure III-10. Preliminary tests showed that some of the wood samples, especially oak and fir, crack along the grain and bend after they have been heated for some time. This bending and cracking disturbed the conditions of uniform irradiance and one-dimensional heating; it also prevented symmetrical heating during two-sided heating. The samples were maintained vertical in the holder throughout the tests by a tongue and groove joint as shown in Figure III-10.

Because some of the samples also expanded upward during the heating, the sides of the sample holder were made longer than the samples. A block of Fiberfrax was used as a top cover, as shown in Figure III-10, to prevent heating from the top. It was likewise free to move in the tongue

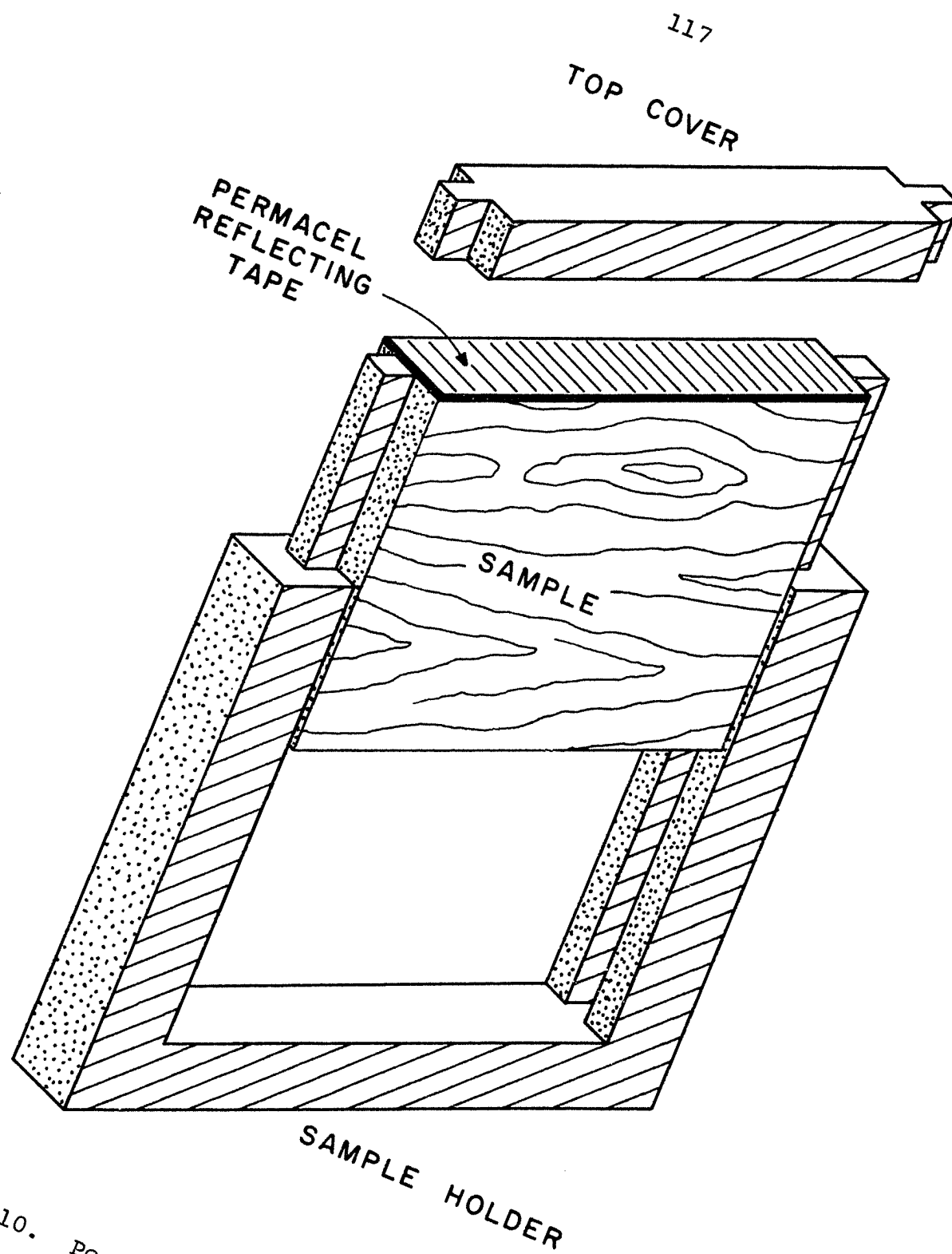


Figure III-10. Position of Sample in Sample Holder.

and groove joint to accomodate shrinkage and expansion. To prevent end effects in case of swelling of the top of the sample, a piece of Permacel reflecting tape was applied such that about 1/8 inch extended down on the faces of the sample (see Figure III-10).

The Permacel tape (Type PE-100) used in these experiments is an aluminum/glass cloth 6.5 mils thick which was specifically designed to reflect radiant heat. The tape is coated with a silicone pressure sensitive adhesive which did not disintegrate prior to ignition. It has been reported by manufacturers to cut the surface temperature rise to less than a factor of one-half that normally experienced. The weight of the tape for a piece 4 x 3/4 inches was less than 0.5 grams. The weight change of the tape due to soot deposit on its surface was found to be far below the experimental accuracy and did not affect the weight loss measurement.

All samples were left in an oven for 24 hours and dried at 102°C. Each was then individually wrapped in a polyethylene bag and several of the individually-wrapped samples were then put in another bag of larger size to ensure that dryness was maintained. For measurements of the properties of the samples, the reader is referred to Appendix B.

At the start of each day's test the exhaust fan was first started and the damper was left half open. The electronic equipment was then turned on and allowed to warm up.

The fuel tank was filled with fuel and the vacuum pump was started. After the instruments were warmed up the weighing system calibration was checked. The linearity of the recorded output from the load cell, and the reproducibility of the system, were examined by applying small weights to the sample holder and removing them. A typical test was carried out as follows: The sample was taken out of the polyethylene bag and positioned in the sample holder as shown in Figure III-10. At this point the focusing of the radiometer (the temperature measuring equipment) on the sample was checked by the focusing light as discussed in previous section. The radiometer was then switched to operating condition and the shields pulled over the sample. The three-way valve was opened and the burners were allowed to fill up to the desired level (about 1 centimeter from the top of the burners). The damper position was set according to the calibration table (see Appendix A). The start of the fire was marked on the recorder; also an electric stop watch was started at the same time. The damper position was adjusted with the timetable throughout the test. When the fires reached steady conditions the shields were pulled, exposing the sample to radiation from the flames (for discussion about the shielding period, refer to Appendix A). The irradiation of the sample was continued until it ignited or was completely charred. Immediately following ignition of the sample, the fires were extinguished and the sample was allowed to burn as long as it continued

flaming. The weight loss and the surface temperature were measured continuously.

According to calibration procedure, explained in more detail in Appendix A, every test started with the damper positioned at the same level. This setting was called starting position. At this starting position, the exhaust duct was open enough to pull all the fumes at the start of the fire. The damper was then opened at appropriate intervals to increase the air velocity through the cabinet. The adjustment of the damper was performed according to a standardized time table to assure the reproducibility of the tests. Opening of the damper in this manner was continued until ignition of the sample occurred. In about the first 50 tests, the damper position was left as it had been at the time of ignition. For the rest of the tests the damper position was returned to the starting position as soon as ignition occurred. No difference in behavior and characteristic of wood burning (after ignition) was noticed.

After the test was completed the recorder was switched to standby condition and the damper opened to permit faster cooling of the cabinet. The vacuum pump was turned off as soon as the fires were completely out. At the end of the test the contents of the vacuum tank were drained into a safety can and the vacuum pump suction filter, which had trapped the condensed vapors, was drained. The system was then ready for the next test.

For pilot ignition tests the pilots were adjusted to give a blue flame of about $1/2$ inch long under the test conditions. The position of the pilots was adjusted such that the tip of the flame was about $1/2$ inch above the sample and edge of the flame was about $1/4$ inch away from the sample. This arrangement is shown in the schematic diagram of Figure III-11.

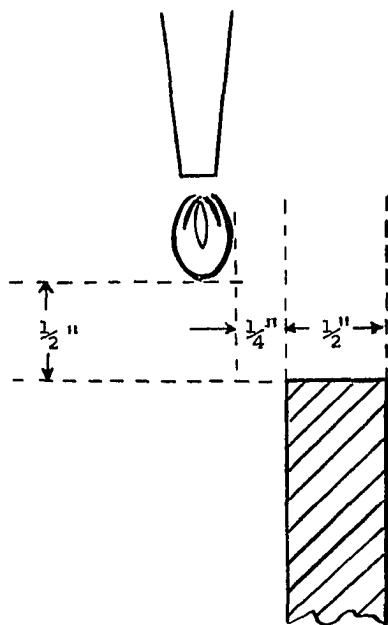


Figure III-11. The Relative Position of the Pilot with Respect to Sample.

For each species, the tests were carried out under conditions of one-sided and two-sided heating and for each of these conditions both spontaneous and piloted cases were studied. Besides these, the systematic variations included the changes in species, sample thicknesses, and irradiance levels.

No serious difficulties were encountered in these tests, but a few minor ones were. After about thirty runs, the edges of the burners above the liquid level were blackened

by soot deposits. The black edges absorbing more heat during the next runs caused higher boiling of the fuel, especially at the corners. The burners, therefore, tended to overflow even with a lower fuel level. Frequent scrubbing and cleaning the burners eliminated this problem. Another problem was the effect of north wind gusts outside the laboratory on the shape of the flames and their fluctuation. The exhaust duct ran through the attic to the north wall and was bent down outside the wall to prevent the accumulation of rain. The fluctuation of wind velocity caused an upset in the flame configuration and intensity although it was not very serious.

The shutdown of the unit at the end of the testing day was carried out by cooling the cabinet, turning off the radiometer, turning the recorder to standby position and draining all the fuel from the system into small safety cans.

CHAPTER IV

DISCUSSION OF RESULTS

A review of previous work on the ignition of combustible solids, as briefly discussed in Chapter II, revealed that:

1. All previous studies of ignition of combustible solids by radiation have utilized radiation sources such as gas-fired panel, tungsten lamp, carbon arc, solar furnace, etc. No ignition study has been made utilizing direct radiation from flames.

2. Throughout literature, references have been given to the work of the investigators who have calculated the rate of evolution of volatiles at ignition point. A fixed rate of volatile evolution at the instant when ignition occurs has been given as a criterion for ignition. No confirmation of this criterion with experimental measurement has been presented in the literature.

3. More recent articles have speculated about a fixed surface temperature criterion for ignition of cellulosic material. The speculation is based on theoretical analysis of heat transfer in an inert solid (no chemical decomposition) with several simplifying assumptions. No

experimental confirmation of surface temperature criterion has appeared in the literature.

4. Studies have shown the rate and mechanism of solid phase pyrolysis to be complex functions of heating rate, temperature, and several other experimental conditions. The pyrolysis prior to ignition in some cases was endothermic and in others exothermic. Information is lacking on heat of decomposition reactions prior to ignition. Other parameters necessary for the inclusion of the effect of thermal decomposition in the mathematical model such as activation energy and frequency factor are also difficult to obtain. Consequently most investigators have attempted to correlate the ignition data with an inert model.

The primary purpose of this investigation was to develop a new method for experimental study of ignition process by irradiating the samples with radiation from buoyant diffusion flames and to provide data for surface temperature and rate of evolution of volatiles from sample. The designed apparatus and the experimental procedure have been discussed in Chapter III.

Ignition Data

A summary of ignition data is given in Appendix D. Measurements have been made for irradiance H , ignition time t , surface temperature T_s , and weight loss of the sample. Irradiance measurements are described in Appendix A. Surface temperature and weight of the sample were measured

as functions of time. The details of temperature measurement are given in Appendix C and weighing measurements are discussed in Chapter III. Physical properties of samples were also determined experimentally and they are explained in Appendix B.

A typical recorder output for weight and temperature measurements of an ignition experiment is shown in Figure IV-1. The curve ABC shows the weight of the sample and the curve DEFGH shows the radiometer output for surface temperature. Point A shows the weight of the sample at the start of exposure time. Point B, a breakpoint on the weight curve, marks the weight of the sample at the instant of ignition. The slope of the curve at point B (approaching from the left) gives the rate of weight loss or evolution of volatiles just before ignition occurred. The slope at point B was found by the method of front-surface mirror image. The values of weight loss rate at the ignition points are reported in Table D-1. The letter C on the weight loss curve shows the area in which pyrolysis is reaching its lowest level and the sample flaming dies out. This area is not marked by a breakpoint. It is not known exactly how much of the volatiles have remained in the sample. Some of the weight loss around point C is due to the burning of charcoal to ash.

The jump between points D and E on radiometer output shows that the sample is exposed to radiation, and the curve between points E and F shows the surface temperature rise

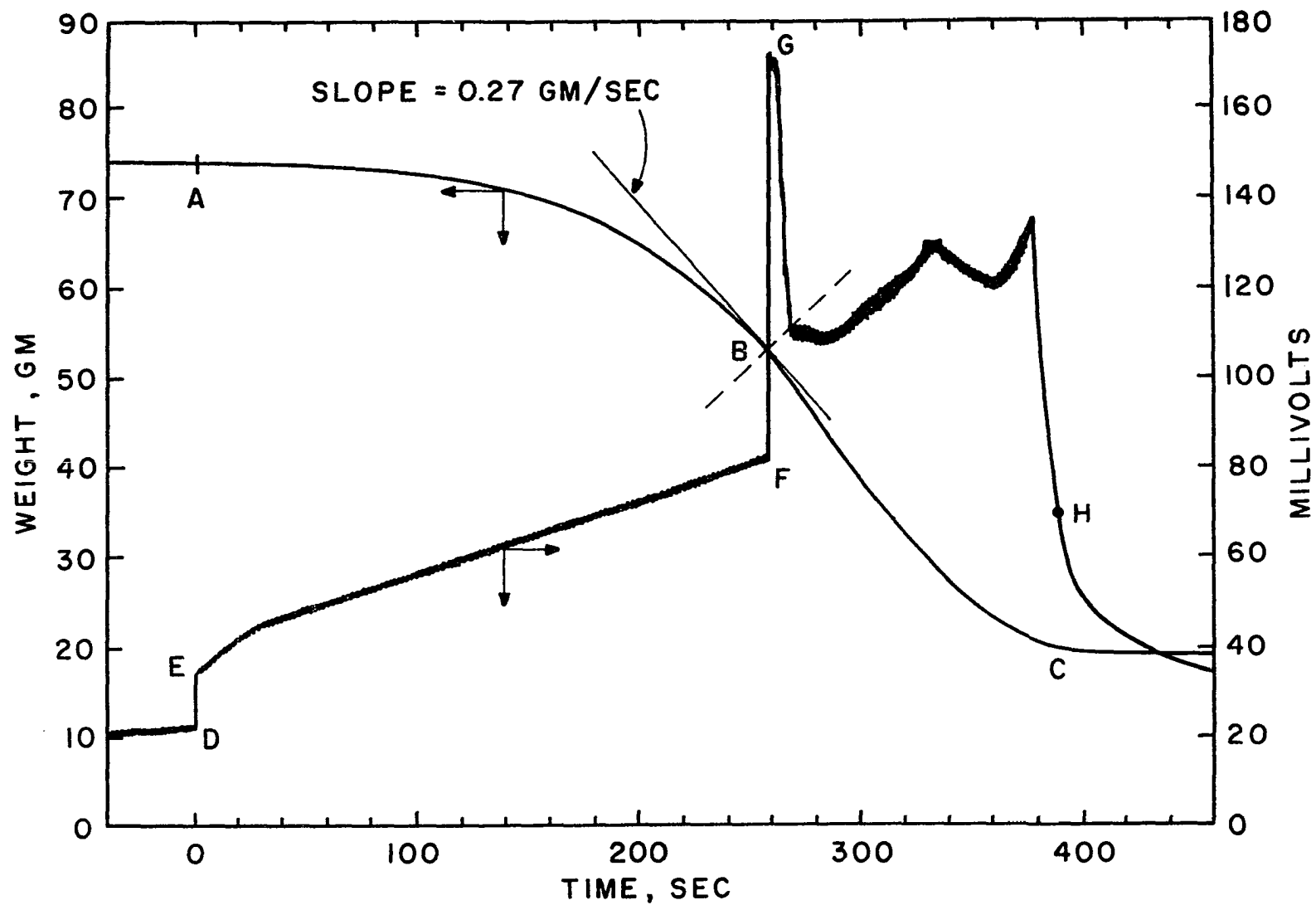


Figure IV-1. Typical Recorder Output for an Ignition Experiment (ABC, Weight Loss Curve; DEFGH, Temperature Curve).

prior to ignition. The breakpoint F denotes the temperature of the surface at ignition, which corresponds to point B on weight loss curve. Point G shows the instant that the flames supplying incident radiation were extinguished.

The missing numbers in the column of ignition time and subsequent columns in Table D-1 indicate that samples did not ignite. In these cases no breakpoints (B and F) on the recorded output data were observed. The weight loss curve changed curvature smoothly, which was normally accompanied by a change of curvature on the temperature curve, indicating that charcoal oxidation and glowing had started.

In some cases an upward change of curvature in the temperature curve and a rapid temperature rise were followed by ignition. In other words flaming occurred after the surface, especially at the corners and edges of the cracks, glowed. These tests are marked with an asterisk (*) in Table D-1. The samples that did not ignite, depending on the irradiance level, either glowed at the surface or continued to char until finally glowing appeared in some of its corners at the end of pyrolysis. Point H on the temperature curve marks the time that the sample flame died out, and it is noted that no significant pyrolysis and weight-loss is detectable after this time.

As noted in Table D-1, ignition experiments were carried out on five different species of wood. Nearly 300 ignition tests were made. The variation in experimental

conditions included one-sided and two-sided heating, pilot, and spontaneous ignition tests. At each of these conditions, and any irradiance, three samples of each species were usually tested.

Irradiance and Ignition Time Relationship

Figure IV-2 shows the typical relation between irradiance and ignition time. The data points shown in Figure IV-2 are averages of three tests. As irradiance is increased the ignition time is reduced. At high irradiance the slope of the curve approaches zero, showing that the change in ignition time is less significant at higher irradiance. On the other hand the ignition time rises rapidly with decreasing the irradiance. The left end of the curve becomes asymptotic to the line $H = H_0$ showing that below H_0 ignition will not occur. The value of H_0 has been termed "critical irradiance for ignition" and depends on the test condition (i.e., one-sided or two-sided heating, spontaneous or pilot ignition, heat losses from the surface, etc.). The critical irradiance, H_0 , refers to the condition where ignition time is infinitely long. However, it has been found by several investigators that if ignition does not occur in a reasonably short time (say about 30 minutes) it will not occur at all. If the volatile products of pyrolysis are exhausted before the conditions of flaming ignition can be satisfied in the gas phase near the solid, ignition will not occur. Therefore the minimum irradiance for which ignition

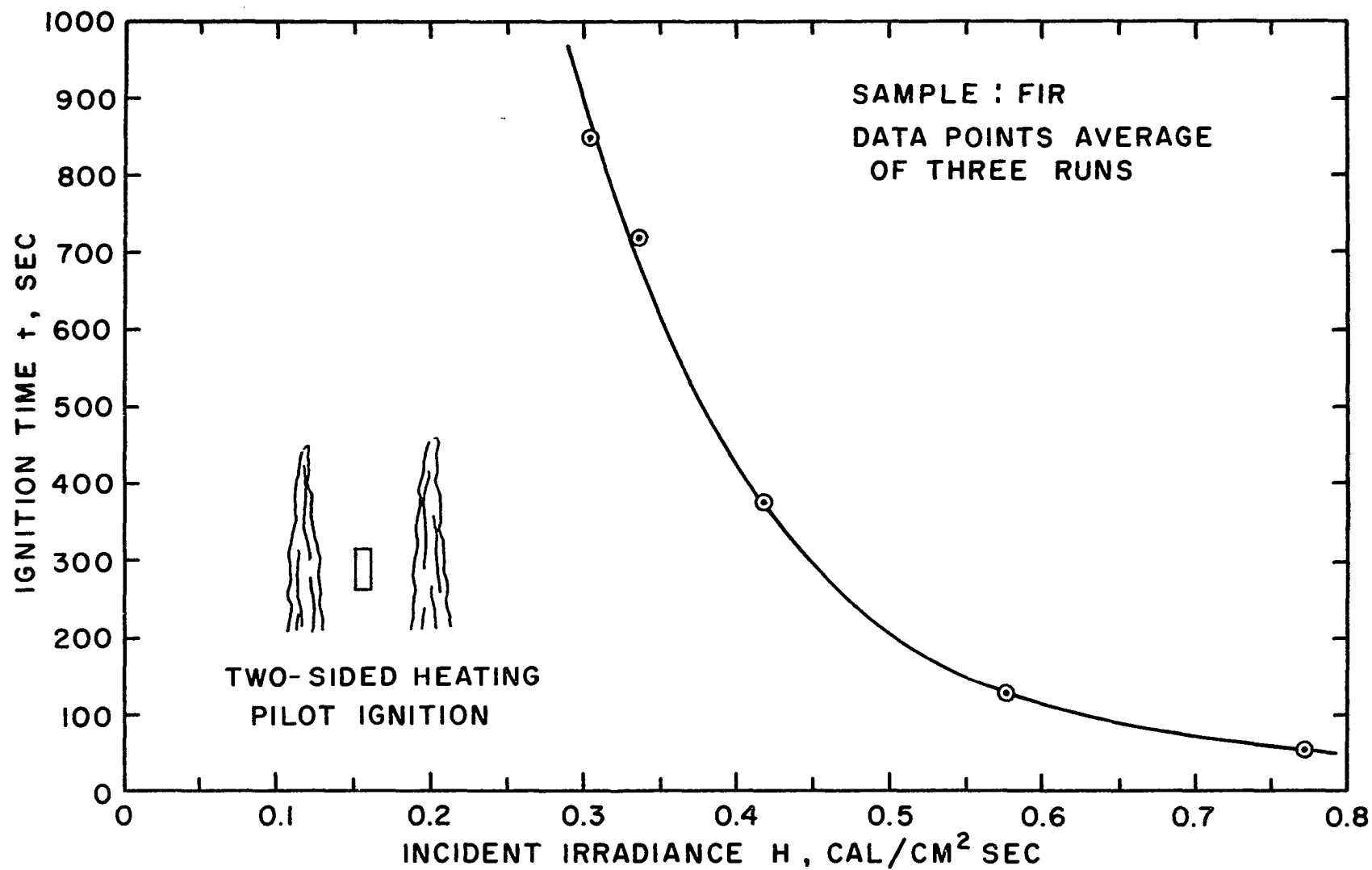


Figure IV-2. Typical Relation between Irradiance and Ignition Time (Two-Sided Heating, Pilot Ignition of Fir).

will occur is larger than the critical irradiance H_0 . In other words minimum irradiance marks the point below which ignition will not occur, whereas critical irradiance H_0 is only a hypothetical value for ignition at infinitely long exposure time. In order to estimate the "critical irradiance" a plot of irradiance against reciprocal of ignition time may be extrapolated to zero abscissa (infinite time). For the purpose of comparison the method adopted by Lawson and Simms (29) is employed and discussed below.

The equation for heat transfer in a semi-infinite, opaque and inert (no chemical decomposition) solid is

$$\alpha \frac{\partial^2 \Delta T}{\partial x^2} = \frac{\partial \Delta T}{\partial t} \quad (\text{IV-1})$$

(Newton's law of cooling for forced convection states the flux across the surface to be proportional to the temperature difference between the surface and the surrounding medium. Therefore, the expression $h(T_s - T_o)$ is frequently referred to as Newtonian type of cooling. The term Newtonian cooling with the above definition will be used in the discussions throughout this chapter).

If the sample is heated at the surface by a constant irradiance and the heat loss is expressed by Newtonian cooling the initial and boundary conditions become:

$$@ t = 0; \text{ for all } x; \Delta T = 0 \quad (\text{IV-2})$$

$$t > 0; x = 0; -K \frac{\partial \Delta T}{\partial x} = H - h \Delta T_s \quad (\text{IV-3})$$

$$t > 0; x \rightarrow \infty; \Delta T = 0 \quad (\text{IV-4})$$

where $\Delta T = T - T_o$

$$\Delta T_s = T_s - T_o$$

T = temperature

T_s = surface temperature

T_o = initial temperature = surrounding temperature

t = time

x = distance in x coordinate

H = irradiance

h = surface heat transfer coefficient

The solution to equation IV-1 with the initial and boundary conditions IV-2 through IV-4 is given by Carslaw and Jaeger (14, page 72) as

$$\frac{\Delta T}{H/h} = \operatorname{erfc} \frac{x}{2(\alpha t)^{1/2}} - e^{\left(\frac{hx}{K} + \frac{h^2 \alpha t}{K^2}\right)} \operatorname{erfc} \left[\frac{x}{2(\alpha t)^{1/2}} + \frac{h(\alpha t)^{1/2}}{K} \right] \quad (\text{IV-5})$$

where $\alpha = K/\rho c$ = thermal diffusivity

$$\operatorname{erfc} x = 1 - \operatorname{erf} x = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-\eta^2} d\eta = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-\eta^2} d\eta.$$

At the surface ($x = 0$), Equation IV-5 becomes

$$\frac{\Delta T_s}{H/h} = 1 - \exp \beta^2 \operatorname{erfc} \beta \quad (\text{IV-6})$$

where $\beta = h(\alpha t)^{1/2}/K = h\sqrt{t}/\sqrt{K\rho c}$. If β is large, following approximation can be used (14, page 483) for $\operatorname{erfc} \beta$

$$\operatorname{erfc} \beta = \pi^{-1/2} e^{-\beta^2} \left[\frac{1}{\beta} - \frac{1}{2\beta^3} + \frac{1 \cdot 3}{2^2 \beta^5} - \frac{1 \cdot 3 \cdot 5}{2^3 \beta^7} + \dots \right] \quad (\text{IV-7})$$

Neglecting all the terms but the first in the above series, Equation IV-7 becomes

$$\operatorname{erfc} \beta = \pi^{-1/2} e^{-\beta^2} \beta^{-1} \quad (\text{IV-8})$$

Substituting Equation IV-8 into Equation IV-6 results in

$$\Delta T_s = \frac{H}{h} \left[1 - \frac{1}{h} \left(\frac{K\rho c}{\pi t} \right)^{1/2} \right] \quad (\text{IV-9})$$

Lawson and Simms (29) applied Equation IV-9 to an infinite slab with the assumption that "there is no appreciable rise in temperature of the back surface during the experiment." Based on the assumption of constant surface temperature criterion for ignition, they plotted equation IV-9 in terms of H versus $H/\sqrt{t}$ and extrapolated the curves to $t = \infty$, i.e., $H/\sqrt{t} = 0$. The value of H at $H/\sqrt{t}=0$ was called

the critical irradiance. Similar plots were made from the data of the present study and are shown in Figures IV-3 through IV-5.

The values of critical irradiance for one-sided heating as reported by Lawson and Simms (29) were about $0.35 \text{ cal/cm}^2\text{sec}$ for pilot ignition and about $0.6 \text{ cal/cm}^2\text{sec}$ for spontaneous ignition. Figure IV-3 gives the critical irradiance for pilot ignition of this study to be about 0.32 which is slightly lower than that of Lawson and Simms. There were not enough data from present study available for spontaneous ignition with one-sided heating to permit extrapolation and comparison of results. However, the critical irradiances for two-sided heating as shown in Figure IV-4 and IV-5 were found to be much lower than those for one-sided heating (about half the values for one-sided heating). The critical irradiances for two-sided heating were about 0.15 and $0.33 \text{ cal/cm}^2\text{sec}$ for pilot and spontaneous ignition, respectively.

In order to generalize the irradiance-ignition time relationship, Lawson and Simms (29) then plotted the irradiance in excess of critical irradiance, $H - H_0$, against ignition time on log-log paper (these plots are not shown in their paper) and found straight line relationships. The slope and intercept of the line was related to physical properties of wood. The resulting equations, as presented in Chapter II, are

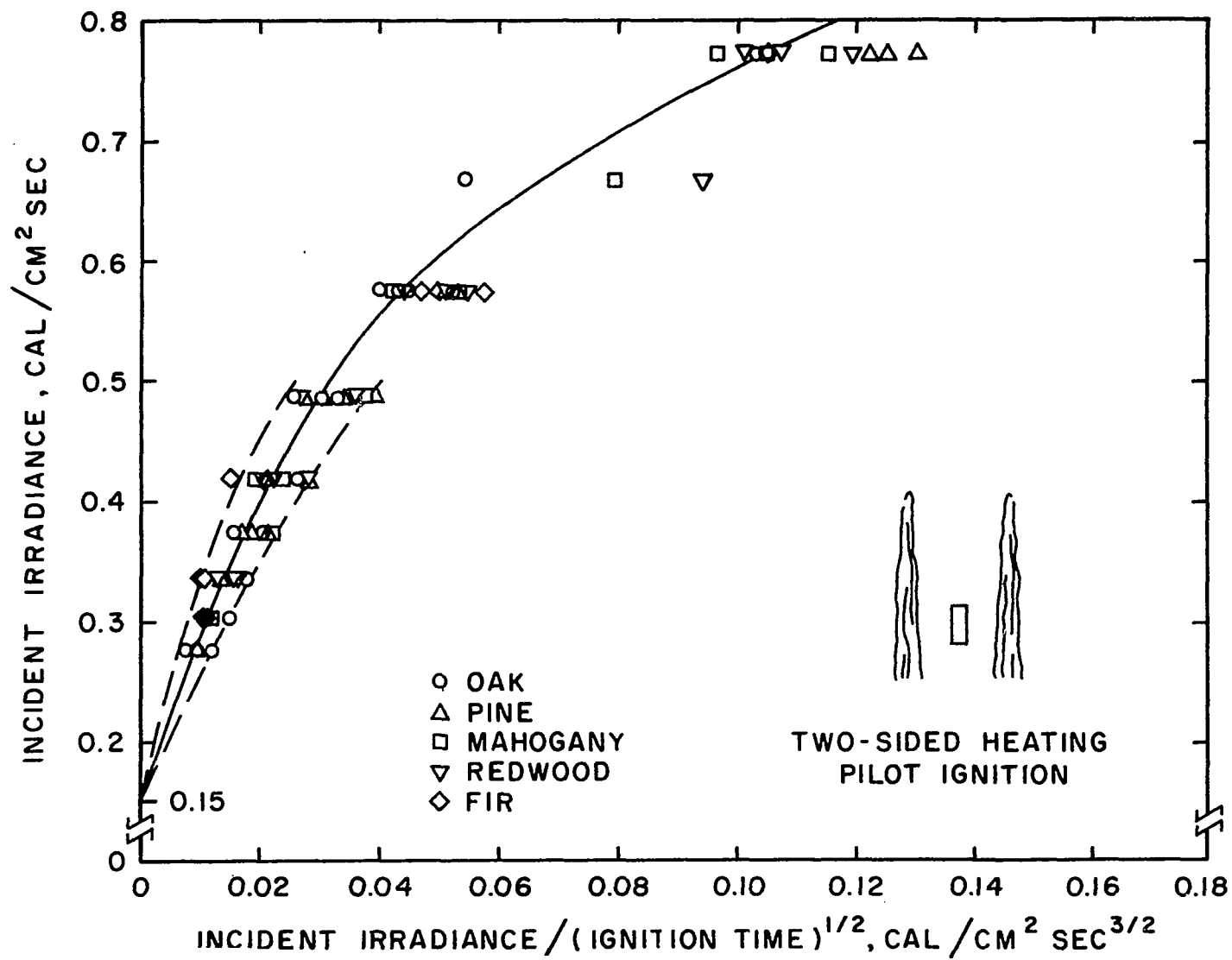


Figure IV-4. Curve for Determining Critical Irradiance (Two-Sided Heating, Pilot Ignition).

$$(H - H_p)t^{2/3} = 0.025 \times 10^6 (K\rho c + 68 \times 10^{-6}) \quad (\text{II-12})$$

and

$$(H - H_s)t^{4/5} = 0.05 \times 10^6 (K\rho c + 35 \times 10^{-6}) \quad (\text{II-13})$$

for pilot and spontaneous ignition respectively. In Equations II-12 and II-13, H_p and H_s refer to critical irradiance of pilot and spontaneous ignition respectively. The properties K , ρ and c as defined in Chapter II are in c. g. s. system.

Buschman (12) using the same method for correlation of his data on pilot ignition of wood found that the constants of the above equations are not the same for all materials, and therefore the Equations II-12 and II-13 cannot be generalized.

If the model described by Equation IV-9, and the assumption of constant surface temperature for ignition, were realistic the curves of Figures IV-3 through IV-5 in this study would be straight lines. The existence of curvature in these plots makes the extrapolation technique questionable and indicates that the assumption leading to Equation IV-9 and/or the postulation of constant ignition temperature were not correct. By referring to Simms' correlation (51, 52) for a semi-infinite solid, it is noted that the values of β are mostly less than unity. In this case the approximations, IV-7 and IV-8, are not justified.

However, extrapolation of the data to infinite time ($H\sqrt{t} = 0$) gives some indication of the critical irradiance which has the virtue of establishing the ignition limit. A critical irradiance for pilot ignition of one-sided heating (about 0.3 to 0.35 cal/cm²sec) as found by Lawson and Simms (29) has been used for estimation of safe separation distances between buildings in the "Building Regulation for Scotland" (55). Present study shows that for pilot ignition of two-sided heating the critical irradiance is about 0.15 cal/cm²sec which is half the value of one-sided heating. Considering that in some circumstances the materials are exposed to radiation from two different angles, the value of 0.15 cal/cm²sec is a safer figure to use.

Correlation of Ignition Data

In this section, an attempt is made to correlate the ignition data of present study. Since temperature is a main parameter in heat transfer problems, and its measurement was one of the primary objectives of this study, a brief analysis of experimental data for surface temperature is given first. Then, the dimensionless groups for correlation of data are derived from mathematical consideration of the problem. Finally, the recommended correlation for ignition data is presented.

Experimental Surface Temperature

As mentioned earlier in this chapter, surface temperature of the specimens was measured continuously during the

tests. The details of surface temperature measurement are given in Appendix C. The preignition data show that surface temperature rise is rapid at the start of exposure to radiation, then it levels off to a constant slope after a short time. The constant surface temperature rise normally continues until the ignition point where a discontinuity in the temperature-time curve appears. This behavior can be seen in the typical recorder output of Figure IV-1. The surface temperatures at ignition are tabulated in Appendix D.

In order to demonstrate the range and distribution pattern of surface temperature (ignition temperature), they were arbitrarily plotted against irradiance. These plots are shown in Figures IV-6 through IV-9. The tests in which glowing of the surface preceded the ignition generally have higher temperatures. In order to avoid inconsistency, these tests have been excluded from plots of Figures IV-6 through IV-9. These plots do not show the ignition temperature to be markedly dependent on species or irradiance levels within the experimental limits of this study. These plots further show that the ignition temperatures are evenly distributed within a band.

For the purpose of comparison, the average (arithmetic mean) and the range of ignition temperatures of Figures IV-6 through IV-9 are given in Table IV-1. Table IV-1 shows that the average ignition temperature of two-

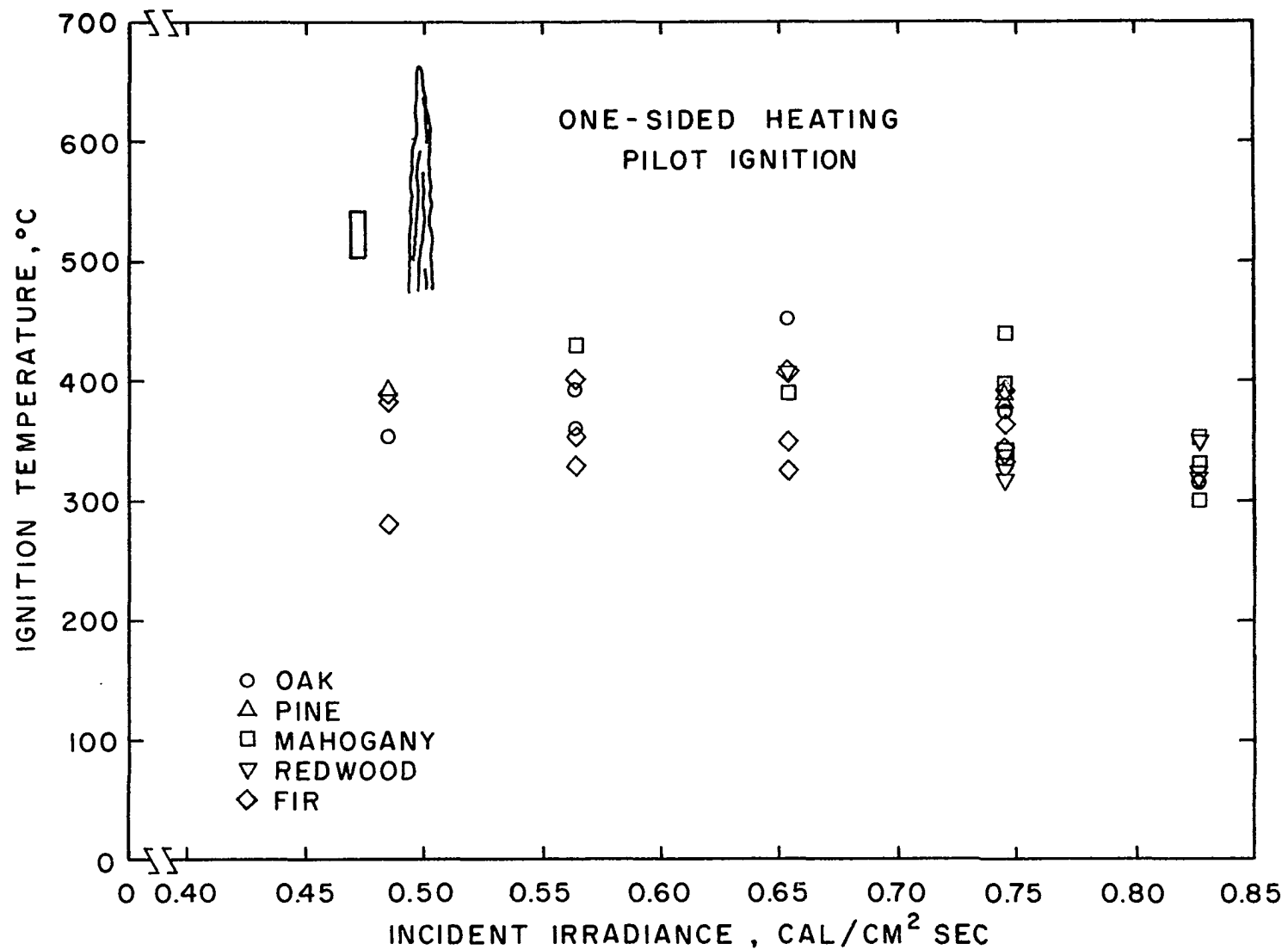


Figure IV-6. Ignition Temperature as a Function of Irradiance (One-Sided Heating, Pilot Ignition).

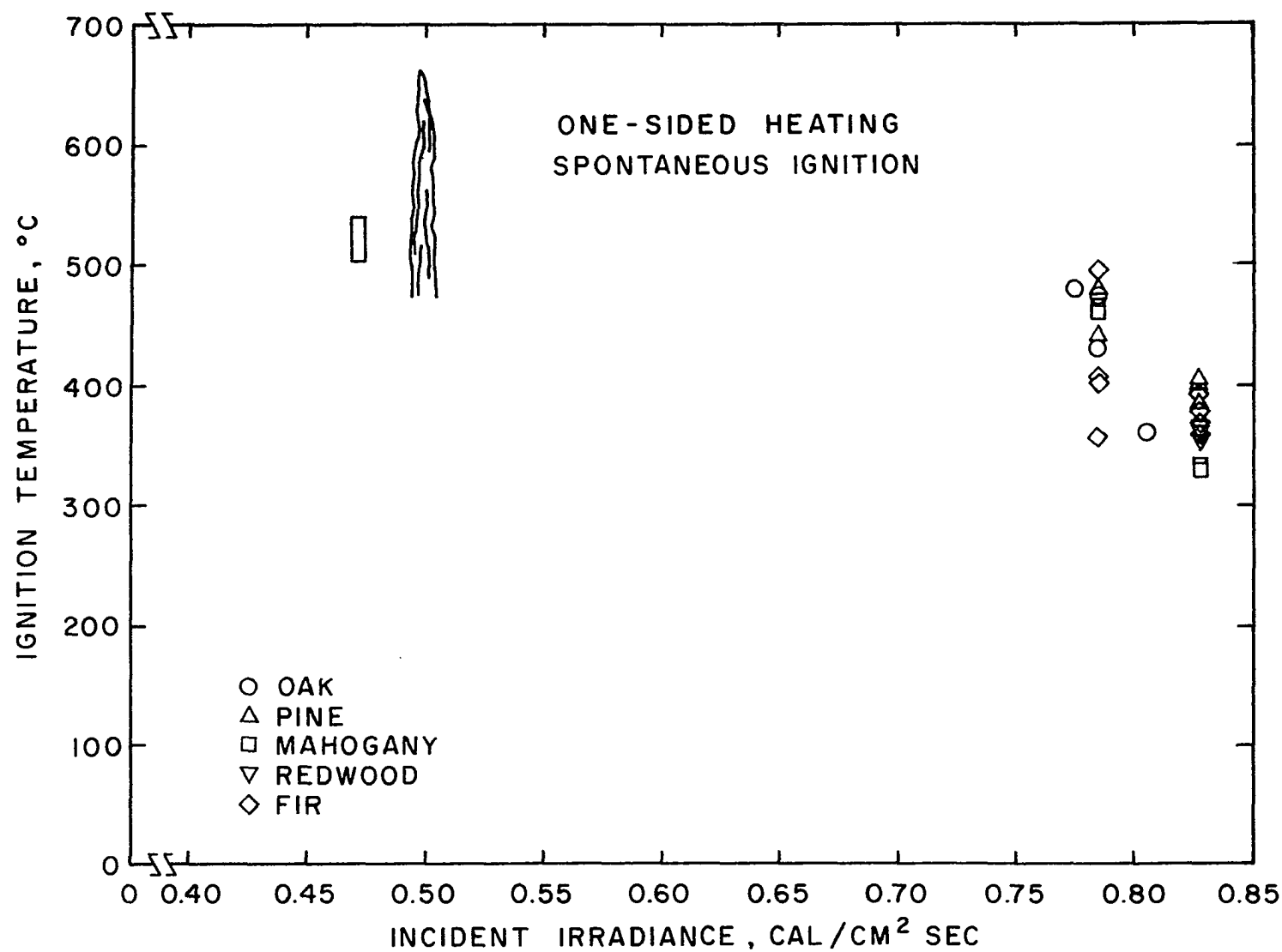


Figure IV-7. Ignition Temperature as a Function of Irradiance (One-Sided Heating, Spontaneous Ignition).

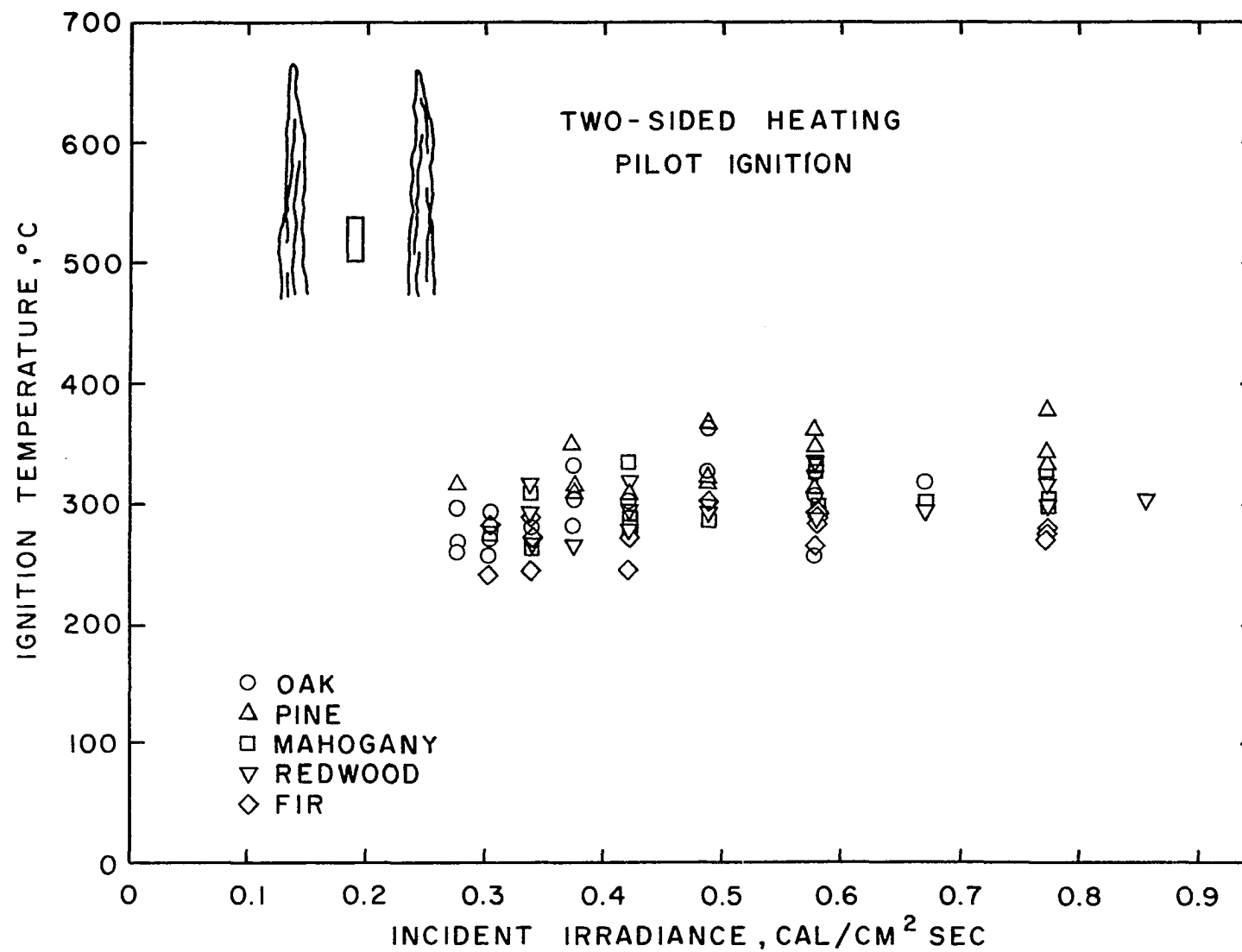


Figure IV-8. Ignition Temperature as a Function of Irradiance (Two-Sided Heating, Pilot Ignition).

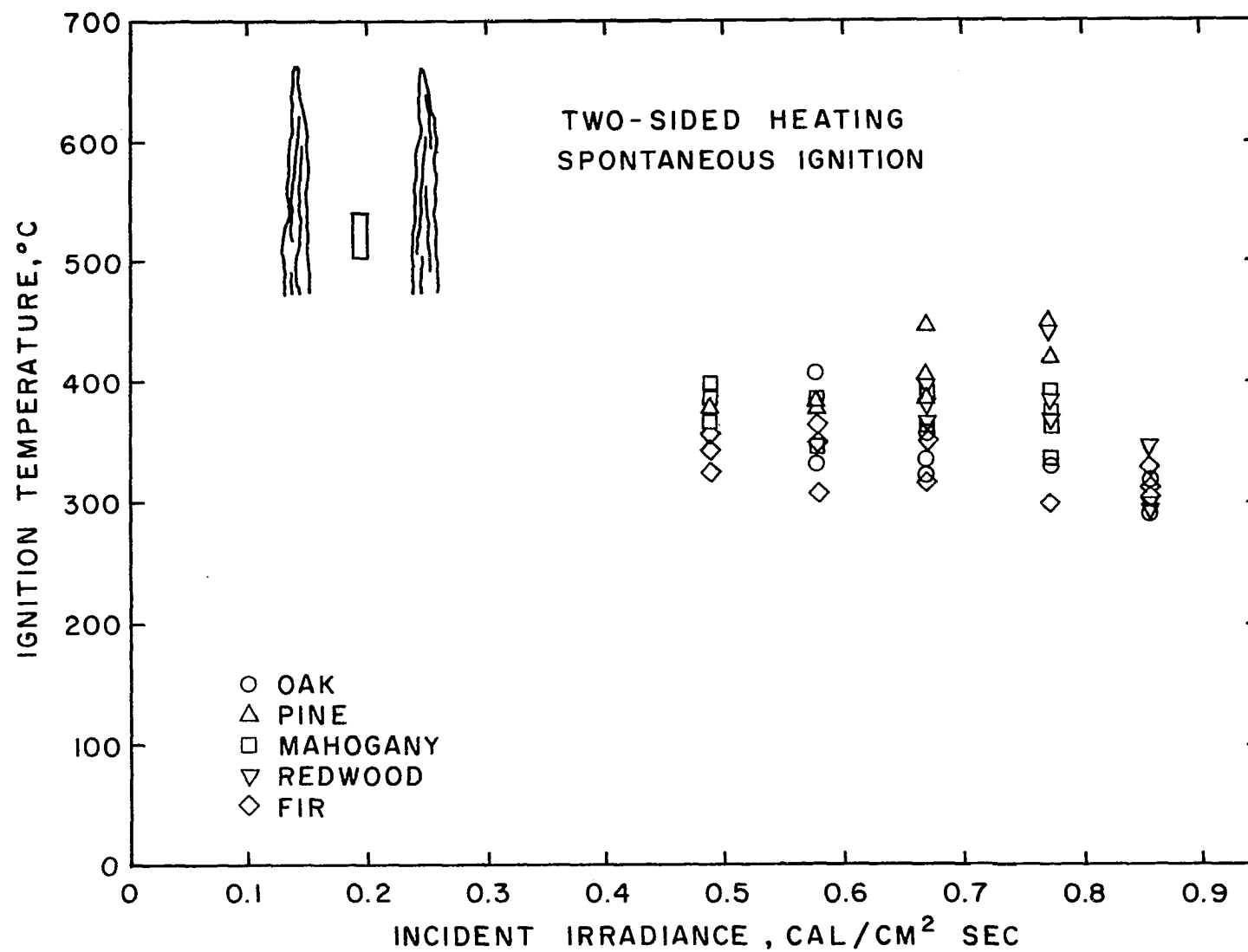


Figure IV-9. Ignition Temperature as a Function of Irradiance
(Two-Sided Heating, Spontaneous Ignition)

TABLE IV-1

EXPERIMENTAL SURFACE TEMPERATURE AT IGNITION

Experimental Condition	Average Temperature (°C)	Range of Temperatures (°C)
One-sided Heating -- Spontaneous Ignition	402	330-495
One-sided Heating -- Pilot Ignition	361	280-450
Two-sided Heating -- Spontaneous Ignition	360	290-450
Two-sided Heating -- Pilot Ignition	300	240-378

sided heating is lower than that of one-sided heating. Also average ignition temperature is lower in the case of pilot ignition as compared with spontaneous ignition. However, by comparing the ranges of ignition temperatures, one cannot conclude such behavior to be necessarily true in general. In other words, although pilot ignition temperature is generally lower than spontaneous ignition temperature, there are cases where pilot ignitions have higher temperature than spontaneous ignitions. The same argument holds for the cases of one-sided and two-sided heatings.

Mathematical Models

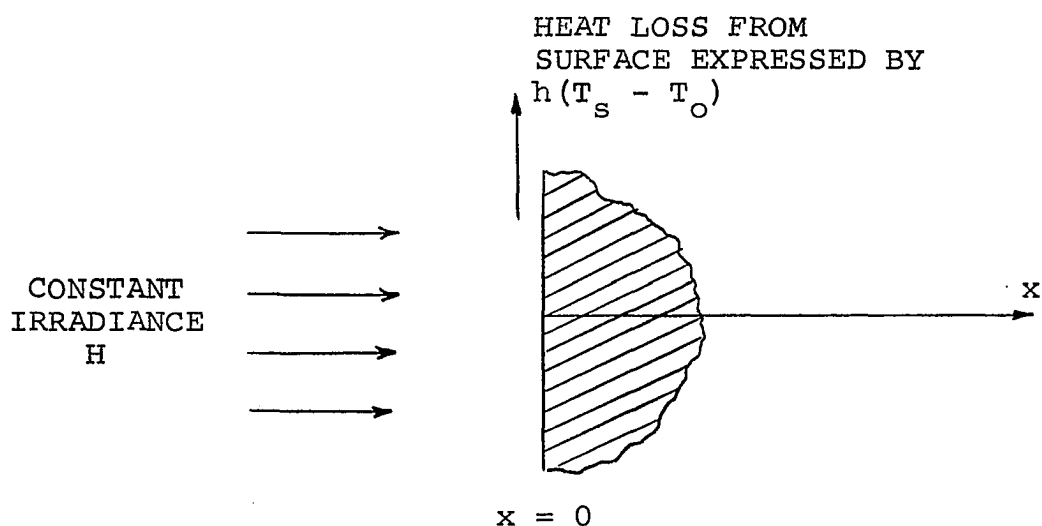
The complete equations describing the ignition phenomena are not amenable to analytical solutions because

of the complexity of process. Pyrolysis of combustible solids involves chemical reactions with measurable rates. Reaction acts as a source or sink depending on whether it is exothermic or endothermic. Pyrolysis at any depth of the sample depends not only upon the temperature at that depth but also upon the time interval at that temperature. The physical and chemical properties of the material are dependent on both time and position. Even with the simplifying assumption of properties being independent of temperature, the equation describing the ignition process is a nonlinear partial differential equation. Consideration of phase change and migration of moisture and gaseous products within the material and several other factors add to the complexity of the problem. However, in order to correlate the ignition data it is desirable to reduce the number of variables by grouping them into dimensionless quantities. Dimensionless groups can be found either by dimensional analysis or from analytical solution of the differential equation describing the process. Ignoring some of the effects such as chemical reaction, it may be possible to find a set of dimensionless variables that correlates the ignition data.

Therefore, in attempts to correlate the ignition data and in order to find the dimensionless groups which are best for correlation, several simplified mathematical models are examined. In these models the physical properties

of the solid are assumed to be constant and uniform. These models are discussed briefly in the following paragraphs.

Model 1: Semi-infinite, opaque, inert solid (no chemical decomposition or phase change) which is irradiated at the surface, and for which the heat losses can be expressed by Newtonian cooling as illustrated below:



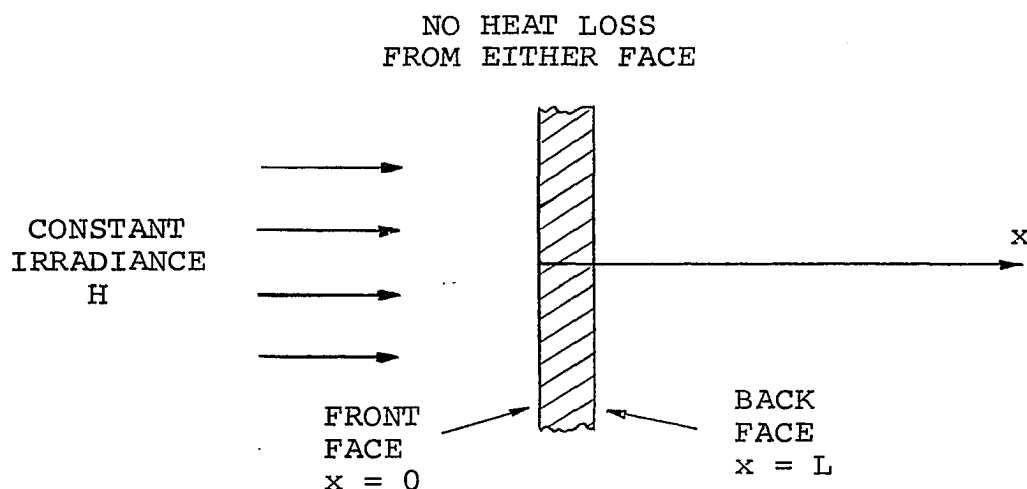
This model was formulated by Equations IV-1 through IV-4 earlier in this chapter. It is the same model used by Simms (51, 52) for his constant surface temperature criterion, and therefore, an analysis of present data with this model is appropriate .

The surface temperature, in this case, is given by Equation IV-6 which can also be written in dimensionless form as

$$\frac{H\sqrt{t}}{\Delta T_s / \sqrt{K\rho c}} = \frac{\beta}{1 - \exp \beta^2 \operatorname{erfc} \beta} \quad (\text{IV-10})$$

where $\beta = h\sqrt{t} / \sqrt{K\rho c} = \text{cooling modulus}.$

Model 2: An infinite slab of thickness L irradiated at the surface ($x = 0$) and without any heat loss. The solid is again assumed to be opaque and inert. This model is illustrated as follows:



The equations for this model are

$$\alpha \frac{\partial^2 \Delta T}{\partial x^2} = \frac{\partial \Delta T}{\partial t} \quad (\text{IV-1})$$

with the initial and boundary conditions

$$@ t = 0; 0 \leq x \leq L; \Delta T = 0 \quad (\text{IV-11})$$

$$t > 0; x = 0; -K \frac{\partial \Delta T}{\partial x} = H \quad (\text{IV-12})$$

$$t > 0; x = L; \frac{\partial \Delta T}{\partial x} = 0 \quad (\text{IV-13})$$

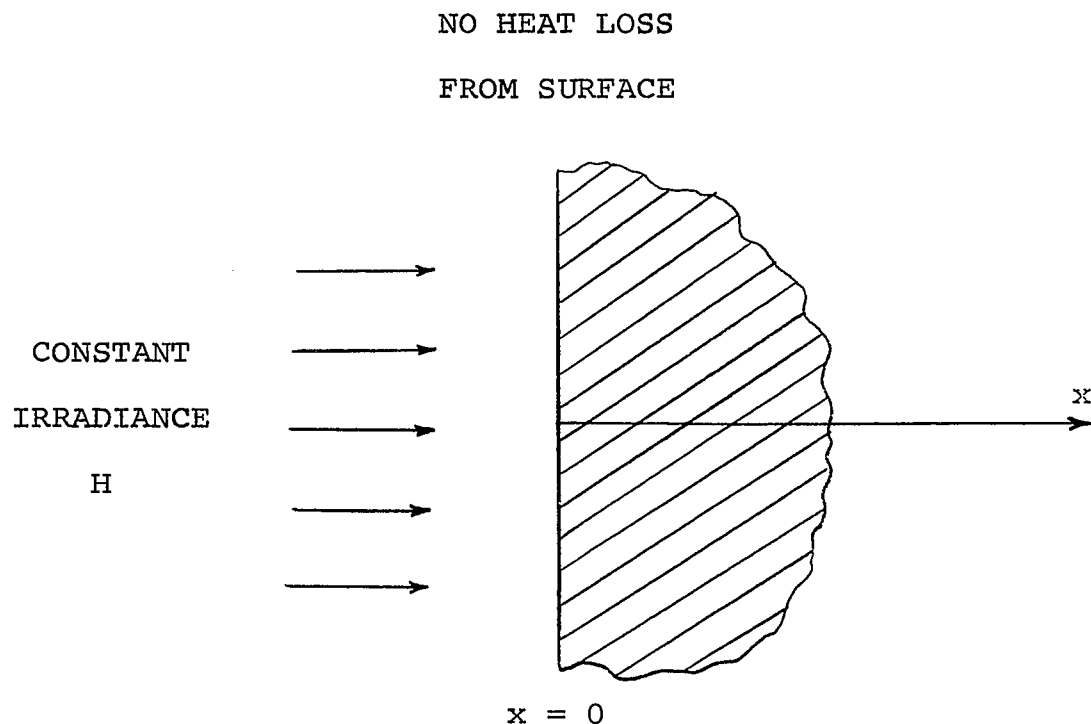
For two-sided heating the same model and boundary conditions are applicable to half of the sample because heating is symmetrical. Therefore in the case of two-sided heating L

is taken as half of the thickness of the sample. The surface temperature rise for this case is given by Carslaw and Jaeger (14, page 112) as

$$\frac{\Delta T_s^K}{HL} = F + \frac{1}{3} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 \pi^2 F} \quad (\text{IV-14})$$

where $F = \alpha t/L^2 = \text{Fourier modulus.}$

Model 3: The same as Model 1 (semi-infinite, opaque and inert solid) except that no losses are assumed.



In this case the boundary condition of Equation IV-3 becomes

$$t > 0; x = 0; -K \frac{\partial \Delta T}{\partial x} = H \quad (\text{IV-15})$$

The surface temperature rise for this case is given by Carslaw and Jaeger (14, page 75) as

$$\Delta T_s = \frac{2H}{K} \left(\frac{\alpha t}{\pi} \right)^{\frac{1}{2}} \quad (\text{IV-16})$$

It should be noted that in cases of semi-infinite solids the thickness L does not appear in the solution. However, for the purpose of comparison of Model 3 and Model 2, both sides of the Equation IV-16 are multiplied by K/HL to obtain

$$\frac{\Delta T_s K}{HL} = \frac{2\sqrt{F}}{\sqrt{\pi}} = 1.1284 \sqrt{F} \quad (\text{IV-17})$$

where again $F = \alpha t/L^2 = \text{Fourier modulus}$. The thickness L in Equation IV-17 (a semi-infinite model) can be thought of as a characteristic distance from surface.

Plots of Equations IV-10, IV-14 and IV-17 which refer to Models 1, 2 and 3 respectively are shown in Figure IV-10. It is noticed that for the value of $\sqrt{F}$ less than 0.6 the presumed Models 2 and 3 behave alike. In other words, for $\sqrt{F} < 0.6$ a slab of inert material is thick enough to be considered semi-infinite.

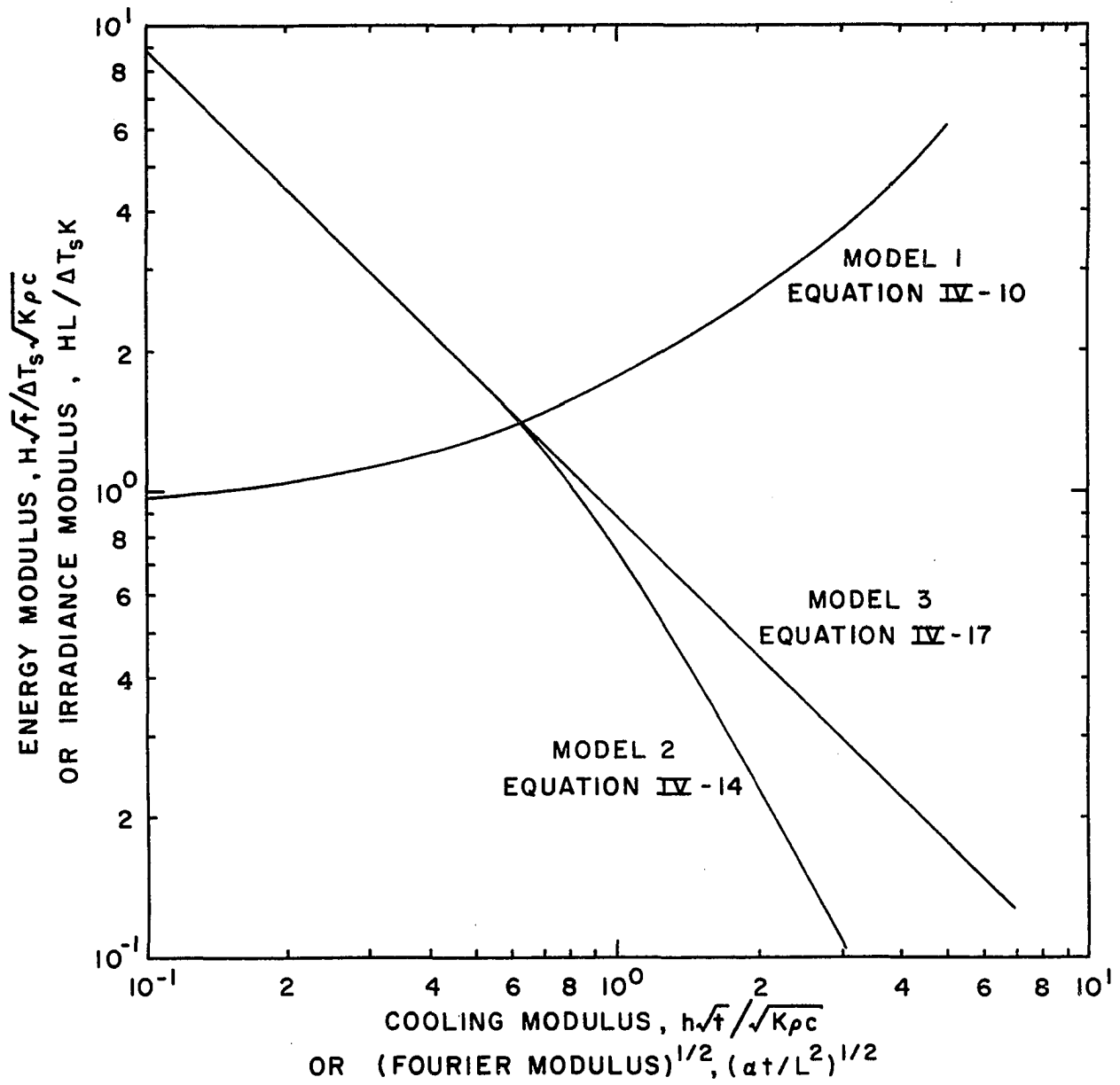


Figure IV-10. Theoretical Curves of Equations IV-10, IV-14 and IV-17.

Correlation of Ignition Data Based on Mathematical Models

In this part, all ignition data of the present study (Table D-1) are correlated with the aid of the dimensionless groups suggested by the mathematical models discussed in the previous section. Figure IV-11 gives the correlation of the ignition data for one-sided heating plotted as $H\sqrt{t}/\Delta T_s \sqrt{K\rho c}$ versus $h\sqrt{t}/\sqrt{K\rho c}$. A surface heat transfer coefficient $h = 0.0008 \text{ cal/cm}^2\text{sec}^\circ\text{C}$ --identical to Simms--was used so that the present results could be compared with his data (51, 52). The theoretical curve of Equation IV-10 correlating these dimensionless groups is also superimposed to show the deviation of experimental values. The correlation of Figure IV-11 is relatively poor and also has the disadvantage of group $\sqrt{t}/\sqrt{K\rho c}$ appearing in both ordinates. Although some of the variables always appear in several dimensionless groups, any correlation of experimental data with the groups in which the same major variable appears in both ordinates is viewed with suspicion. For example, if $\sqrt{t}/\sqrt{K\rho c}$ is plotted versus $\sqrt{t}/\sqrt{K\rho c}$ in cartesian coordinates, a straight line with the slope of unity is produced. If the x-coordinate is multiplied by h , which is a constant, the slope of the straight line is changed. Now when the y-coordinate is multiplied by the variable $H/\Delta T_s$, it may scatter the data around the straight line and make the correlation appear better than it really is. In the case of Simms' correlation (51, 52) ΔT_s was also a constant

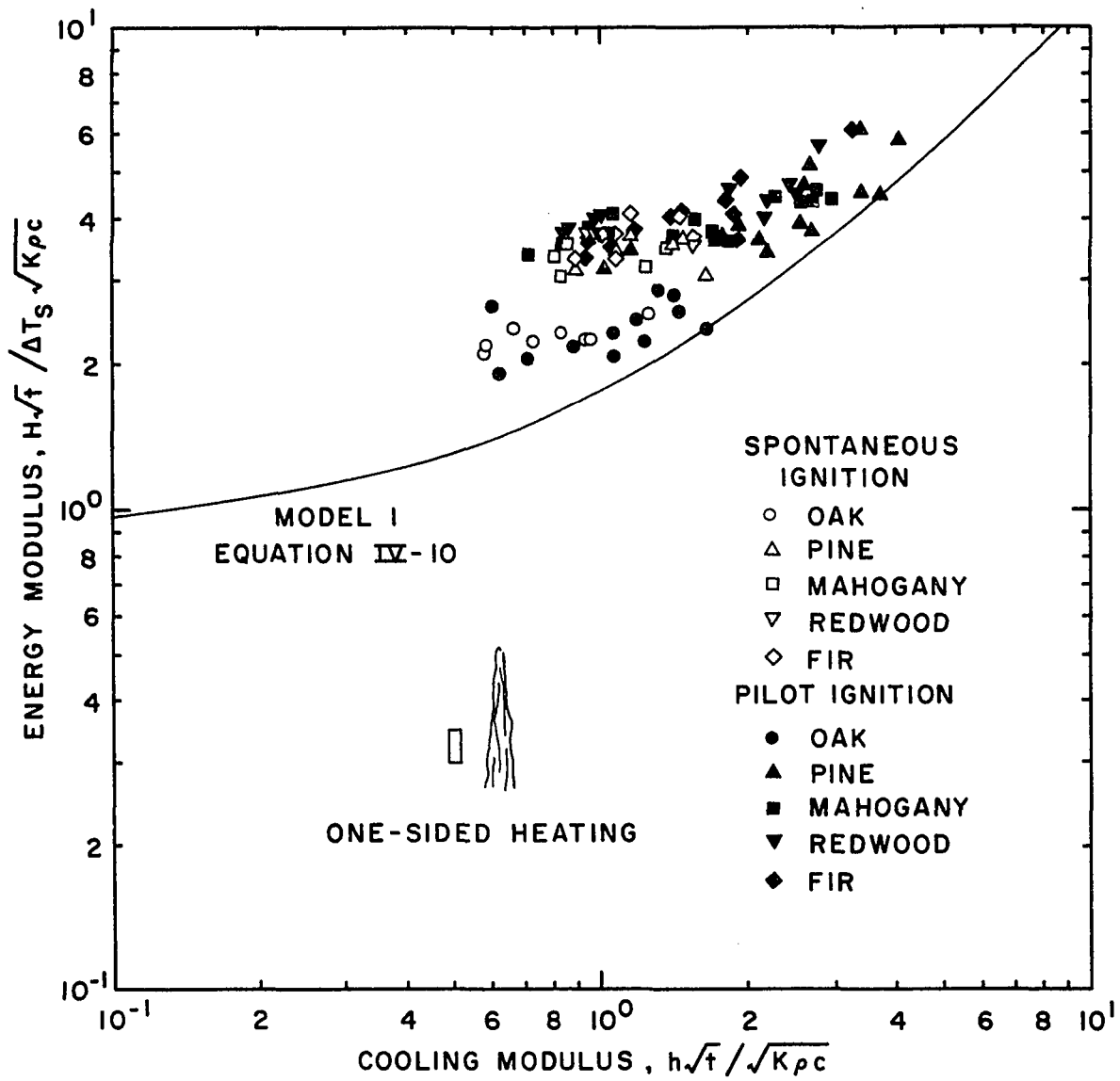


Figure IV-11. Correlation of Ignition Data Based on Equation IV-10 [Suggested by Simms (51,52)].

value. Therefore, if one has to use the same variables in both ordinates, he must make sure that some variables are not overshadowed by others. Further discussion of Model 1 is postponed until other dimensionless groups have been tried.

Equations IV-14 and IV-17 both suggest the correlation of the data with irradiance modulus $HL/\Delta T_s K$ versus the square root of Fourier number or dimensionless time variable $(\alpha t/L^2)^{1/2}$. In this case the time variable appears only in one of the moduli. Figures IV-12 and IV-13 give the correlations of ignition data based on these moduli. Figure IV-12 gives the correlation for one-sided heating and Figure IV-13 for two-sided heating. The quantity L in these groups is the thickness of the sample in the case of one-sided heating and half thickness for symmetrical heating.

The correlations of Figure IV-12 show that $(\alpha t/L^2)^{1/2}$ for almost all of the ignition data of one-sided heating is less than 0.6. In this region, for the appropriate ignition times, the thickness L is large enough so that the sample behaves as semi-infinite (the smallest size was 0.5 inch thick). In other words, up to the time of ignition heat has not penetrated enough to reach the back face of the sample. In two-sided heating (Figure IV-13), where L is half the thickness of the sample, the range of $(\alpha t/L^2)^{1/2}$ extends up to about 2.0 for lower irradiances and longer ignition times. However, these data do not show any marked tendency to bend down as predicted by the theoretical curve of Equation IV-14

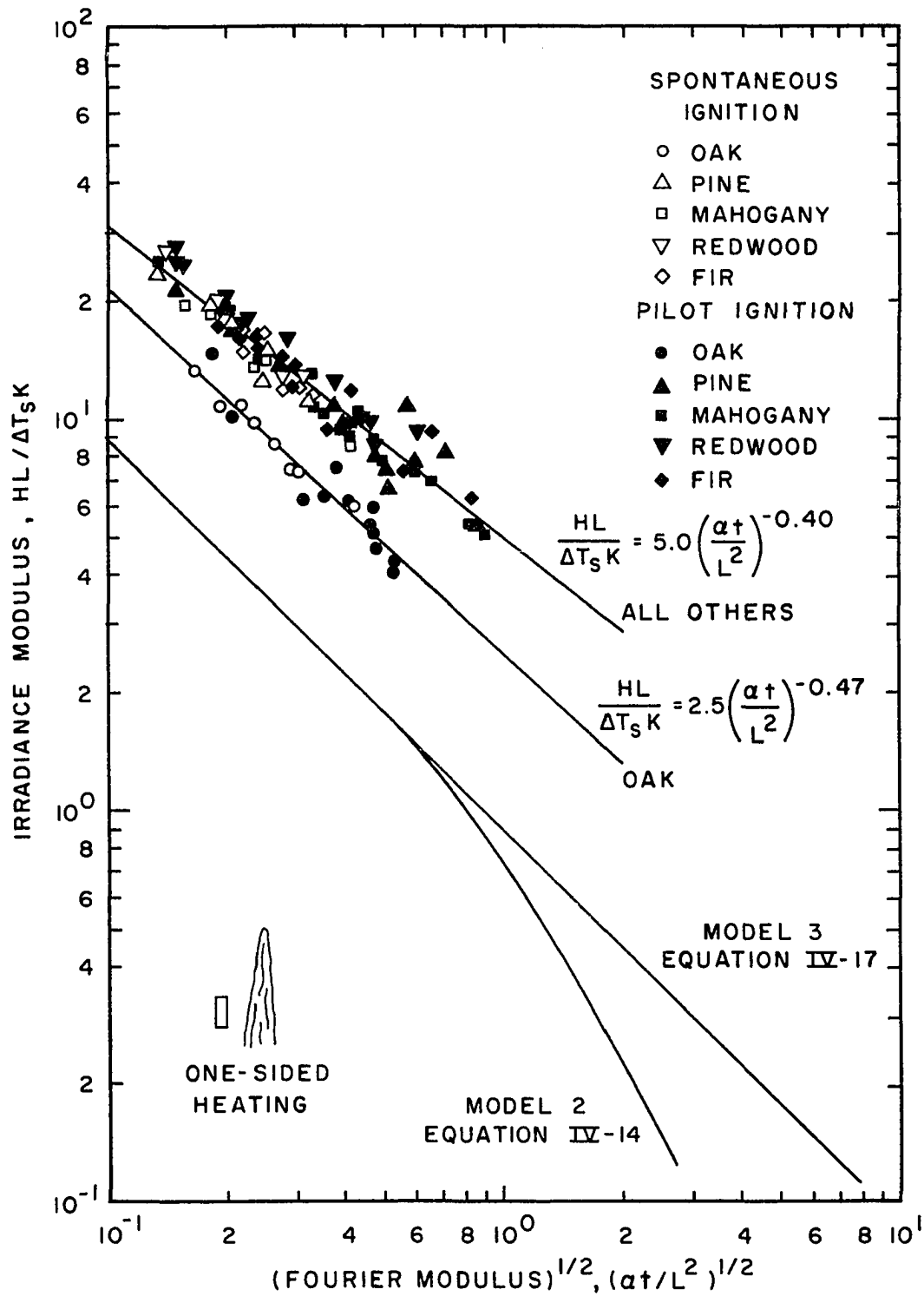


Figure IV-12. Recommended Correlation of Ignition Data Based on Equation IV-14 (One-Sided Heating).

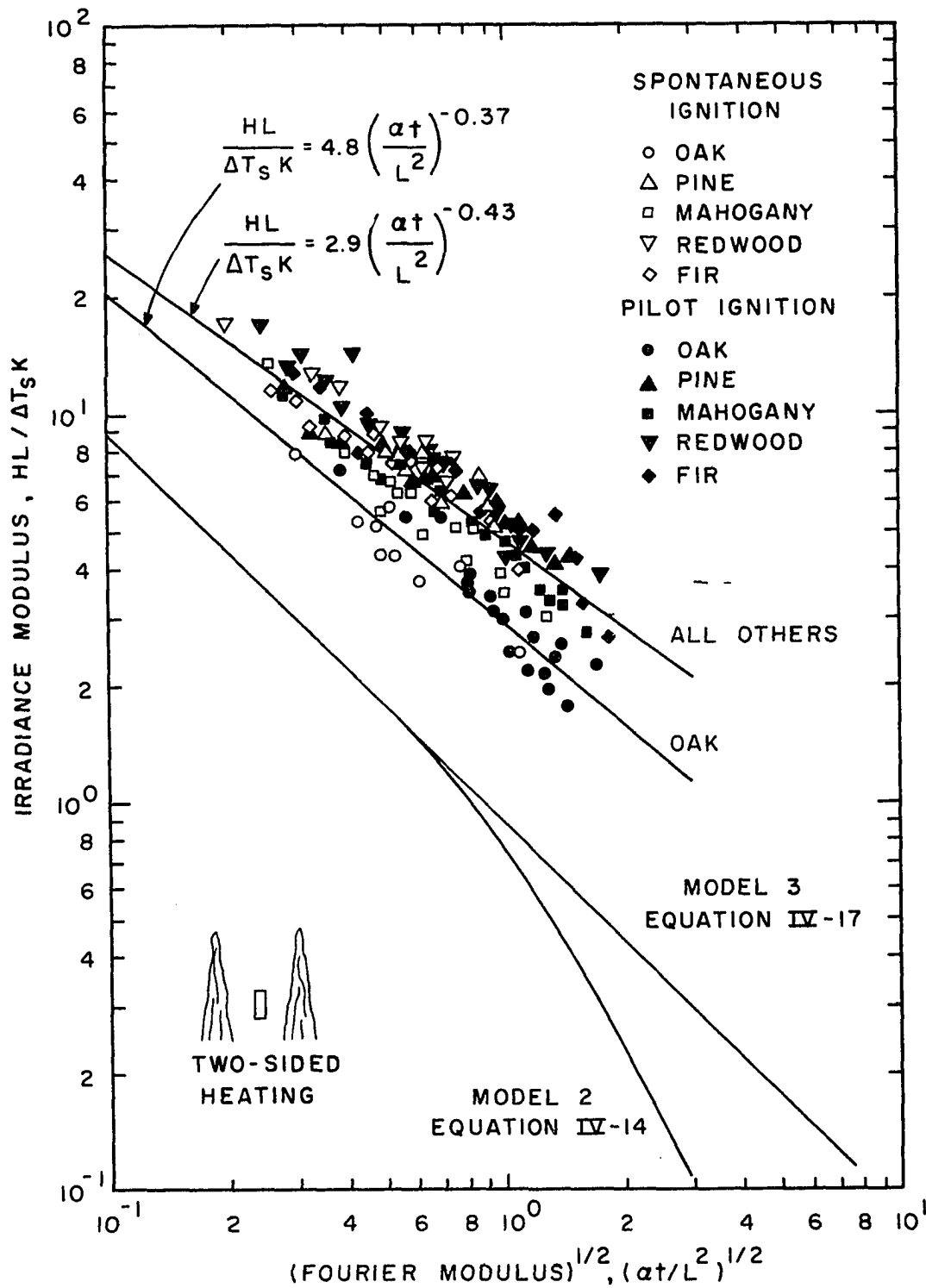


Figure IV-13. Recommended Correlation of Ignition Data Based on Equation IV-14 (Two-Sided Heating).

for an infinite slab.

A striking characteristic of ignition data as shown in plots of Figures IV-11 through IV-13 is that oak, with the highest density (or highest thermal conductivity), falls on the lower side of the data. The same behavior is noticed in the data of Simms (55) for pilot ignition. The data of other species, however, do not separate from each other although it is noticed that pine and redwood (lower density) are mostly above the line, but fir and mahogany are below the line (in Figures IV-12 and IV-13). Since the temperature range was the same for all species and physical properties appear in the dimensionless groups, the data separation according to density indicates that the rate of chemical reaction of pyrolysis, and overall heat of reaction, are dependent on density or grain structure of wood. MacLean (36) in investigating a number of hardwoods and soft woods also found that hardwoods disintegrate more rapidly than soft woods.

Correlations of Figures IV-12 and IV-13 are relatively good as compared with other correlations in the literature. It should be noted that both pilot ignition and spontaneous ignition follow approximately the same correlations. Although the time for pilot ignition is generally shorter than that for spontaneous ignition for the same irradiance level, the value of irradiance modulus is correspondingly increased (caused by a decrease in temperature) such that both

spontaneous and pilot ignition fit in the same pattern. The lines drawn through the data plotted in Figures IV-12 and IV-13 are found by the least square method. A separate line was found for oak because of its significant difference in properties (primarily density and grain structure) from the other species.

Every data point appearing on Figures IV-12 and IV-13 refers to the ignition point of one sample. The temperature-time data prior to ignition have not been shown in these plots. In order to see whether the process prior to ignition can really be described by the heat transfer model employed, the same dimensionless groups were calculated for all ignition tests at 30-second intervals. Several checks with different tests showed that the data prior to ignition also follow the same pattern of correlation. Figure IV-14 for example, gives a few points from each test for one-sided heating. The lines drawn through the data in this plot are the same lines as in Figure IV-12.

Butler et al. (13) worked with another dimensionless group, the energy modulus, $Ht/\Delta T_s \rho cL$, which is obtained by dividing both sides of the Equation IV-14 by Fourier number $\alpha t/L^2$ to obtain

$$\frac{\Delta T_s \rho cL}{Ht} = 1 + \frac{1}{F} \left[\frac{1}{3} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 \pi^2 F} \right] \quad (\text{IV-18})$$

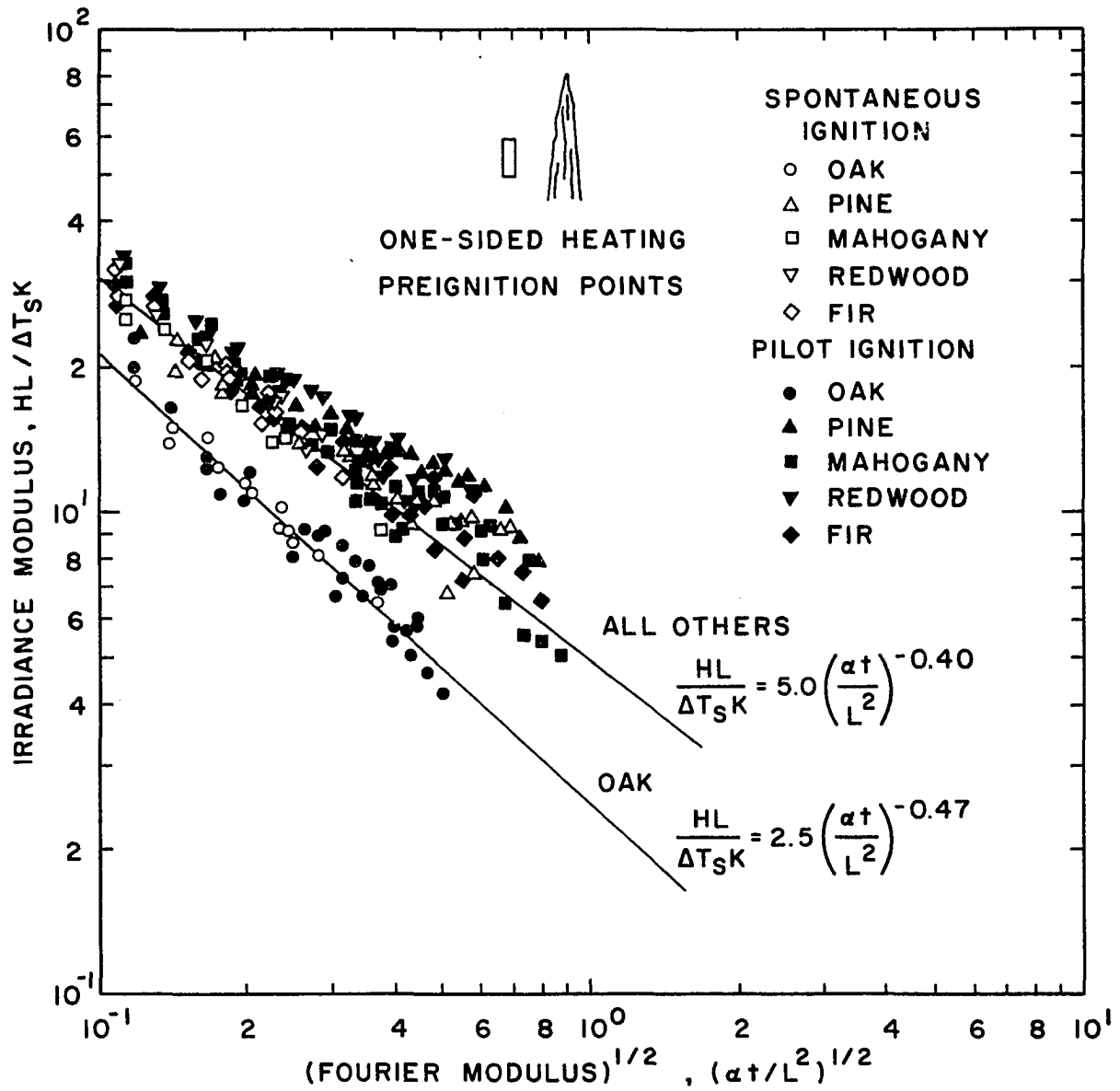


Figure IV-14. Correlation of Preignition Points Based on Equation IV-14 (One-Sided Heating).

By using the energy modulus, $Ht/\Delta T_s \rho cL$, one has in effect multiplied the y-coordinate of Figures IV-12 and IV-13 by the Fourier number $\alpha t/L^2$, i.e.,

$$\left[\frac{Ht}{\Delta T_s \rho cL} \right] = \left[\frac{HL}{\Delta T_s K} \right] \cdot \left[\frac{\alpha t}{L^2} \right] \quad (\text{IV-19})$$

$$\left[\begin{array}{c} \text{Energy} \\ \text{Modulus} \end{array} \right] = \left[\begin{array}{c} \text{Irradiance} \\ \text{Modulus} \end{array} \right] \cdot \left[\begin{array}{c} \text{Fourier} \\ \text{Modulus} \end{array} \right]$$

In this case time will appear in both ordinates so that the total energy, rather than the irradiance, is being calculated.

However, instead of using the energy modulus, $[Ht/\Delta T_s \rho cL]$, Butler et al. (13) employed an incomplete energy modulus, $Ht/\rho cL$. Their reasons for dropping ΔT_s from energy modulus were: (a) " . . . certain difficulties attendant on attaching physical significance to ΔT_s and its arbitrary selection based on a very limited knowledge of the processes." (b) It is more appropriate to use a dimensionless group in which one of the thermodynamic or kinetic quantities is incorporated. Such a group can then reflect the chemical potential of the materials in the reactions that are anticipated. Because of the lack of appropriate thermochemical data and failure to find a good substitute for ΔT_s (which they had to assume), Butler et al. sacrificed the property of a dimensionless group and used the group $Ht/\rho cL$.

For the purpose of comparison, the incomplete energy modulus, $Ht/\rho cL$, for the present study was calculated and plotted versus the square root of Fourier modulus. These plots are shown in Figures IV-15 and IV-16. It should be mentioned that the data of Butler et al. (13), shown for comparison, were for ignition of thin sheets (12-30 mils) of blackened alpha-cellulose of 0.73 gm/cm^3 nominal density, irradiated on one face by a source which simulated a nuclear pulse. Their samples had been irradiated in the range of about $3\text{-}25 \text{ cal/cm}^2\text{sec}$ for which the ignition time was within $0.1\text{-}1.0 \text{ sec}$. However, the agreement of the data appears to be good and shows that "ignition energy-time" relationships with physical properties correlate the same in the experimental region considered.

Correlation of Weight Loss Data

As described in Chapter III, samples were weighed continuously throughout the ignition tests. The slope of weight curve at any time gives the rate of evolution of volatiles at that time (see Figure IV-1). The rate of weight loss at the ignition point (approaching from the left) was measured by the front surface mirror image method and are tabulated in Appendix D in terms of $\text{gm/cm}^2\text{sec}$. The weight loss data, as well as surface temperature prior to ignition, are on file at the Flame Dynamics Laboratory, University of Oklahoma Research Institute.

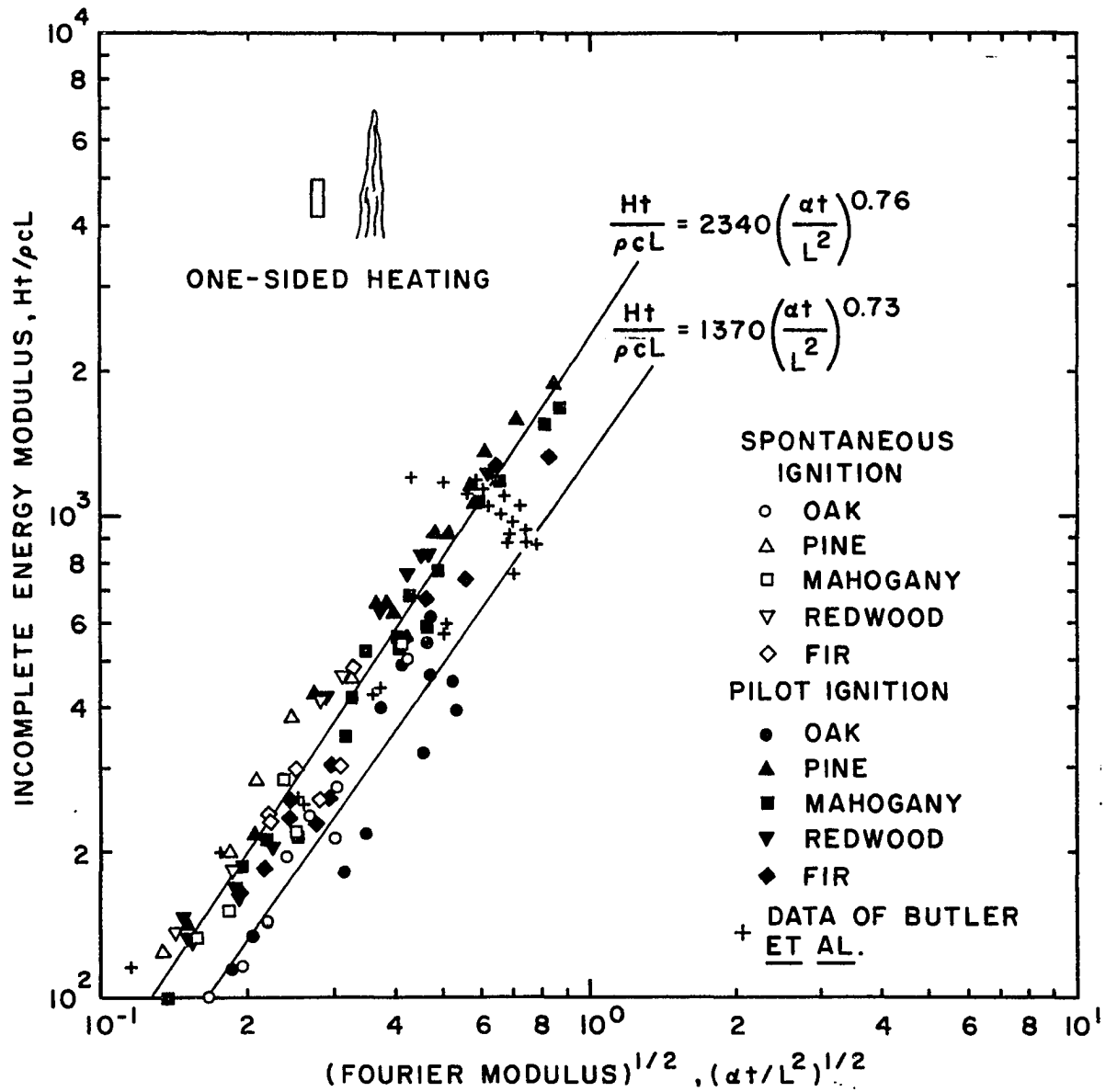


Figure IV-15. Comparison of Ignition Data of Present Study with the Data of Butler et al. (13) (One-Sided Heating).

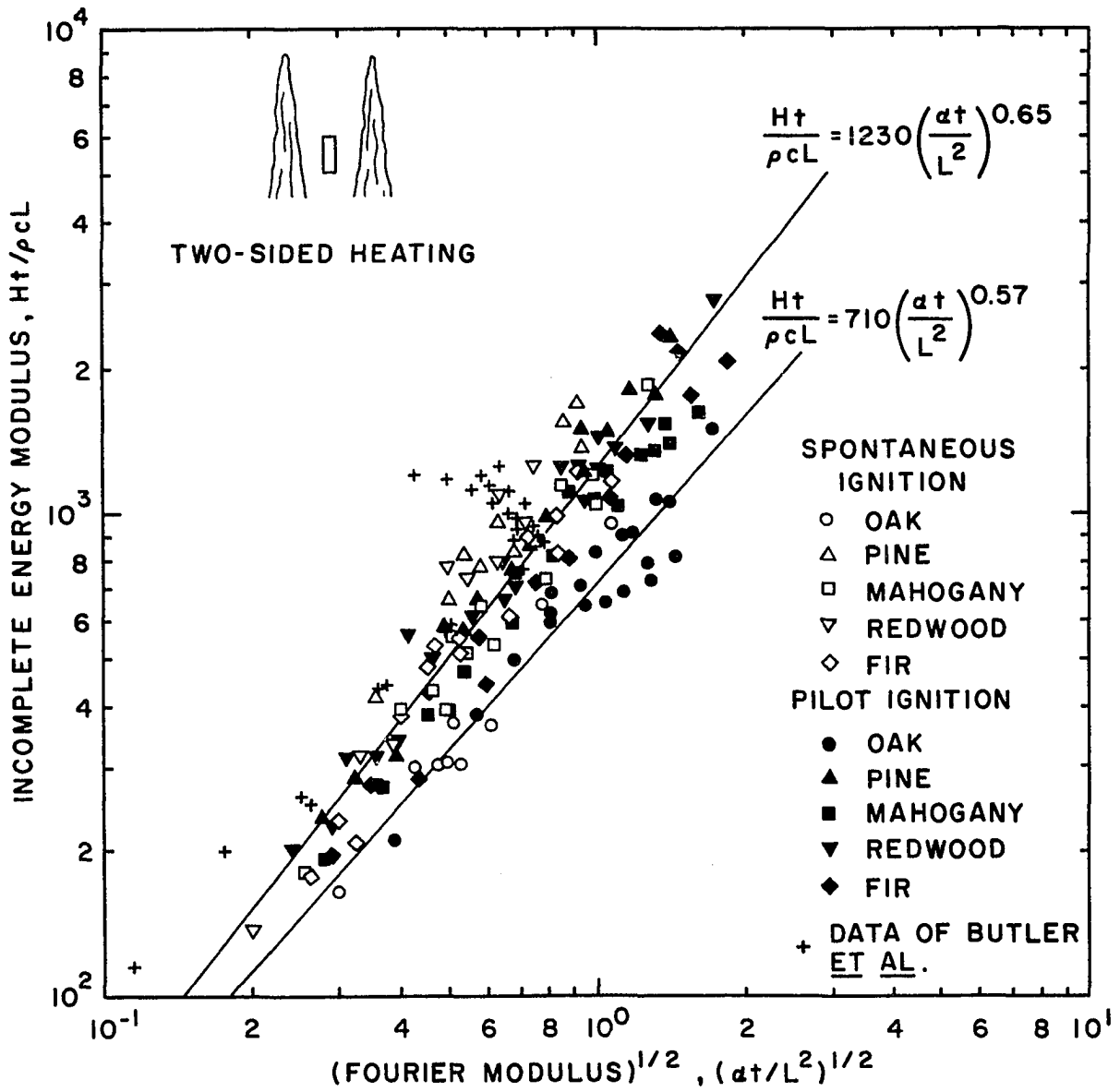


Figure IV-16. Comparison of Ignition Data of Present Study (Two-Sided Heating) with the Data of Butler *et al.* (13) which is for One-Sided Heating.

The achievement of a certain level for the rate of evolution of volatiles from sample has been mentioned as a criterion of ignition. Bamford et al. (5), as a result of their calculations reported a value of 2.5×10^{-4} gm/cm²sec to be a minimum rate required for sustained flaming. The experimental result of this present study, as seen in Table D-1, gives the rate of weight loss at ignition in the range of 1.0×10^{-4} to 21.7×10^{-4} gm/cm²sec. The majority of the tests showed a rate of weight loss more than three times the minimum value of 2.5×10^{-4} gm/cm²sec reported by Bamford et al. (5). Although a minimum weight loss rate is necessary for ignition, ignition need not necessarily occur if that minimum is exceeded. The quality of the gaseous products should also be such that, upon mixing with air, it produces an ignitable mixture. The present data show the minimum weight loss rate at ignition may be less than that reported by Bamford et al., but do not necessarily show the minimum weight loss rate at which ignition can occur.

As mentioned in Chapter II, Sauer (45) postulates that charring, at any depth, occurs when the ratio of the density to original density falls to a given value. He assumed the pattern as the weight loss; namely, a first order reaction formula. Based on the mathematical model of a semi-infinite solid, neglecting heat losses and chemical reactions, he derived a set of dimensionless groups for a diffusion controlled process and correlated the weight

loss data of other investigators. For the purpose of comparison the data of the present study were plotted with Sauer's (45) correlation. These plots are shown in Figures IV-17 through IV-19. The ignition points are plotted as solid symbols. Several intermediate weight loss data (prior to ignition) which follow the same pattern are also included and are shown in open symbols. Figure IV-17 gives the data for both pilot and spontaneous ignitions of one-sided heatings. Figure IV-18 and IV-19 give the correlations for two-sided heating of pilot and spontaneous ignition respectively.

It is noticed again that in the correlation of Figures IV-17 through IV-19, oak falls on the lower irradiance side of the plots and pine and redwood fall on the other side. These figures further show that the data of the present study approach Sauer's (45) correlation (which is based on constant E/RT_0) at higher energy moduli. It should be noted that the energy modulus corresponding to Sauer's curve includes a correction factor, $F(\gamma\sqrt{at})$, which is based on the effect of diathermancy. This factor for an exposure time of 30 seconds was about 0.95. For the longer exposure times of this present study, it approaches unity and does not affect the position of the data significantly.

Discussion of Ignition Data Correlations

In this section, the correlations of ignition data based on two different sets of dimensionless groups which were used in previous sections are briefly discussed. It may

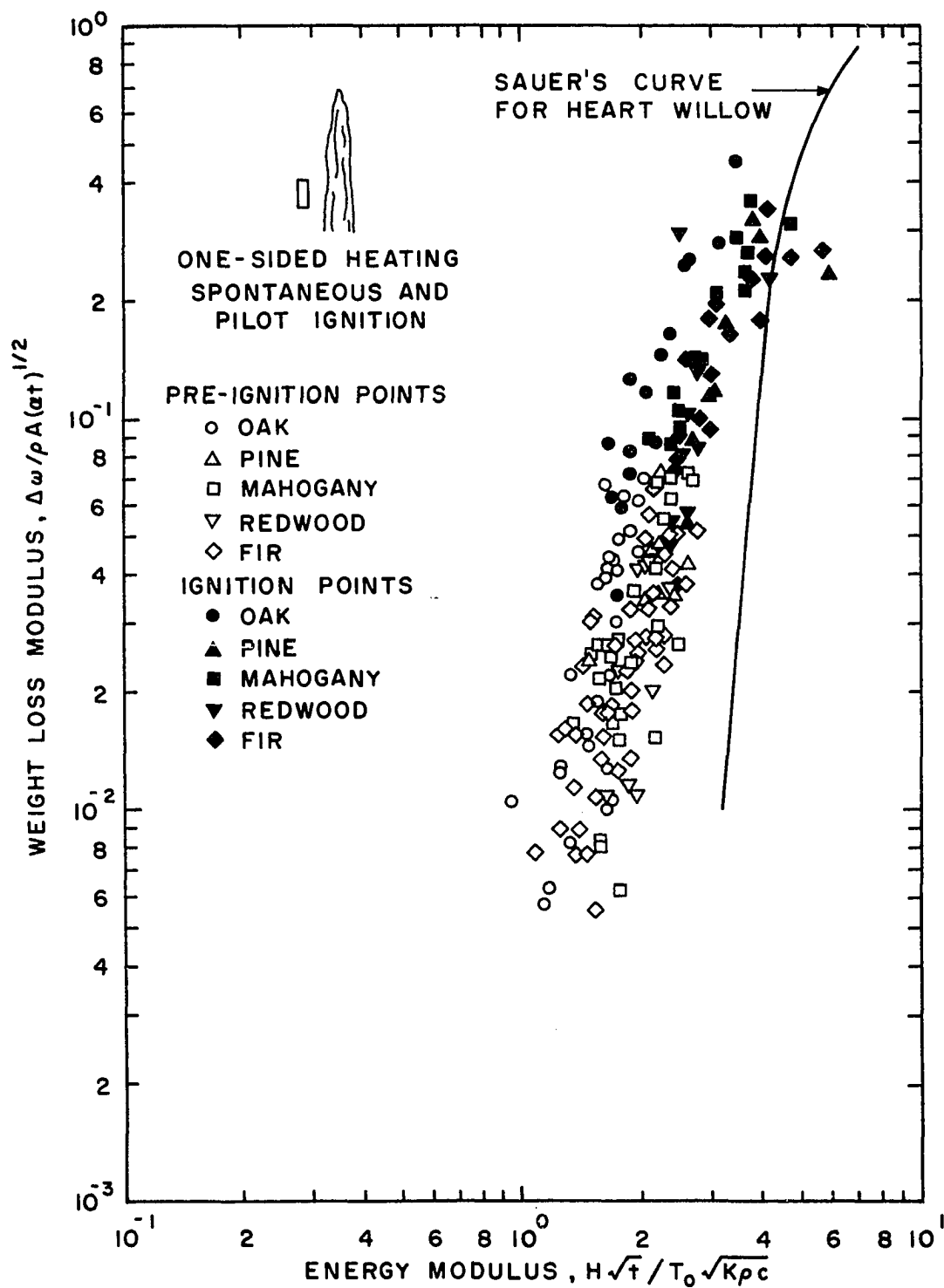


Figure IV-17. Correlation of Weight-Loss Modulus and Energy Modulus (One-Sided Heating, Pilot and Spontaneous Ignition) as Compared with Sauer's Curve (45).

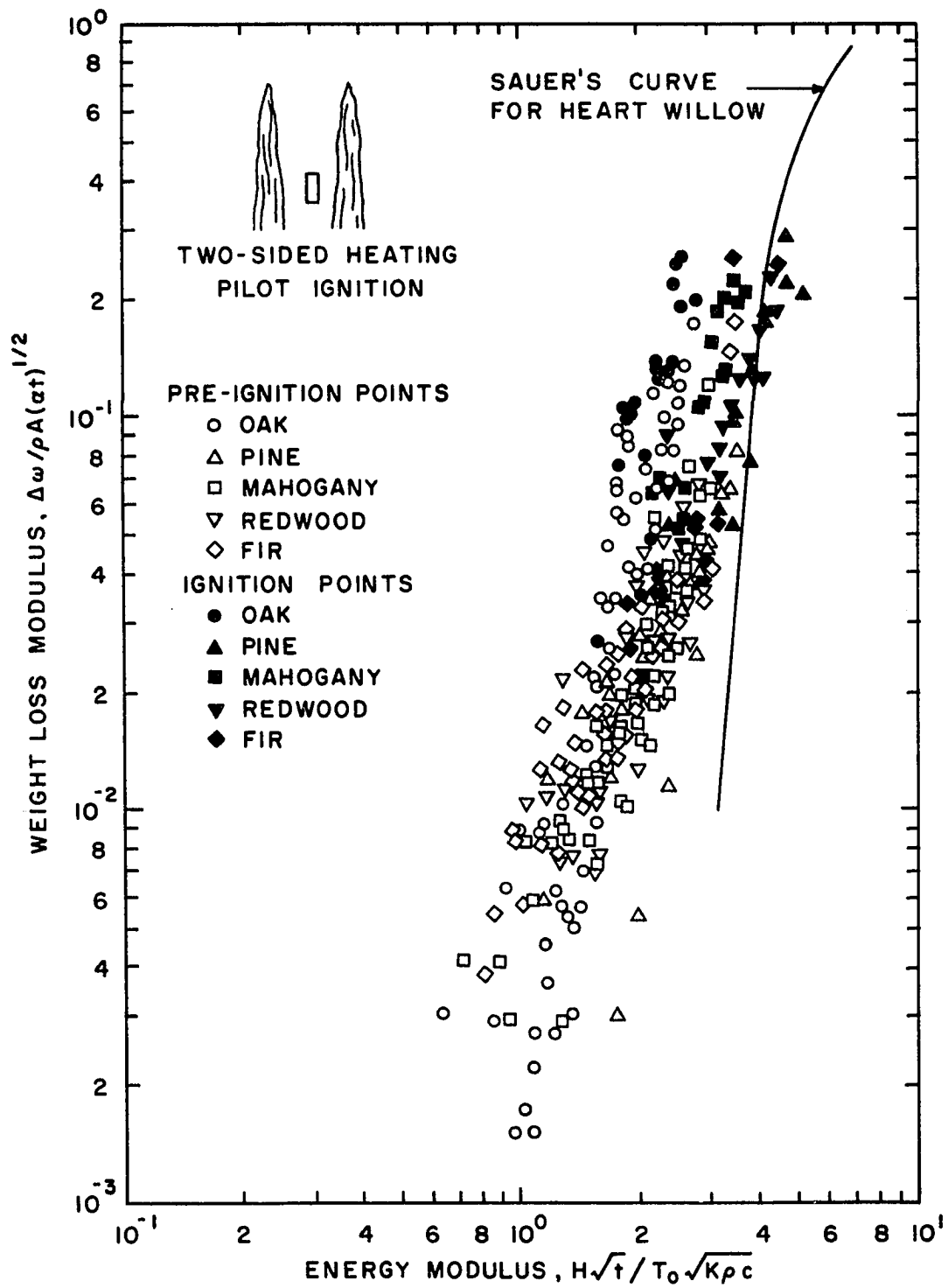


Figure IV-18. Correlation of Weight-Loss Modulus and Energy Modulus (Two-Sided Heating, Pilot Ignition) as Compared with Sauer's Curve (45).

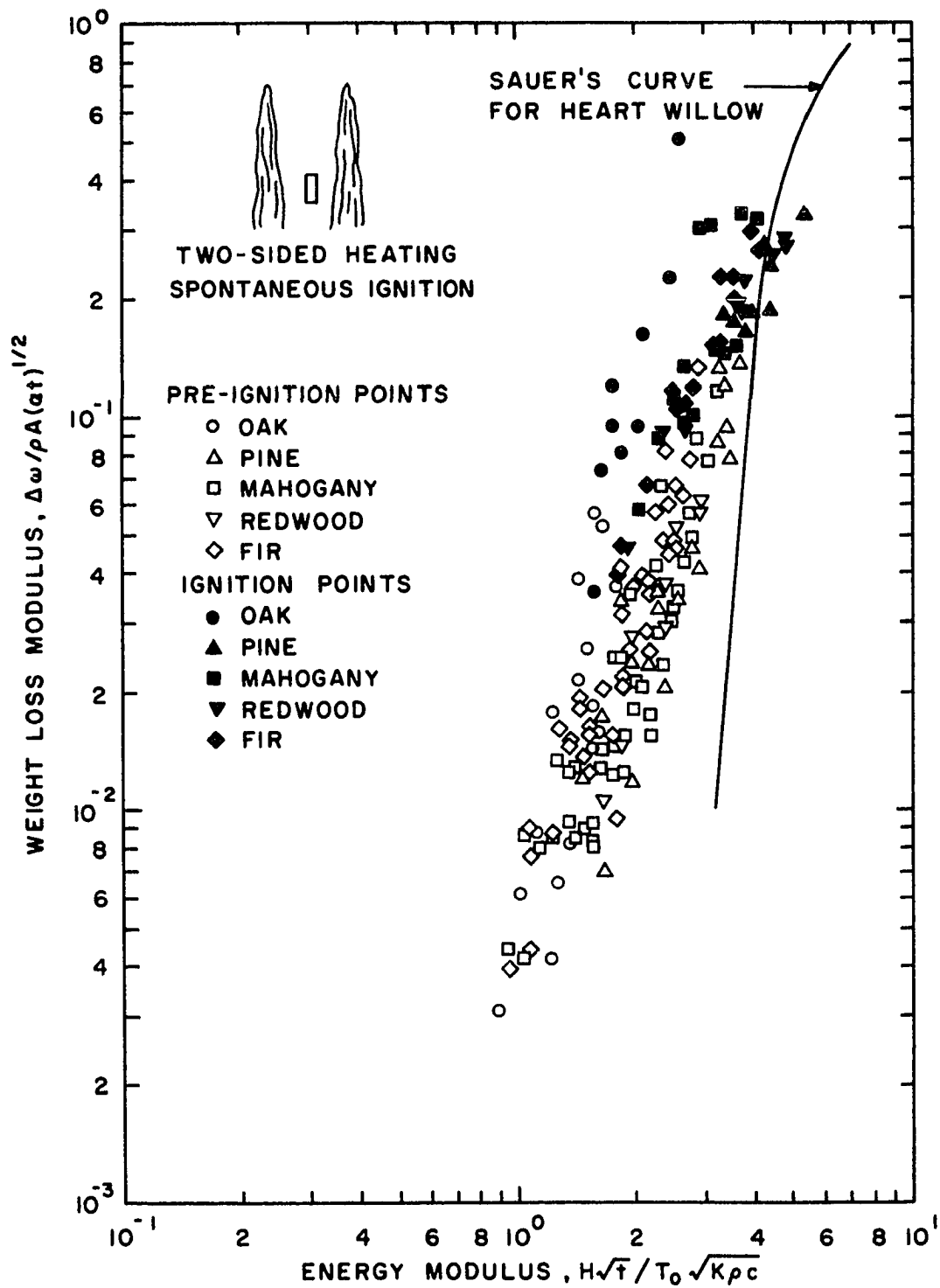


Figure IV-19. Correlation of Weight-Loss Modulus and Energy Modulus (Two-Sided Heating, Spontaneous Ignition) as Compared with Sauer's Curve (45).

be recalled from preceding equations of this chapter that the assumptions of an inert solid (no chemical decomposition) and constant, uniform properties were assumed. The presumed conditions and the resulting equations were:

Model 1: Semi-infinite solid, constant irradiance and Newtonian cooling, $h(T_s - T_o)$, at the surface. The Newtonian cooling constant h has been assumed to be an overall heat transfer coefficient which accounts for all types of energy losses. The resulting solution describing the surface temperature was

$$\frac{H\sqrt{t}}{\Delta T_s \sqrt{K\rho c}} = \frac{\beta}{1 - \exp \beta^2 \operatorname{erfc} \beta} \quad (\text{IV-10})$$

where $\beta = h\sqrt{t}/\sqrt{K\rho c} = \text{cooling modulus}$.

Model 2: Infinite slab of thickness L with constant irradiance at the surface ($x = 0$) and no heat loss from either surface. The solution to this model for the surface was

$$\frac{\Delta T_s K}{HL} = F + \frac{1}{3} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 \pi^2 F} \quad (\text{IV-14})$$

Model 3: The same as Model 1 but with no heat loss at the surface. This model resulted in

$$\frac{\Delta T_s K}{HL} = 1.1284 \sqrt{F} \quad (\text{IV-17})$$

where again $F = \alpha t/L^2 = \text{Fourier number}$.

Therefore Model 1, assuming Newtonian cooling for heat loss, resulted in Equation IV-10 which introduces one set of dimensionless groups as an energy modulus, $(H\sqrt{t}/\Delta T_s \sqrt{K\rho c})$ and a cooling modulus, $h\sqrt{t}/\sqrt{K\rho c}$. Models 2 and 3, which assume no cooling effect, suggest another set of dimensionless groups, namely irradiance modulus, $HL/\Delta T_s K$, and Fourier modulus, $\alpha t/L^2$.

It is obvious that some of the incident and absorbed radiation energy in heating a combustible solid is lost through:

1. Surface reflection.
2. Natural or forced convection.
3. Surface back radiation.
4. Sensible heat of the pyrolysis gases.

The net absorbed energy is consumed in heating the sample to higher temperature and in endothermic reactions of pyrolysis. If the reactions are exothermic they will add to the effect of external heating.

Correlation with Inert Model and Newtonian Heat Loss (Model 1)

Simms (51-52) employed Model 1 and correlated his data with the dimensionless groups of Equation IV-10. Based on this correlation he suggested a constant surface temperature criterion for ignition. Application of this model to the ignition data of present study, Figure IV-11, showed a poor correlation. As discussed previously, in plotting $(H\sqrt{t}/\Delta T_s$

$\sqrt{K\rho c}$) versus $h\sqrt{t}/\sqrt{K\rho c}$ the group, $\sqrt{t}/\sqrt{K\rho c}$, appears in both ordinates which even in the case of a good correlation is misleading. In this section the correlation with this model is analyzed further, and in the light of this analysis the constant temperature criterion of Simms is discussed.

Validity of Model 1: In employing an inert model such as Model 1 with only Newtonian cooling, it has been assumed in effect that all the above-mentioned heat losses, as well as the algebraic result of the heats of reactions, are combined and expressed by a constant surface heat transfer coefficient. In the following paragraphs, the validity of this assumption is evaluated by two independent methods.

1. Equation IV-10 is the solution to Model 1, and its curve is shown in both figures IV-10 and IV-11. If the assumption of constant overall heat transfer coefficient for the actual combustible model is valid, one should be able to find h by using the actual data and the theoretical curve of Equation IV-10. The procedure is to calculate the energy modulus, $(H\sqrt{t}/\Delta T_s \sqrt{K\rho c})$, from the experimental data and to find its corresponding cooling modulus, $(h\sqrt{t}/\sqrt{K\rho c})$, from the theoretical curve. A value of h can then be calculated. Using all the ignition data for one-sided heating, the values of h were found with this method for every test. Figure IV-17 shows the calculated values of h plotted versus ignition time. This figure shows the overall surface heat

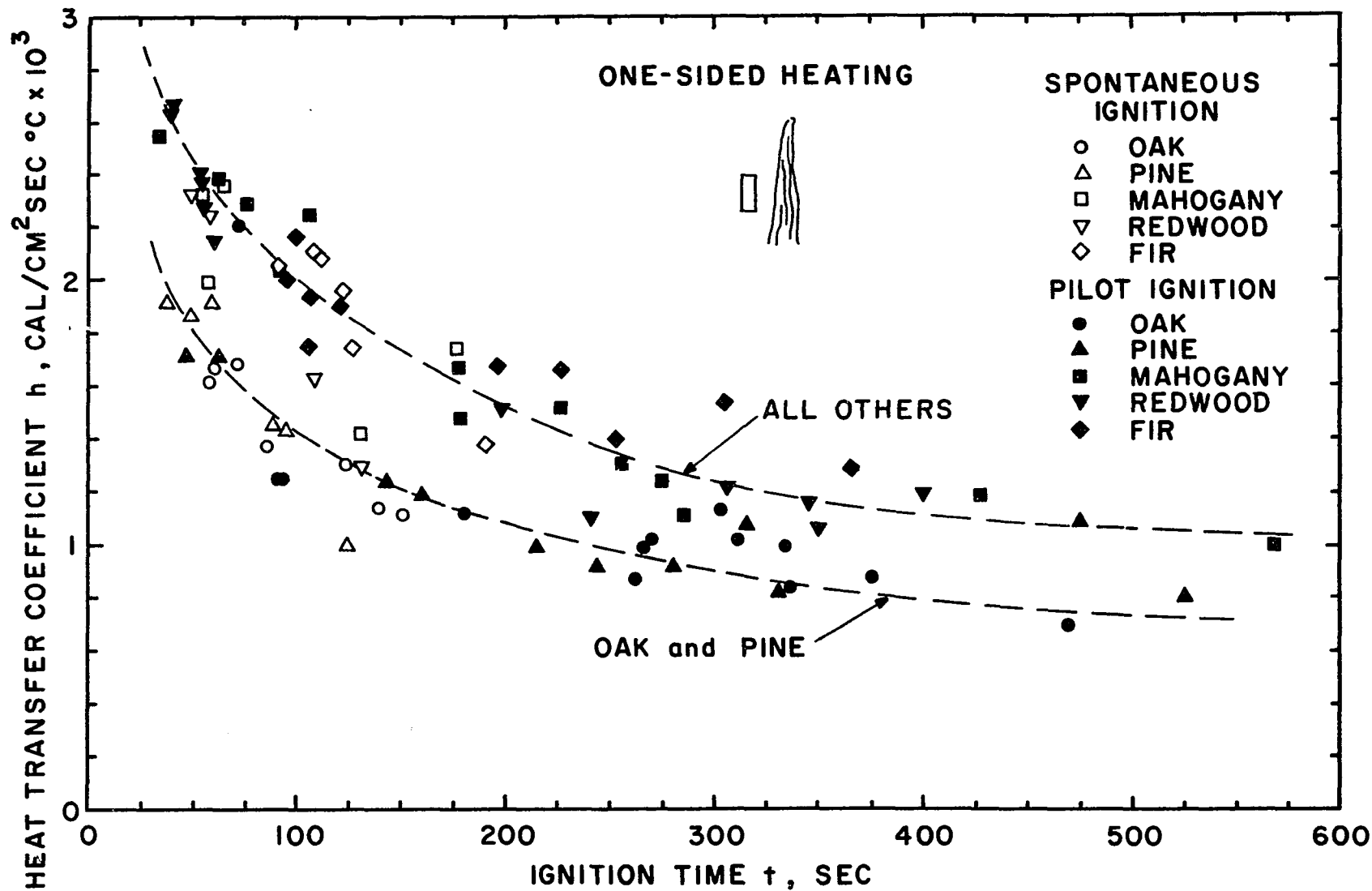


Figure IV-20. Correlation of Overall Heat Transfer Coefficient Found from Equation IV-10 (Model 1) with Ignition Time.

transfer coefficient is not constant and ranges from about 0.0007 to 0.0027 cal/cm²sec°C. Two particular characteristics of this plot are: (a) The overall heat transfer coefficient, h , is higher for the samples that ignited in shorter time (higher irradiance) and it decreases exponentially as the ignition time becomes longer. (b) The overall heat transfer coefficient is lower for oak and pine. The departure for oak is not unexpected in view of Figure IV-11 through IV-16 and is attributed to the dependence of rate and heat of reaction on density and grain structure of wood. However, the reason for deviation of pine from the other woods, and its similarity to oak, in Figure IV-20 is not known.

2. Another method for estimation of h is by direct calculation. It may be recalled that the surface boundary condition was described by (valid only if h is a constant):

$$-K \frac{\partial T}{\partial x} = H - h (T_s - T_o) \quad (\text{IV-20})$$

where $-K \frac{\partial T}{\partial x}$ = heat transfer from the surface into the solid by Fourier's law of conduction

H = radiation incident on the surface (irradiance)

and $h(T_s - T_o)$ = total heat loss from the surface by convective cooling, radiation from the surface to the surroundings, and surface reflection.

Since the quantity, $h(T_s - T_o)$ represents all heat losses from the surface, Equation IV-20 can be written as

$$-K \frac{\partial T}{\partial x} = H - [q_c + q_r + q_p] \quad (\text{IV-21})$$

where q_c = heat loss due to surface convection = $h_c(T_s - T_o)$

q_r = heat loss due to radiation from the surface to the surroundings = $\epsilon \sigma T_s^4$, where T_s = surface temperature, ϵ = surface emittance and

$$\sigma = 1.356 \times 10^{-12} \text{ cal/cm}^2 \text{sec}^\circ \text{K}^4$$

q_p = heat loss due to surface reflection

= ρH , where ρ = surface reflectance, H = irradiance.

Thus Equation IV-21 can be rewritten as

$$-K \frac{\partial T}{\partial x} = H - [h_c(T_s - T_o) + \epsilon \sigma T_s^4 + \rho H] \quad (\text{IV-22a})$$

or equivalently, multiplying through by $\frac{T_s - T_o}{T_s - T_o}$

$$-K \frac{\partial T}{\partial x} = H - h_c(T_s - T_o) - \epsilon \sigma T_s^4 \frac{T_s - T_o}{T_s - T_o} - \rho H \frac{T_s - T_o}{T_s - T_o}$$

Defining
$$h_r^* = \frac{\epsilon \sigma T_s^4}{T_s - T_o} \quad (\text{IV-23})$$

$$h_\rho^* = \frac{\rho H}{T_s - T_o} \quad (\text{IV-24})$$

Then Equation IV-22a becomes

$$\begin{aligned}
 -K \frac{\partial T}{\partial x} &= H - (h_c + h_r^* + h_\rho^*) (T_s - T_o) \\
 &= H - h (T_s - T_o)
 \end{aligned}
 \tag{IV-22b}$$

where $h \equiv h_c + h_r^* + h_\rho^*$

The quantities, h_c , h_r^* , h_ρ^* , in Equation IV-22b are instantaneous values since T_s varies with time, and consequently, so do the properties at the boundary. In Equation IV-23 and IV-24 an asterisk designation is used on the proportionality coefficients, h_r^* and h_ρ^* , to emphasize that they are basically different from the conventional radiative heat transfer coefficient, h_r , commonly used in the literature. As will be seen later, h_r is properly defined according to Equation IV-31.

Typical values for h_c , h_r^* and h_ρ^* were calculated for arbitrary values of the surface temperature, T_s , while holding all the other pertinent quantities such as temperature of the surrounding air, reflectance, emittance, irradiance and the free stream air velocity constant.

(a) Calculation of h_c : The mean value of the heat transfer coefficient due to forced convection may be estimated by the Pohlhausen equation (41, page 224) derived from boundary layer theory; thus

$$\left[\frac{h_c}{c_p V \rho} \right] \left[\frac{c_p \mu}{K} \right]^{2/3} = \frac{2}{3} \left[\frac{l V \rho}{\mu} \right]^{-1/2} \quad (\text{IV-25})$$

where all the quantities are the properties of air at average film conditions,

c_p = heat capacity of air at constant pressure

V = free stream air velocity

ρ = density

μ = viscosity

K = thermal conductivity

l = height of sample

The average film temperature was found by averaging the free stream air temperature T_o and the surface temperature T_s , that is, $(T_s + T_o)/2$. The air temperature in the ignition cabinet under test conditions was about 70°C. The free stream air velocity V was about 3.4 ft/sec. For these conditions, h_c is calculated from Equation IV-25 for a range of surface temperatures, and the results are given in Table IV-2. As would be expected, h_c is practically constant since the free stream air velocity, V was assumed to be constant and the other terms in Equation IV-25 do not vary appreciably with surface temperature over the temperature range involved.

(b) Calculation of h_r^* : from Equation IV-23

$$h_r^* = \frac{\epsilon \sigma T_s^4}{T_s - T_o}$$

Assuming a surface (hemispherical) emittance, ϵ , of 0.9 and $T_o = 70^\circ\text{C}$, h_r^* was calculated for several surface temperatures. The values are given in Table IV-2.

(c) Calculation of h_ρ^* : For calculation of h_ρ^* from Equation IV-24, at any surface temperature, the reflectance ρ and irradiance H should be known. Since the model has been assumed to be opaque, then

$$\rho = 1 - \alpha \quad (\text{IV-26})$$

where α = surface absorptance. Assuming the samples to behave as gray bodies then $\epsilon = \alpha$ (41, page 63) and

$$\rho = 1 - \epsilon \quad (\text{IV-27})$$

Therefore, since $\epsilon = 0.9$, a total (or hemispherical) reflectance of 0.1 can be applied. For the irradiance, H , any arbitrary value in the experimental range may be chosen. The irradiance level in the present study ranged from 0.275 to 0.855 cal/cm²sec. For the purpose of these calculations a value of $H = 0.484$ cal/cm²sec from one experimental condition of the present study (6-inch burner distance) is employed. The

values of h_{ρ}^* were calculated from Equation IV-24 for a constant value of ρH according to

$$h_{\rho}^* = \frac{\rho H}{T_s - T_o} = \frac{(0.1)(0.484)}{T_s - T_o}$$

Table IV-2 shows that although h_c is essentially constant, the instantaneous values of h_r^* and h_{ρ}^* vary with surface temperature. The last column of Table IV-2 shows that $h_c = h_r^* + h_{\rho}^* = h$, which is used in the boundary condition of Equation IV-20 (Model 1) is not constant.

Since the instantaneous values for h vary significantly with surface temperature while holding all other parameters constant, the question arises whether an average value of h obtained by graphical integration over the duration of a particular test would be more applicable to Equation IV-20 (Model 1) in comparisons with other tests. Average h 's were calculated for several selected tests on fir, redwood and pine, pilot and spontaneous ignition, and one-sided heating for which the ignition times varied from 196 to 252 seconds and the irradiances ranged from 0.484 to 0.827 cal/cm²sec. As shown in Table IV-3, these average h 's showed a much lesser variation from test to test than did the instantaneous values of h throughout the duration of a particular test as given in Table IV-2. Thus, if one desired to employ Model 1, in which h is assumed to be constant, it appears that an appropriate average value for h would be

TABLE IV-2

ESTIMATION OF h FOR VARIABLE SURFACE TEMPERATURE
AND ALL OTHER QUANTITIES CONSTANT^(a)
(cal/cm²sec°C x 10⁴)

T_s (°C)	$T_s - T_o$ (°C)	h_c	h_r^*	h_ρ^*	h
100	30	3.0	8.0	16.1	27.1
200	130	3.0	4.7	3.7	11.4
300	230	3.0	5.7	2.1	10.7
400	330	2.9	7.6	1.5	12.0
500	430	2.9	10.1	1.1	14.0
600	530	2.9	13.4	0.9	17.2

(a) $T_o = 70^\circ\text{C}$, $\epsilon = 0.9$, $\rho = 0.1$, $H = 0.484 \text{ cal/cm}^2\text{sec}$,
 $V = 3.4 \text{ ft/sec}$.

TABLE IV-3

COMPARISON OF AVERAGE OVERALL HEAT TRANSFER
COEFFICIENT h FOR SEVERAL TESTS

Test No.	Ignition Time (sec)	H (cal/cm ² sec)	Average h (cal/cm ² sec°C x 10 ⁴)
274 F P 1S	196	0.484	11.0
264 F P 1S	252	0.653	12.5
207 R S 1S	108	0.827	13.7
91 P S 1S	122	0.774	14.9

about 13×10^{-4} rather than the value, 8×10^{-4} , used by Simms (51, 52, 55). Referring to Figure IV-11, if a value of $h = 13 \times 10^{-4}$ were used instead of 8×10^{-4} , the data would be shifted to the right indicating a closer fit with the theoretical curve given by Equation IV-10.

Before concluding this discussion, the difference between $h_r^* + h_\rho^*$ used above and the conventional h_r used in the literature will be demonstrated. A heat balance at the surface can be written as

$$-K \frac{\partial T}{\partial x} = H - \rho H - \epsilon \sigma T_s^4 - h_c (T_s - T_o) \quad (\text{IV-28})$$

Assuming the irradiated sample is a "gray body"

$$\rho = 1 - \alpha = 1 - \epsilon$$

so that Equation IV-28 becomes

$$-K \frac{\partial T}{\partial x} = \epsilon \sigma \left[\left(\frac{H}{\sigma} \right) - T_s^4 \right] - h_c (T_s - T_o) \quad (\text{IV-29})$$

The first term on the right hand side can be expanded

$$\epsilon \sigma \left[\left(\frac{H}{\sigma} \right) - T_s^4 \right] = \epsilon \sigma \left[\left(\frac{H}{\sigma} \right)^{\frac{1}{2}} + T_s^2 \right] \left[\left(\frac{H}{\sigma} \right)^{\frac{1}{4}} + T_s \right] \left[\left(\frac{H}{\sigma} \right)^{\frac{1}{4}} - T_s \right] \quad (\text{IV-30})$$

Defining

$$h_r = \epsilon \sigma \left[\left(\frac{H}{\sigma} \right)^{\frac{1}{2}} + T_s^2 \right] \left[\left(\frac{H}{\sigma} \right)^{\frac{1}{4}} + T_s \right] \quad (\text{IV-31})$$

Equation IV-30 becomes

$$\epsilon \sigma \left[\frac{H}{\sigma} - T_s^4 \right] = h_r \left[\left(\frac{H}{\sigma} \right)^{\frac{1}{4}} - T_s \right] \quad (\text{IV-32})$$

Substituting Equations IV-32 into IV-29 yields

$$-K \frac{\partial T}{\partial x} = h_r \left[\left(\frac{H}{\sigma} \right)^{\frac{1}{4}} - T_s \right] - h_c (T_s - T_o) \quad (\text{IV-33})$$

By adding and subtracting $h_r T_o$ in the right hand side one gets

$$-K \frac{\partial T}{\partial x} = h_r \left[\left(\frac{H}{\sigma} \right)^{\frac{1}{4}} - T_o \right] - (h_r + h_c) (T_s - T_o) \quad (\text{IV-34})$$

Comparing Equations IV-33 with IV-22b,

$$H - (h_r^* + h_\rho^*) (T_s - T_o) = h_r \left[\left(\frac{H}{\sigma} \right)^{\frac{1}{4}} - T_s \right] \quad (\text{IV-35})$$

from which

$$(h_r^* + h_\rho^*) = \frac{H - h_r \left[\left(\frac{H}{\sigma} \right)^{\frac{1}{4}} - T_s \right]}{T_s - T_o} \quad (\text{IV-36})$$

The alternative form of Equation IV-36 is obtained by comparing IV-34 with IV-22b

$$(h_r^* + h_\rho^*) = h_r + \frac{H - h_r \left[\left(\frac{H}{\sigma} \right)^{1/4} - T_o \right]}{T_s - T_o} \quad (\text{IV-37})$$

As can be seen from Equations IV-36 and IV-37, $(h_r^* + h_\rho^*)$ is related in a complex manner to h_r . Basically h_r includes the effect of both radiation and reflection and when multiplied by $\left[\left(\frac{H}{\sigma} \right)^{1/4} - T_s \right]$ gives the net radiative heat transfer between the surface and the surroundings (see Equation IV-35). On the other hand, $(h_r^* + h_\rho^*)$ when multiplied by $(T_s - T_o)$ gives the heat lost from the surface to the surroundings by radiation and reflection.

Finally, Equation IV-34 gives the boundary condition in terms of h_r and h_c as contrasted to the boundary condition of Equation IV-22b in terms of h_r^* , h_ρ^* and h_c . Equation IV-34 is preferred in the sense that the definition of h_r corresponds to the common usage in the literature.

The variation of h_r with surface temperature for a typical test is shown in Table IV-4. It is noted that h_r increases monotonically with temperature, whereas from Table IV-2 the sum, $h_r^* + h_\rho^*$, passes through a minimum at some intermediate temperature.

TABLE IV-4

CALCULATION OF h_r FROM EQUATION IV-31
FOR VARIABLE SURFACE TEMPERATURE
AND CONSTANT IRRADIANCE (a)

T_s °C	T_s °K	h_r cal/cm ² sec°K
100	373	10.3
200	473	12.5
300	573	15.2
400	673	18.5
500	773	22.5
600	873	27.3

(a) $H = 0.484 \text{ cal/cm}^2\text{sec}$; $\epsilon = 0.9$; $\sigma = 1.356 \text{ cal/cm}^2\text{sec}^\circ\text{K}^4$

Constant surface temperature criterior for ignition:

In the above discussions it was shown by two independent methods, that the application of an inert model with Newtonian cooling does not describe the ignition process satisfactorily. In the following the work of Simms, suggesting a constant surface temperature criterion for ignition of wood, is analyzed briefly.

By using Model 1 and Equation IV-10, Simms (51, 52, 54, 55) took the limit of the energy modulus, $H\sqrt{t}/\Delta T_s \sqrt{K\rho c}$, as the cooling modulus, $\beta = h\sqrt{t}/\sqrt{K\rho c}$, approached zero.

$$\lim_{\beta \rightarrow 0} \left[\frac{H\sqrt{t}}{\Delta T_s \sqrt{K\rho c}} \right] = \frac{\pi^{1/2}}{2} \quad (\text{IV-38})$$

From Equation IV-38, a first approximation to ΔT_s was then obtained. By using this ΔT_s , Simms estimated the appropriate value of the Newtonian cooling constant, h , to be $0.0008 \text{ cal/cm}^2\text{sec}^\circ\text{C}$ as reported in reference (55). Simms then adjusted ΔT_s such that the theoretical curve of Equation IV-10 gave the best fit (within about ± 30 percent) through his experimental data. This adjusted surface temperature rise was found to be 525°C .* In effect Simms fixed two parameters, h and ΔT_s , forcing his data to fall around the theoretical curve of Model 1. Even then the scatter in his data is so great that a straight line is probably as valid a fit as the theoretical curve. Therefore, the conclusion of constant surface temperature criterion, based on Simms' plot, does not seem to be justifiable.

In addition the experimental surface temperatures which were presented in Figures IV-6 through IV-9 and summarized in Table IV-1 do not validate a constant surface temperature criterion for ignition. The criterion of constant temperature implies that when the surface of wood

*There appears to be an error in Simms' paper. The theoretical curve drawn through the experimental data in Simms' papers (51,52) does not represent Equation IV-10. Using the values of " $\exp \beta^2 \operatorname{erfc} \beta$ " tabulated in Carslaw and Jaeger (14, page 485) it can be shown that the theoretical curve calculated from Equation IV-10 should be considerably higher than Simms showed. In order to bring the data and calculated curve into correspondence a ΔT_s of about 465°C , as compared with the 525°C used by Simms, should be assumed.

reaches a certain temperature, the rate and concentration of volatiles are such that ignition occurs. From consideration of reaction kinetics and mechanism of pyrolysis, discussed mainly in Chapter II, it is known that the quantity and the quality of the pyrolysis products of wood depend not only upon the temperature but also on the time of exposure, rate of heating, and the properties of the material, such as density and grain structure.

In summary, the result of this present study by mathematical consideration and experimental investigation show that a constant surface temperature criterion for ignition is not valid for the following reasons:

1. Applications of an inert model with Newtonian cooling (Model 1) does not describe the ignition process because all energy losses and the net effect of the chemical reactions cannot be combined and expressed as a constant overall surface heat transfer coefficient.

2. Simms (51, 52) used Model 1 and fixed two parameters h and ΔT_s forcing his data to scatter around the theoretical curve of Model 1 (Equation IV-10). Since he plotted $H\sqrt{t}/\Delta T_s\sqrt{K\rho c}$ versus $h\sqrt{t}/\sqrt{K\rho c}$, in which case $\sqrt{t}/\sqrt{K\rho c}$ appeared in both ordinates, and since h and ΔT_s were assumed constant, the only variable which does not appear in both ordinates is H . Therefore, any conclusion based on this approach is not very significant.

3. The quantity and the quality of the gaseous products initiating the ignition depend not only on temperature but also on several other factors such as rate of net heating and physical and chemical properties of material.

4. The variation in the measured surface temperatures, tabulated in Table IV-1, support the arguments raised in items 1, 2, and 3, which reject the constant surface temperature criterion for ignition.

Correlation with Inert Model and Assumption of No Heat Loss

The recommended correlation of ignition data (Figures IV-12 and IV-13) was based on a mathematical model which employed an inert solid and assumed no heat loss from the boundary. The actual processes involved in ignition are complex, and the experimental data for ignition do not provide complete information concerning all phases of energy transactions. Even if complete information were available, the problem could not be solved analytically (although it might become amenable to numerical solution). In employing a simplified model for ignition, once several drastic assumptions (such as choosing an inert solid) are made one might as well take the simplest model which ignores all unknown parameters. For example, in trying to describe all types of heat losses, including those due to chemical reactions, by means of Newtonian-type cooling, one might introduce additional complications which make the interpretation of the result more difficult. For this reason Models 2 and 3 of "mathematical Models" discussed earlier

in this chapter were assumed to be inert solids with constant irradiance (a known value) and no heat loss.

Models 2 and 3 suggested the dimensionless groups of irradiance modulus, $HL/\Delta T_s K$, and Fourier modulus, $\alpha t/L^2$. Plots of ignition data with these dimensionless variables, as shown by Figures IV-12 and IV-13, give reasonably good correlations. Both pilot and spontaneous ignitions are correlated on the same chart. The equations of the lines drawn through experimental data are described by $(HL/\Delta T_s K) = a(\alpha t/L^2)^b$ where a and b are constants. The values of a and b are different in the case of one-sided and two-sided heatings. They are also different for oak as compared with other species.

In both Figure IV-12 and IV-13, the data points fall above the theoretical lines of Equations IV-14 and IV-17. The reason for this behavior is that the heat losses were neglected in the theoretical models. In other words, the H used in the theoretical models corresponds to the net heat gain by the sample. In actual practice the irradiance H is higher than the net heat input to the sample, and therefore the experimental data fall above the theoretical curves. Since the lines drawn through the data points (found by the least square method) are not parallel with the theoretical line of Equation IV-17, a definite conclusion cannot be made as to what fraction of the incident energy is lost or used in chemical reactions. Neglecting this minor difference in the slope of the two lines, if the

values of the ordinate for oak are multiplied by a factor, $\kappa = 0.4$, and for all other woods tested are multiplied by $\kappa = 0.23$, the data points for all materials approach the theoretical curve as shown in Figures IV-21 and IV-22. Better agreement would have been obtained if κ had been assumed to be a slight function of temperature. Thus, the experimental results show that the simple mathematical model of an inert and opaque solid with the surface boundary condition

$$-K \frac{\partial T}{\partial x} = \kappa H \quad (\text{IV-39})$$

describes the ignition process of wood by flames within the range of experimental conditions employed.

Since the factor κ was applied to the irradiance modulus, $HL/\Delta T_s K$, the quantity $(1-\kappa)$, which is equal to 0.6 for oak and 0.77 for all other woods tested, is a measure of the fraction of irradiance at the surface that is not accounted for by an inert model with the assumption of no heat loss.

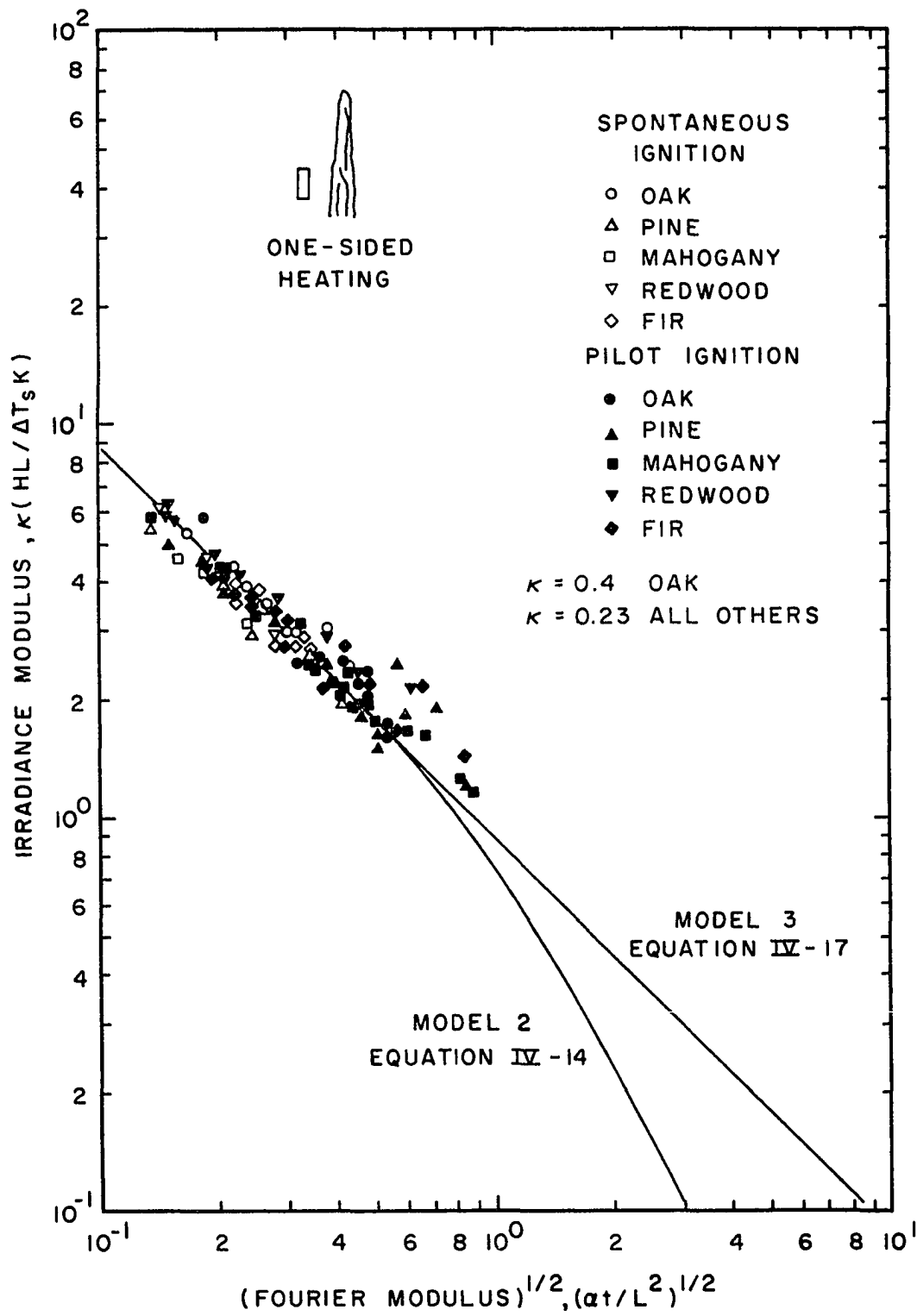


Figure IV-21. Correlation for Ignition Data Based on Equation IV-14 with Modifying Factor κ (One-Sided Heating).

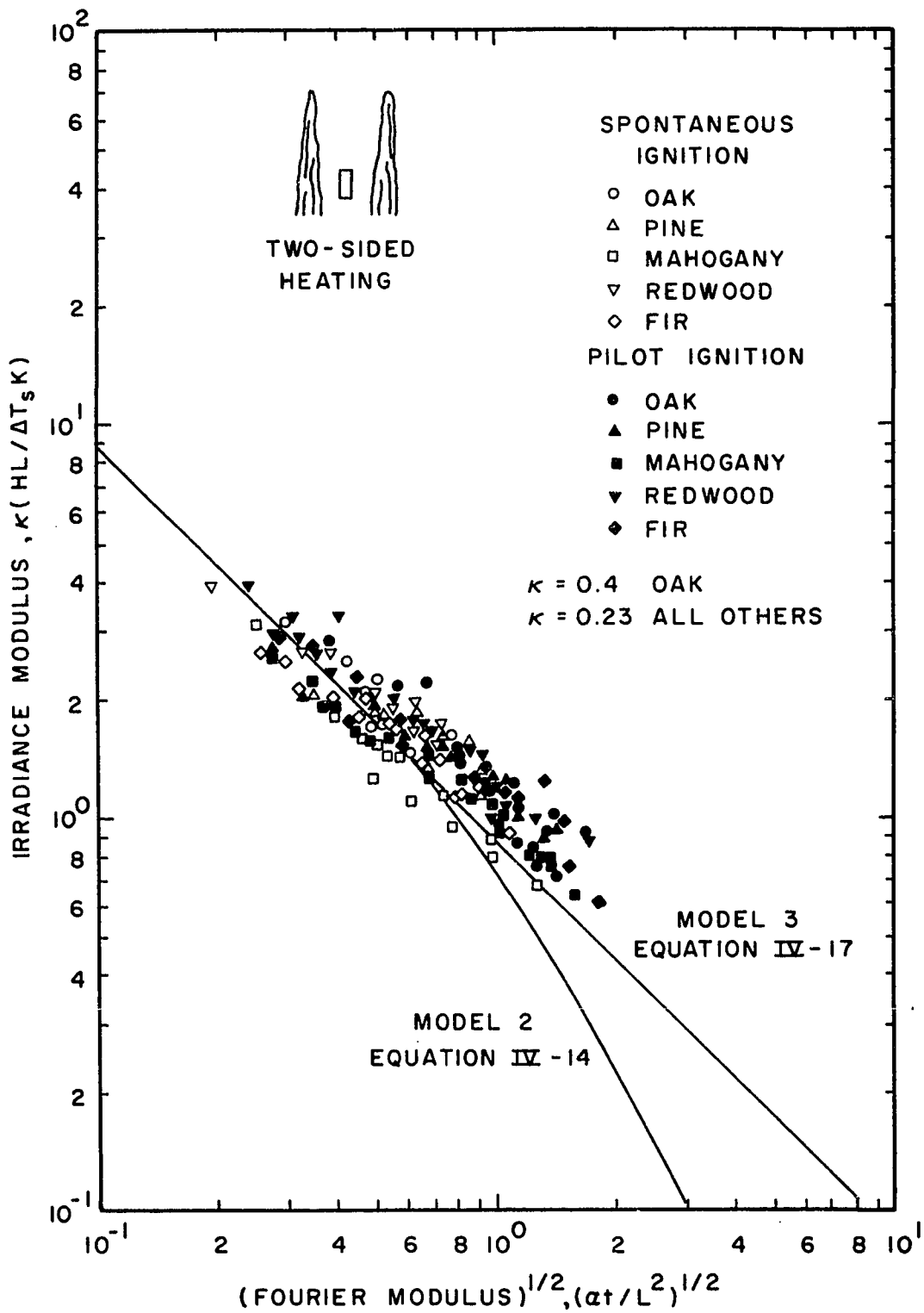


Figure IV-22. Correlation for Ignition Data Based on Equation IV-14 with Modifying Factor κ (Two-Sided Heating).

CHAPTER V

CONCLUSIONS

This study constitutes the first experimental study of ignition phenomena in which open flames from liquid pools were used for sample irradiation. The oven-dried wood samples of five different species were irradiated under the different conditions of one-sided and two-sided heatings. Both spontaneous and pilot ignition tests were carried out. The physical properties of samples were found experimentally. The level of irradiances used in this study ranged from 0.275 to 0.855 cal/cm²sec and the ignition times were in the range of 24-1254 seconds. Surface temperature and weight loss of irradiated samples were measured continuously.

A semi-quantitative analysis, as well as the measured surface temperature data, show that a single constant surface temperature criterion as suggested by Simms (29, 51, 52, 54, 55, 62) is not correct. The ranges of surface ignition temperatures for different experimental conditions are presented in Table IV-1. Generally, the average surface temperatures for pilot ignition are less than for spontaneous ignition and are lower in the case of two-sided heating than in the case of one-sided heating.

The rate of evolution of volatiles from samples at the instant when ignition occurred ranged from 1.0×10^{-4} to 21.7×10^{-4} gm/cm²sec. The majority of the tests showed a rate of weight loss more than three times the minimum value of 2.5×10^{-4} gm/cm²sec reported by Bamford et al. (5) as a criterion for ignition and burning. Although a minimum weight loss rate is necessary for ignition, ignition need not necessarily occur if that minimum is exceeded. The quality of the gaseous products should also be such that, upon mixing with air, it produces an ignitable mixture. The present data show the minimum weight loss rate at ignition may be less than that calculated by Bamford et al., but do not necessarily show the minimum weight loss rate at which ignition can occur. Therefore a minimum rate of evolution of volatiles is a necessary but not a sufficient condition for ignition to occur; an ignition criterion based only on the rate of weight loss is not correct.

The "critical irradiances" for ignition for one-sided heating of wood were reported by Lawson and Simms (29) to be about 0.35 and 0.6 cal/cm²sec for pilot and spontaneous ignitions respectively. The data of present study showed that the critical irradiance of pilot ignition in the case of one-sided heating is about 0.32 cal/cm²sec which is almost the same as the data of Lawson and Simms. However the data of two-sided heating showed the critical irradiance is half of the value for one-sided heating; namely, about

0.15 and 0.30 cal/cm²sec for the cases of pilot and spontaneous ignitions respectively.

In an attempt to correlate the ignition data three simplified mathematical models were employed. Model 1 which was based on the assumption of inert solid with Newtonian cooling gave a poor correlation. It was shown that all the energy losses from the samples as well as the effect of chemical reactions cannot be combined and expressed by a constant overall heat transfer coefficient, h . Therefore Model 1 (inert solid with Newtonian cooling) does not describe the ignition process. Models 2 and 3 which are based on an inert solid but no heat loss suggested the dimensionless group $HL/\Delta T_s K$ (irradiance modulus) and $\alpha t/L^2$ (Fourier modulus) and gave a relatively good correlation. The recommended correlations of ignition data are shown in Figures IV-12 and IV-13. In both of these figures oak falls below the other species. Since the physical properties of the samples appear in the dimensionless groups, the deviation of oak from other species shows that the rate of pyrolysis and the heat of reaction is also dependent on the density or grain structure of wood.

Finally, it was found that the ignition process of wood can be described by a mathematical model of an inert and opaque solid with constant and uniform properties. The appropriate equation for this model is

$$\alpha \frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t}$$

The applicable boundary condition for the irradiated surface is found to be

$$-K \frac{\partial T}{\partial x} = \kappa H$$

where H = irradiance (constant)

and κ = constant depending on species

The factor κ was found to be 0.40 for oak and 0.23 for all other species in this present study. However, it should be pointed out that although the above equations describe and correlate the overall results of the ignition test, they do not provide means of predicting ignition behavior. Besides the thermal properties of the material (K , ρ and c) two of the three parameters H , ΔT_s and t must be known before an estimate of the ignition behavior can be made.

APPENDIX A

IRRADIANCE MEASUREMENT

The knowledge of the rate of irradiance of the sample in the ignition studies is of fundamental importance. The pertinent literature shows that different devices have been employed to measure the rate of energy transfer or the total energy transferred to the sample. These instruments are, in general, called calorimeters. Two fundamental concepts are used for measurements.

1. Thermal Capacity: In this technique the amount of energy transferred to the surface of the instrument is measured by the rise in temperature of a known mass of substance such as water or a block of copper contained in the calorimeter. In the case of phase change in the calorimeter the measurement is made for the amount of heat supplied in a certain time to change the medium from one equilibrium phase to another. Another calorimeter in this category is the slug or slope calorimeter, which relates the rate of heat transfer to a thermally isolated mass of known constant thermal capacity to the time derivative of the temperature of the slug at any given instant. The temperature history in this case is measured with a

fine thermocouple wire attached to the slug.

2. Thermal Gradient: In this technique the rate of energy transfer to a substance, usually a solid, is related to a measurable temperature gradient on or within the substance. For example, in one instrument of this type the temperature history of specific points inside a sample can be measured. Then the temperature gradient at the surface may be found by either extrapolation of data or by an analytical method. Other kinds of calorimeters in this category are thermopiles and asymptotic rapid response calorimeters. In these types a finite thickness of the material is so oriented that the heat passes through a known path (for example in radial direction such as the instrument shown in Figure A-1). The temperature difference across this path is a measure of the thermal energy incident on the material.

In general the instruments using the thermal capacity concept have slower response, and in most cases the data reduction is time-consuming. On the other hand the technique using the thermal gradient concept offers fast response and, especially in the case of the thermopile and the asymptotic rapid response calorimeter, the output signals are directly proportional to the incident energy.

The instrument used to measure the incident energy in the present work was an asymptotic rapid response calorimeter based on the thermal gradient technique. The instrument was Hy-Cal Engineering Model P-1401-B pyrheliometer.

The principles of operation of this instrument are easily understood by referring to the schematic diagram of Figure A-1.

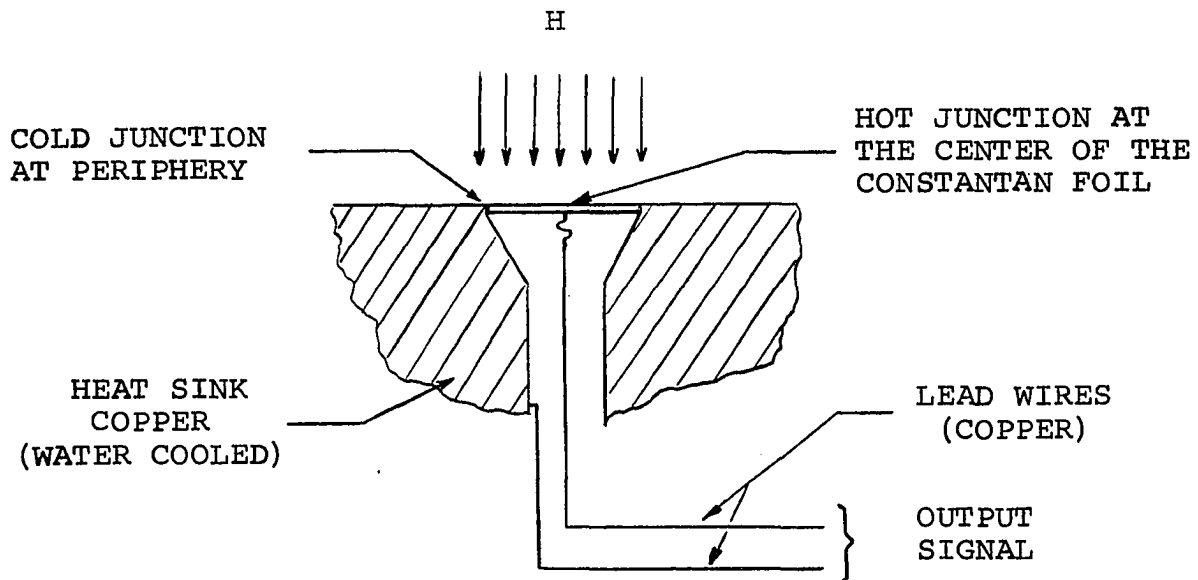


Figure A-1. Schematic Diagram of Pyrheliometer

A circular constantan foil is suspended over a cavity in a block of copper which acts as a heat sink. This foil is thermally and electrically bonded to the heat sink at the periphery. By attaching a fine copper wire at the center of the foil, a differential thermocouple is formed with the hot and cold junctions at the center and periphery of the foil respectively. The energy, H , absorbed by the foil flows radially to the copper block which acts as a constant temperature heat reservoir (in operation this block was kept cool by running water through appropriate cavities provided

for this purpose). As a result of this radial heat flow the temperature of the center rises above that of the periphery. This temperature difference is directly proportional to the incident flux over the surface of the foil. Gardon (19) and Stempel and Rall (61) give detailed information for mathematical evaluation of sensitivity and time constant of this instrument.

The response of the water cooled pyrliometer used in these experiments is on the order of five seconds. This response is quite adequate for the long exposure period of the ignition tests where the incident flux is less than 1 cal/cm²sec.

The pyrliometer contains a quartz window in front of the foil which blocks the effect of convective heat transfer to the foil; therefore, it senses only the radiation transmitted through the window. However, the two major disadvantages of quartz windows are (a) they block infrared radiation beyond about 4 or 5 microns and (b) for a long exposure time the window gets hot and reradiates. To eliminate these problems the pyrliometer was also calibrated with a NaCl window and without a window. When no window was used, the calibration was carried out under natural convection. All calibrations were carried out by the manufacturer, and were supplied in terms of incident black body radiation.

Before carrying out the ignition tests, the pyrheliometer described above was used to calibrate the ignition apparatus for the incident heat flux at the surface of the sample as a function of burner distance. In doing so the pyrheliometer was housed in the sample holder panel in a location where the samples would be positioned during normal tests (see Figure A-2). After 165 calibration runs, the following characteristics of the ignition apparatus were established:

1. In order to get a constant and reproducible heat flux, the damper position, which altered the amount of induced draft through the apparatus, had to be regulated. Two standardized time tables were prepared, one for one-sided heating and one for two-sided heating, that gave the position of the damper at any time after the start of the tests.

2. The thermal flux incident on the surface of the samples was calibrated as a function of burner distance. It was found that the calibration by the pyrheliometer with the quartz window showed a higher value than with the NaCl window or without a window for greater burner distances as shown in Figure A-3. The results with the salt window and without a window were the same. These differences may have been caused by absorption and reradiation by the quartz window, the effect of moisture on the salt window which may have reduced the transparency of the salt crystal and/or by

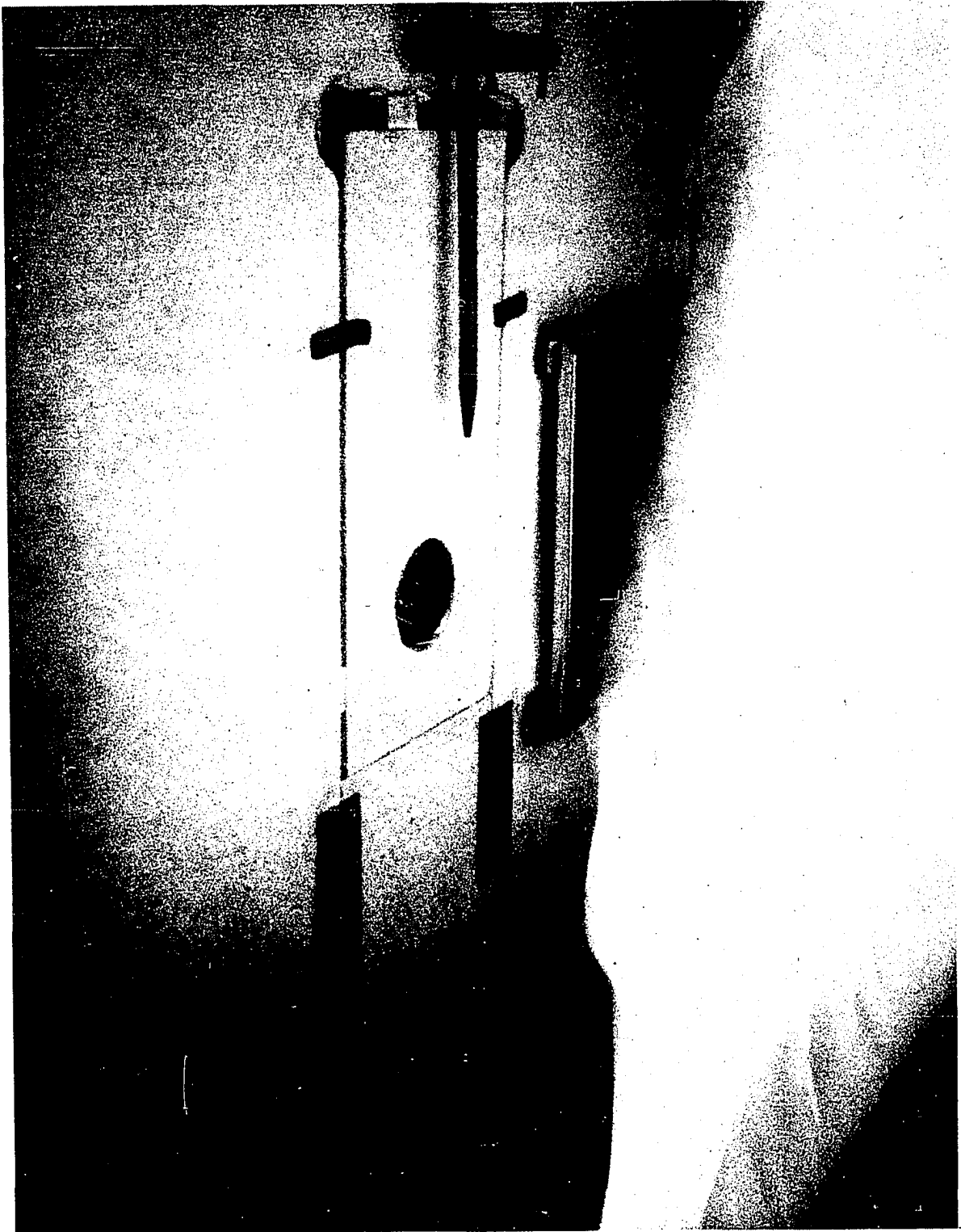


Figure A-2. Pyrheliometer Positioned in Sample Location.

the convective cooling effect for the case without a window. The salt window, as it could be judged visually, stayed clear throughout the tests. When the salt windows were not in use they were kept in plastic bags containing silica gel. To estimate the convective cooling, an anemometer probe was inserted into the apparatus, and an attempt was made to measure the air velocity at different locations. It was noticed that as the probe was moved toward the pyrheliometer, the velocity of air was reduced until it was practically zero when the probe was nearly touching the surface. Therefore the convective cooling could not be more than the order of natural convection. Considering that the samples are also subject to the convective cooling effect, although their surface conditions may be different from that of the pyrheliometer, it was logical to accept the calibration results obtained with the salt window and without a window. The calibration curves for two-sided and one-sided heatings are given in Figure A-3.

3. Although the damper settings were regulated to obtain consistent conditions, it was found that the fuel and air temperatures had some effect on the intensity of radiation. The direction of wind outside the laboratory also affected the amount of induced draft through the apparatus. However, the effect of all these and other variables did not cause significant variation from average results.

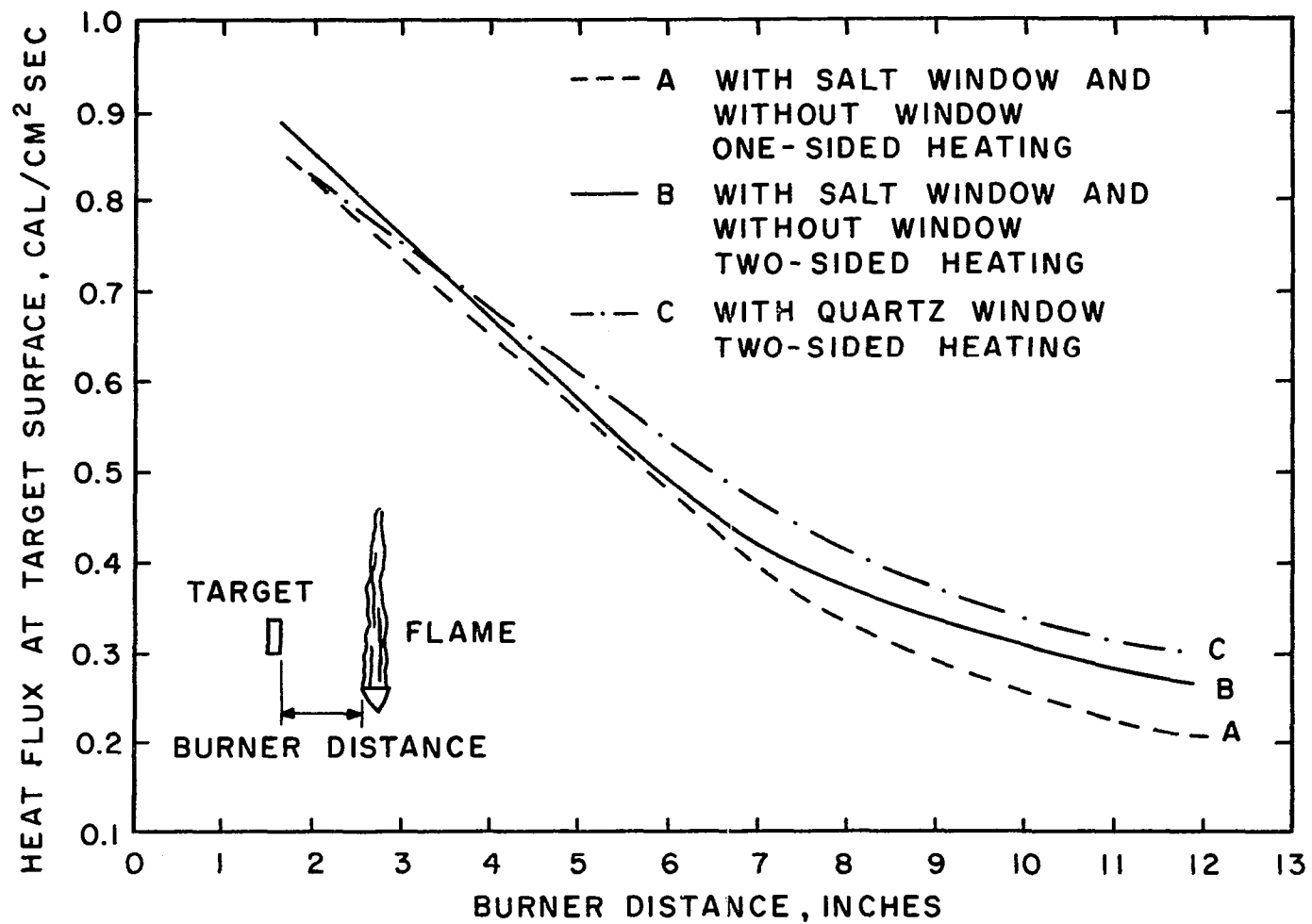


Figure A-3. Irradiance Calibration Curves for the Ignition Cabinet (Cyclo-hexane Fuel).

4. As checked by the pyrliometer output, it took some time from the start of the fire before the flame reached a steady condition and the pyrliometer gave a constant output signal. This time was accepted as the shielding time. In other words, during the normal ignition tests the samples were shielded until constant radiation intensities were obtained, then the shield was pulled suddenly and the sample was exposed to radiation. The shielding time for burner distances of 2 and 3 inches was 8 minutes. For burner distances of greater than 3 inches, it was 10 minutes. These figures apply both to one-sided and two-sided heating.

APPENDIX B

EXPERIMENTAL DETERMINATION OF THE THERMAL PROPERTIES OF WOOD SAMPLES

In order to correlate the results of ignition experiments, the thermal properties of the specimens were determined. The reported values of the thermal diffusivity and thermal conductivity of wood specimens in the literature (26, 34, 35) show that these properties depend on factors such as density, moisture content, direction of heat flow with respect to grain, defects (like checks, knots, and cross grain structures). For example, the thermal diffusivity, which is a measure of the rate of temperature change, is about 3 times higher along the grain than it is across the grain. The proportion and the relative density of the springwood and summerwood in the board also affect the thermal properties. Therefore all samples of each species of wood were cut from the same board and their average thermal properties were determined experimentally.

Thermal diffusivity, designed by α is given by

$$\alpha = \frac{K}{\rho c} \quad (B-1)$$

The determination of complete thermal properties requires the experimental measurement of either α or K provided that ρ and c are known. The following method of the determination of thermal diffusivity was proposed by Chung and Jackson (15), and has the advantages of simplicity and reliability.

The equation for unsteady-state heat transfer in the radial direction of an infinitely long cylindrical rod is

$$\alpha \left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right] = \frac{\partial T}{\partial t} \quad (\text{B-2})$$

If the rod is initially kept at a uniform temperature, the initial condition which applies to Equation B-2 is

$$T = T_o \quad (\text{B-3})$$

If the rod is then immersed in a fluid having a uniform temperature T_a , which is different from T_o , heat is transferred to or from the rod, and one boundary condition, at the surface, $r = R$, becomes

$$\frac{\partial T}{\partial r} = - \frac{h}{K} (T_a - T) \quad (\text{B-4})$$

Because the rod is symmetrical the second boundary condition at the center of the rod, $r = 0$, becomes

$$\frac{\partial T}{\partial r} = 0 \quad (\text{B-5})$$

The solution to Equation B-2 and the initial and boundary conditions given by Equations B-3, B-4 and B-5 is given by Jakob (25) as

$$\frac{T_a - T}{T_a - T_o} = \sum_{\nu=1}^{\nu=\infty} \frac{2J_1^2(\chi_\nu)}{\chi_\nu [J_0^2(\chi_\nu) + J_1^2(\chi_\nu)]} [\exp - (\chi_\nu^2 \frac{\alpha t}{R^2})] [J_0(\chi_\nu \frac{r}{R})] \quad (\text{B-6})$$

The series in Equation B-6 converges rapidly and after a comparatively short time all terms after the first become negligible. Equation B-6 then reduces to the form

$$Y = A e^{-bt} \quad (\text{B-7})$$

where

$$Y = \frac{T_a - T}{T_a - T_o} \quad (\text{B-8})$$

$$A = \frac{2J_1^2(\chi_1)}{\chi_1 [J_0^2(\chi_1) + J_1^2(\chi_1)]} [J_0(\chi_1 \frac{r}{R})] \quad (\text{B-9})$$

and

$$b = \frac{\chi_1^2 \alpha}{R^2} \quad (\text{B-10})$$

Equation B-7 may be written as

$$\ln Y = -bt + \ln A \quad (B-11)$$

Equation B-11 is linear when $\log Y$ is plotted versus t . From the slope of the line ($-b$) and from Equation B-10 the thermal diffusivity α can then be calculated.

The value of χ_1 in equation B-10 is the smallest root of the transcendental equation

$$\frac{\chi}{(hR/K)} = \frac{J_0(\chi)}{J_1(\chi)} \quad (B-12)$$

and depends on the dimensionless group (hR/K) . The limiting value of χ_1 when $(hR/K) \rightarrow \infty$ is 2.405 (Table 13-9 of Reference (25)). For practical application, if (hR/K) is greater than 100, no significant error will result.

To determine α experimentally, the temperature at some point inside a cylindrical specimen is observed as a function of time. A plot of $\log Y$ versus t is prepared; the slope of the straight portion of the curve is found; and the thermal diffusivity α is calculated.

The experimental conditions required to meet the above mathematical model are:

1. The rod must be long enough to eliminate the end effects. It has been found (15) that a ratio of rod length to diameter of 4 would make the result inaccurate by only 1

part in 10,000 for an isotropic material. Even considering that the value of thermal diffusivity of wood along the grain is about three times that across the grain, a length to diameter ratio of 10 is considered to give results within the experimental accuracy.

2. The sample must initially be at uniform temperature T_0 . This initial condition was fulfilled by using room temperature as the initial temperature.

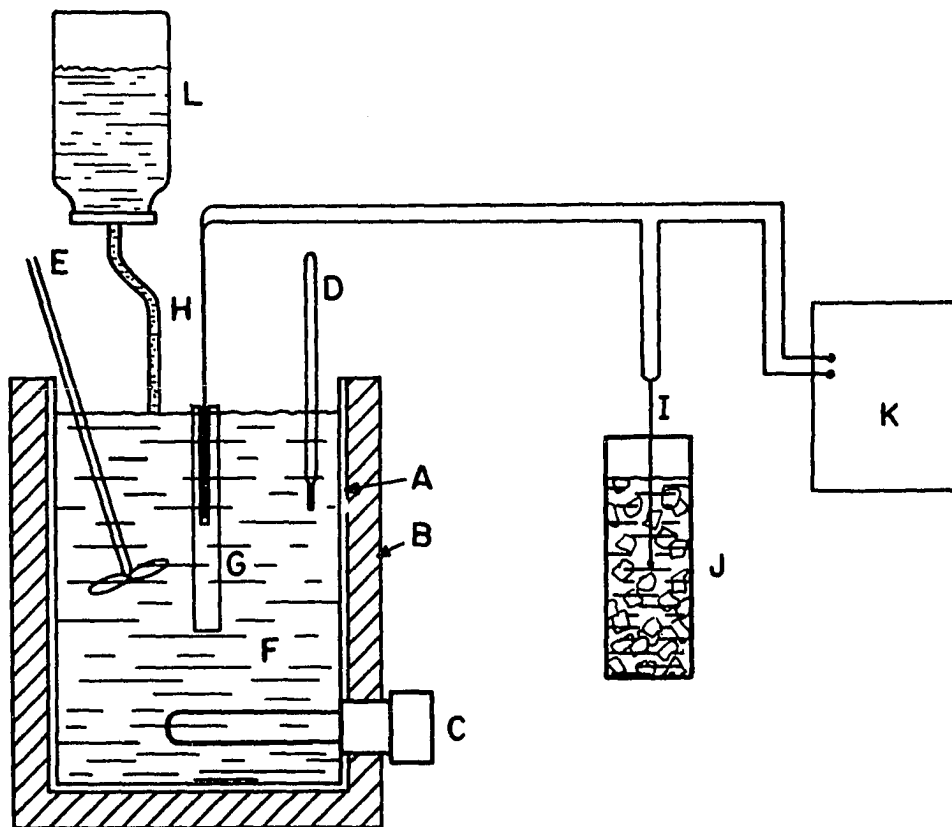
3. The surrounding temperature to which the sample is suddenly exposed must be constant. For this condition boiling water (about 98.8 to 99.8°C depending on the atmospheric pressure) was used as the surrounding medium.

4. The heat transfer coefficient should be high enough so that the limiting values of $\chi_1 = 2.405$ can be used. To provide this condition an electric stirrer was used to circulate the turbulent boiling water. The result of the thermal diffusivity was cross checked with the graphical solution of Equation B-2 given by Jakob (25), which showed that the heat transfer coefficient was high enough to meet the required condition.

The point of temperature measurements need not necessarily be in the center of the cylinder because the heating lines for all radial points are parallel. Therefore the deviation of the thermocouple hole from the axis of the sample rod does not affect the result.

The equipment used in obtaining the experimental data is shown schematically in Figure B-1. It consists of an insulated 2-gallon bucket having two electrical immersion heaters, of 1650 Watts total, fitted in the bottom. An inverted Mason jar fixed above the bucket serves to keep the water level in the system constant. An electric stirrer provides a higher heat transfer coefficient at the surface of the sample. The supplementary parts of the equipment are an ice bath Thermos for keeping the cold junction of the thermocouple constantly at 0°C and a recorder to record the thermocouple output.

Two pieces of wood cut from each end of each board were turned down to rods approximately 8 inches long and 3/4 inch in diameter. A 1/16-inch diameter hole was drilled along the center axis from one end to a depth of about 4.25 inches. All samples were oven-dried at about 102°C for 24 hours. Then they were placed in plastic bags to cool down to room temperature. After accurate measurements of their length and diameter they were tagged and painted with epoxy resin. The thin film of epoxy prevented the wood from becoming moistened; its comparatively high thermal conductivity did not introduce any significant error in the final result. The hot junction of the thermocouple (Conax Con-O-Clad of 40 mil sheath diameter) was placed in the bottom of the sample hole and the specimen was suddenly immersed into the boiling water. The millivolt output



- A GALVANIZED BUCKET
- B INSULATION
- C IMMERSION HEATER
- D THERMOMETER
- E ELECTRICAL STIRRER
- F WATER
- G SPECIMEN
- H HOT JUNCTION OF THERMOCOUPLE
PLACED IN SPECIMEN
- I COLD JUNCTION OF THERMOCOUPLE
PLACED IN ICE BATH
- J ICE BATH
- K RECORDER
- L LEVEL CONTROLLER

Figure B-1. Schematic Diagram of Thermal Diffusivity Apparatus.

of the thermocouple was continuously recorded.

Table B-1 shows the sample calculation of the specimen No. 2 of pine and the values of Y which are plotted against t in Figure B-2. The rest of the calculation is as follows:

$$\text{Slope} = -b = \left[\frac{\ln 0.4258 - \ln 0.0680}{1.0 - 5.0} \right]$$

$$= \left[\frac{2.68825 - 0.85379}{3.0} \right]$$

$$b = 0.612$$

$$\alpha = \frac{(0.394)^2 (.612)}{5.784} = 0.0164 \frac{\text{in}^2}{\text{min}}$$

$$= 0.00684 \text{ ft}^2/\text{hr}$$

To check the reproducibility of the tests each sample was tested four times. The maximum variation of the results from the average of the four tests was less than 4.7, 3.5, 3.2, 2.6, and 2.4 percent for oak, pine, fir, mahogany and redwood respectively.

The value reported in Table B-2 for the thermal diffusivity of each species was the numerical average of the results obtained from all samples of that species in all four tests. The maximum percent variation of each individual result from this overall average was less than 9.9, 9.6, 6.6, 4.6 and 4.0 for oak, redwood, pine, mahogany

TABLE B-1

EXAMPLE OF THERMAL DIFFUSIVITY MEASUREMENT DATA

Sample: PINE

Diameter, $D = 0.788$ in.Radius, $R = 0.394$ in.Length, $L = 8.469$ in. $L/D = 10.75$ Ambient Temperature, $T_a = 99.3^\circ\text{C}$ Initial Temperature, $T_o = 25.8^\circ\text{C}$

t Min	T $^\circ\text{C}$	$T_a - T$ $^\circ\text{C}$	Y
0	25.8	73.5	1.0000
0.5	27.4	71.9	0.9782
1.0	41.8	57.5	0.7823
1.5	56.3	43.0	0.5850
2.0	68.0	31.3	0.4258
2.5	76.2	23.1	0.3143
3.0	82.2	17.1	0.2326
3.5	86.8	12.5	0.1701
4.0	90.2	9.1	0.1238
4.5	92.3	7.0	0.0952
5.0	94.3	5.0	0.0680
5.5	95.4	3.9	0.0531

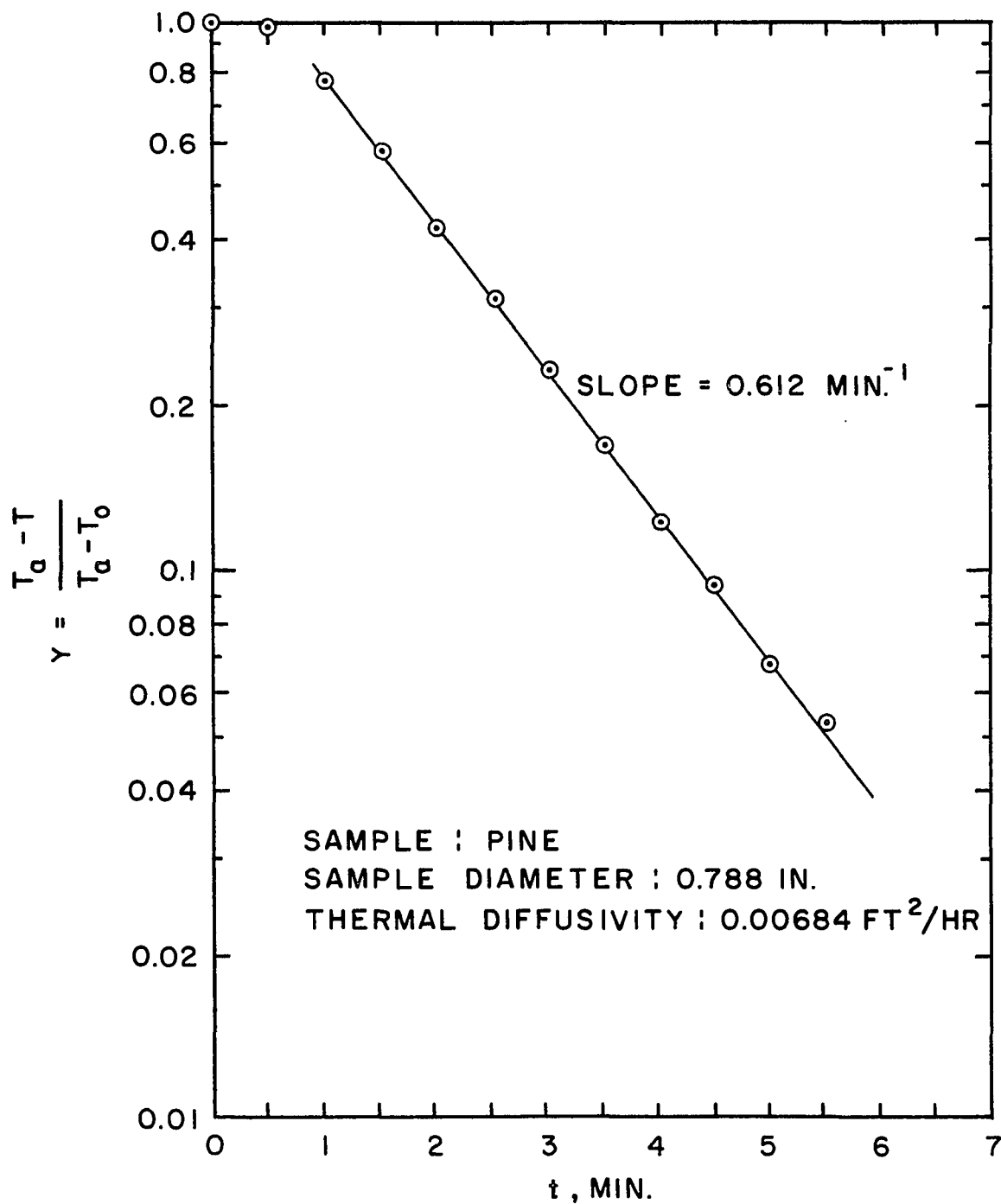


Figure B-2. Example Plot of Y versus t for Thermal Diffusivity Measurement.

and fir respectively. These show the variation in the structure of the wood in different parts of the board from which the samples were prepared.

As mentioned in Chapter III all samples of each species of wood were cut from the same board. The samples were made in thicknesses of $1/2$, $5/8$ and $3/4$ inch. The other dimensions of the samples did not vary significantly. To find the average density of each species two samples from each size, randomly chosen from among all samples of that species, were oven dried and weighed by an analytical balance. The dimensions of each sample were measured with a micrometer and their individual density was found by dividing each sample's weight by its calculated volume. The average density of each species was then found by numerical average of densities of 6 samples, two from each size.

It was found that the range of densities in each species, especially in oak and fir (0.720-0.891 and 0.544-0.678 gm/cc respectively), was rather wide and it was decided to calculate the individual density of each sample. This calculation consisted in dividing the initial recorded weight of the sample during weight loss measurement by the average volume of ten samples of each size. The maximum variation in average volume was 2.2 percent. The values found in this manner were used for correlation of ignition data. The density of every sample is reported in Table D-1 of Appendix D.

The thermal conductivity of each sample was found from Equation B-1

$$\alpha = \frac{K}{\rho c} \quad (B-1)$$

or

$$K = \alpha \rho c \quad (B-13)$$

The values used on the right hand side of Equation B-13 were as follows:

α = The average thermal diffusivity of each species as found by the experimental method described earlier in this Appendix.

ρ = The individual density calculated on an oven-dry basis as described earlier in this Appendix.

c = An average value of 0.34 cal/gm°C which is widely used in literature.

An average value of density was used to calculate the average thermal conductivity in order to see the magnitude of the results. These data are summarized in Table B-2. The individual values of thermal conductivity may be found by using the average thermal diffusivity of Table B-2, and individual density of Table D-1.

TABLE B-2

SUMMARY OF AVERAGE PHYSICAL PROPERTIES
OF WOOD SAMPLES

Wood	α (Thermal Diffusivity)		*K (Thermal Conductivity)		ρ (Density)	
	cm ² /sec	ft ² /hr	cal/cm sec°C	Btu/ft hr°F	gm/cm ³	lb/ft ³
Fir	0.00140	0.00542	0.000290	0.0703	0.610	38.1
Mahogany	0.00154	0.00598	0.000291	0.0706	0.555	34.7
Oak	0.00168	0.00652	0.000440	0.1067	0.770	48.1
Pine	0.00177	0.00685	0.000229	0.0555	0.381	23.8
Redwood	0.00150	0.00580	0.000232	0.0561	0.455	28.4

* C = .34 cal/gm°C and .34 Btu/lb°F for calculation of K from experimental values.

APPENDIX C

SURFACE TEMPERATURE MEASUREMENT

The attainment of a given surface temperature as a criterion for ignition has been used by several investigators. Temperature measurement is important because the decomposition of organic materials and the reactions which precede and accompany their ignition are dependent upon the temperature of the exposed surface.

The determination of ignition temperature has been found to be difficult and the results of different studies usually do not agree with each other. The techniques of surface temperature measurements found in literature consist of the following:

1. The most common procedure is to attach a thermocouple to the surface of the sample. The results of this method are difficult to interpret because: (a) An unknown portion of the recorded signal is due to the direct absorption of radiant energy by thermocouple. (b) The temperature of thermocouple may not be the same as the surface, due to the conduction along the thermocouple leads. (c) The thermocouple bead may lose its intimate contact with the surface as soon as charring, shrinkage and cracking start. (d) The

thermocouple bead senses a temperature which is different from the surface temperature because it is only in partial contact with the surface.

2. A second method is to place thermocouple junctions at various depths in the sample and extrapolate the results to the surface. The results of this method are also questionable, due to the nature of contact, the distance from the surface and especially the extrapolating technique.

3. The third general method is by means of radiation pyrometers which allow remote measurement of the surface temperature and do not require physical contact. This last method therefore seems better than the others and is broadly classified in two groups: (a) optical pyrometers, which are instruments in which the brightness (for a narrow wavelength interval) of a hot object is visually compared to that of a source of standard brightness, and (b) radiation pyrometers, which measure the rate of energy emission per unit area over a relatively broad range of wave lengths.

A pyrometer of the latter type may be used for surface temperature measurement of samples in the ignition studies. This instrument should cover the range of incandescent and non-incandescent temperatures and also have a rapid response to permit the measurement of rapidly varying temperatures. If an instrument of this type is employed, the optical properties of the samples should be known or measured.

The portion of the electromagnetic spectrum called the "thermal radiation" band lies in the range of wave lengths from about 0.1 to 100 microns. The visible light portion of the spectrum is very narrow and extends from about 0.35 to 0.75 micron. The electromagnetic energy in the thermal radiation band is generated by molecular thermal action in all objects at temperatures above absolute zero. The Stefan-Boltzmann law gives the amount of this energy radiated per unit area as follows:

$$E = \sigma \epsilon T_s^4 \quad (C-1)$$

where E = energy, watts/cm²

σ = Stefan-Boltzmann constant

$$= 5.67 \times 10^{-12} \text{ watts/cm}^2 \text{ } ^\circ\text{K}^4$$

ϵ = surface emittance

T_s = absolute temperature, $^\circ\text{K}$

The spectral distribution of radiation represents the statistical molecular energy distribution and was derived by Plank by introducing the quantum concept. The resulting expression is given by

$$E_{b\lambda} = \frac{2\pi hc^2 \lambda^{-5}}{e^{(hc/k\lambda T_s)} - 1} \quad (C-2)$$

where $E_{b\lambda}$ = monochromatic emissive power of a black body,
 $\text{erg/cm}^2 \text{ sec cm}$

c = velocity of light = $2.9979 \times 10^{10} \text{ cm/sec}$

h = Planck's constant = $6.6236 \times 10^{-27} \text{ erg/sec}$

k = Boltzmann constant = $1.3802 \times 10^{-16} \text{ erg/}^\circ\text{K}$

and λ = wavelength, cm

The subscript (b) in $E_{b\lambda}$ designates "Black body" or perfect emitter ($\epsilon = 1$). Spectral distribution curves calculated from Equation C-2 are shown in Figure C-1.

Wien's Displacement Law states that the wavelength of the maximum intensity is inversely proportional to the absolute temperature. It is derived from Equation C-2 and results in

$$\lambda_{\max} T_s = 0.2898 \text{ cm}^\circ\text{K} \quad (\text{C-3})$$

where $\lambda_{\max}$ = wavelength at which the maximum intensity occurs for a black body at $T^\circ\text{K}$

This fact is also shown on Figure C-1. For higher temperature objects the peak shifts to the left.

The spectral or monochromatic emittance is defined as the ratio of monochromatic-emissive power of the body to the monochromatic-emissive power of a black body at the same wave length and temperature ($\epsilon_\lambda = E_\lambda / E_{b\lambda}$). A gray body is defined such that the monochromatic emittance ϵ_λ of the body is independent of wave length, that is $\epsilon_\lambda = \text{constant}$, which is always less than one.

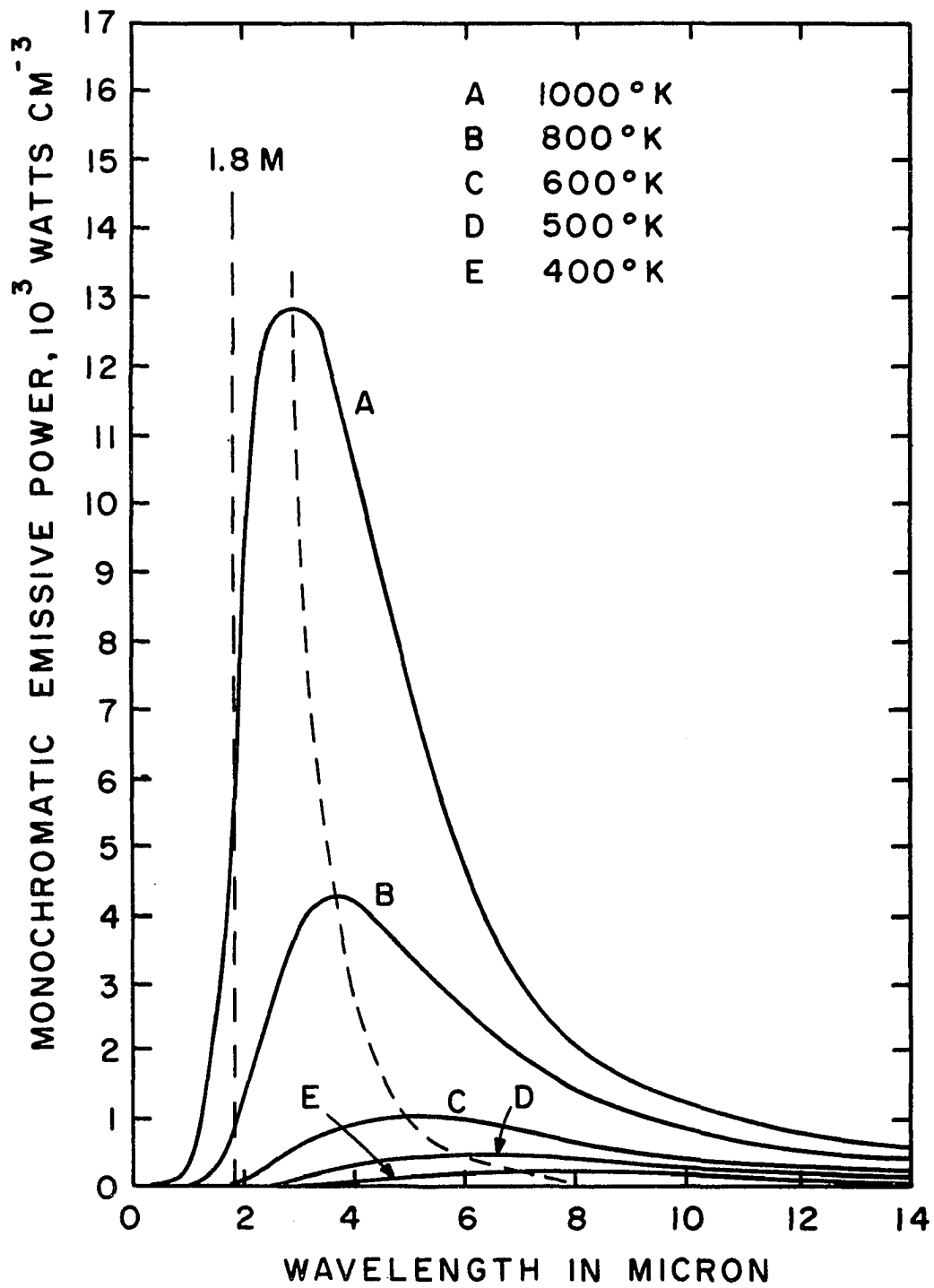


Figure C-1. Black Body Radiation Curves.

The absorptance, α , of a surface depends not only on the surface condition and the material but also on the quality of incident radiation, characterized by its spectral distribution. For gray bodies, the monochromatic absorptance α_λ is also independent of the wave length or spectral distribution of incident radiation. In this case $\alpha = \epsilon$ even though the temperature of the radiator and its receiver are not the same (41, page 63).

The Barnes Engineering Industrial Radiometer Model R-4D1 used to measure the surface temperatures of the samples has been discussed previously (see Chapter III). In operation, the radiometer converts the radiant energy entering the radiometer into an electrical voltage through a system constant k . As checked with calibration curves and a black body cavity source, it was found out that the following equation allows the calculation of target radiance and target temperature from the panel meter voltage

$$\frac{\sigma \epsilon T_s^4}{\pi} = \frac{2kV_s}{1 - 0.005(T_r - 25)} + N_r \quad (C-4)$$

where k = system constant = 130 (for the focal distance used)

V_s = measured output signal voltage, rms volts

T_r = reference source temperature in radiometer head,
°C (an average operating temperature $T_r = 30^\circ\text{C}$)

N_r = reference source radiance (for 30°C , $N_r = 6.5$
m watts/cm²steradian)

ϵ = target emittance

and σ = Stefan-Boltzmann constant
 $= 5.67 \times 10^{-9} \text{ m watts/cm}^2 \text{ } ^\circ\text{K}^4$

If emittance (ϵ) of the target is known Equation C-4 permits the target temperature T_s to be calculated from the measured value of V_s .

However, if the target is heated by a radiation source, the problem is not so easy because the energy received by the radiometer is contributed not only by the surface emittance but also by the reflected energy from the radiating source itself. In this study, the energy incident on the surface, at any burner distance, was measured by an Asymtotic Rapid Response Calorimeter, as explained in Appendix A. The fraction of this incident energy which is reflected in the direction toward the temperature measuring system is unknown unless a comprehensive study of the surface properties and other factors involved is made.

If the directional reflectance ρ_d is known, Equation C-4 becomes

$$\frac{\epsilon_d \sigma T_s^4}{\pi} + \frac{\rho_d H}{\pi} = \frac{2kV_s}{1 - 0.005(T_r - 25)} + N_r \quad (\text{C-5})$$

where ϵ_d = directional emittance = $1 - \rho_d$

ρ_d = directional reflectance

H = radiant energy incident on the surface of the sample, m watts/cm^2

Substituting the values of σ , k , T_r and N_r in consistent units, the temperature, T_s , is then given by

$$T_s (^{\circ}\text{K}) = 100 \left[\frac{1477.5(V_s) - 7379.2(\rho_d)(H) + 36.0}{1 - \rho_d} \right]^{\frac{1}{4}} \quad (\text{C-6})$$

in which H is in $\text{cal/cm}^2\text{sec}$ and V_s is in volts. It still remains necessary to estimate ρ_d with some reliable experimental technique before Equation C-6 can be used. The estimation of the values of ρ_d to be used for temperature measurement of wood samples will be discussed later in this Appendix.

The radiometer output was directly and continuously recorded by a Honeywell ElectroniK 19 Lab Recorder whose reading was calibrated against the radiometer output V_s . The calibration curve was linear and V_s could be calculated from the following equation

$$V_s = 0.01694(\text{MV}) - 0.03$$

where MV denotes recorder output in milli-volts.

The value of ρ_d necessary to calculate the surface temperature from Equation C-6 is a surface property. The term surface here denotes the interface between a transparent medium and an opaque sample. The radiant energy emerging from the surface originates within the body and does not result from transmission of energy incident on some other

part of the body. Emission is thus a characteristic of the interface composition and configuration. The reflectance and the emittance of a surface are related to each other, and if one of them is determined, the other will be known.

An optically smooth surface is defined as a surface whose irregularities are smaller than the wavelength of the energy incident upon it. The reflected ray always leaves such a surface at an angle equal to the angle of incidence. The reflection in this case is thus mirror-like and is called specular reflection. Many surfaces encountered in engineering practice are not perfectly smooth and their irregularities are on the order of a few microns, which is the order of magnitude of the wavelength of thermal radiation. If the size of the irregularities is greater than the wavelength of the incident ray the reflection is "broken up" and a mono-directional beam will be distributed uniformly in all directions after reflection. Such a surface is called a diffuse surface. Information on the diffuse or specular character of actual surfaces is almost totally lacking for ignitable materials. Tables of previous data cannot be used because the properties depend on surface conditions such as roughness, dust, color, the nature of the material, etc. and also on the spectral distribution of radiant energy. If a surface is specular in the visible region it is specular in the infrared region. Generally the specular behavior of any surface increases with increases in wavelength, angle of incidence, and smoothness.

For the purpose of evaluation of ignition data and calculation of surface temperature from Equation C-6 it was necessary to estimate the directional reflectance ρ_d . This reflectance, because of the characteristics of the ignition cabinet and spectral distribution of radiant energy, was a mixture of specular and diffuse components. An attempt was made to estimate ρ_d from the results of experiments carried out with the apparatus set up for reflectance measurement in the school of Aerospace and Mechanical Engineering as described by Francis (18). The results of the calculations seemed to underestimate ρ_d .

It was desirable to carry out some experiments which allowed estimation of ρ_d under conditions which closely reproduced the ignition tests. The idea was to measure the surface temperature using both the radiometer and some other independent method which eliminated the effect of reflection. This work was accomplished by attaching a 28-gage wire thermocouple to the surface of the sample, a short distance away from the area that could be seen by the radiometer. The sample was then shielded and the burner fire started. The thermocouple output was continuously recorded throughout the test. At the instant when the sample was exposed to radiation a breakpoint in the recording of the thermocouple output showed the surface temperature at that time. No significant inaccuracy occurred prior to opening the shutter because the thermocouple hot junction was shielded

from direct irradiation by the flame prior to exposure time. At the time of exposure the surface was also seen by the radiometer, whose output signal was recorded.

Figure C-2 shows a schematic diagram of the experimental set up. Figure C-3 shows typical output signals from the thermocouple and radiometer. Point 2 on the thermocouple output gives the surface temperature just before the exposure time. Point 2 occurs at the same time as Point 1 on the radiometer output, but by using a high chart speed it was noticed that the initial exposure temperature as indicated by the radiometer was not reached until after a time lag which was due to the mechanical response of the recorder pen. Therefore the initial exposure temperature (shown by the radiometer) would be the initial surface temperature as indicated by the thermocouple plus the surface temperature rise during this time lag period. The time lag, depending on the initial surface temperature and the length of the path that the recorder pen had to travel, ran from about 0.09 to 0.20 seconds and could be read from the charts close to 0.01 second. Due to the very low conductivity of the wood, the surface temperature rise as compared with the temperature indicated by Point 2, appeared to be significant.

If the actual surface temperature corresponding to Point 3 is estimated, then the directional reflectance ρ_d can be calculated from the following equation

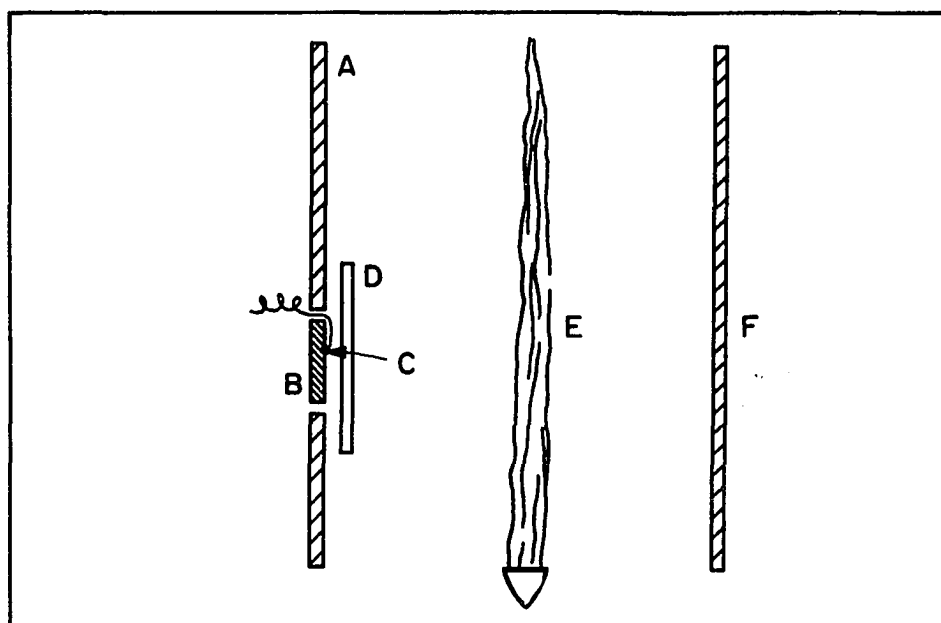


Figure C-2. Schematic Diagram of Experimental Setup for Reflectance Measurement. (A) Sample Panel, (B) Sample, (C) Thermocouple Bead, (D) Shielding Panel, (E) Flame from Liquid Pool, (F) Guide Panel.

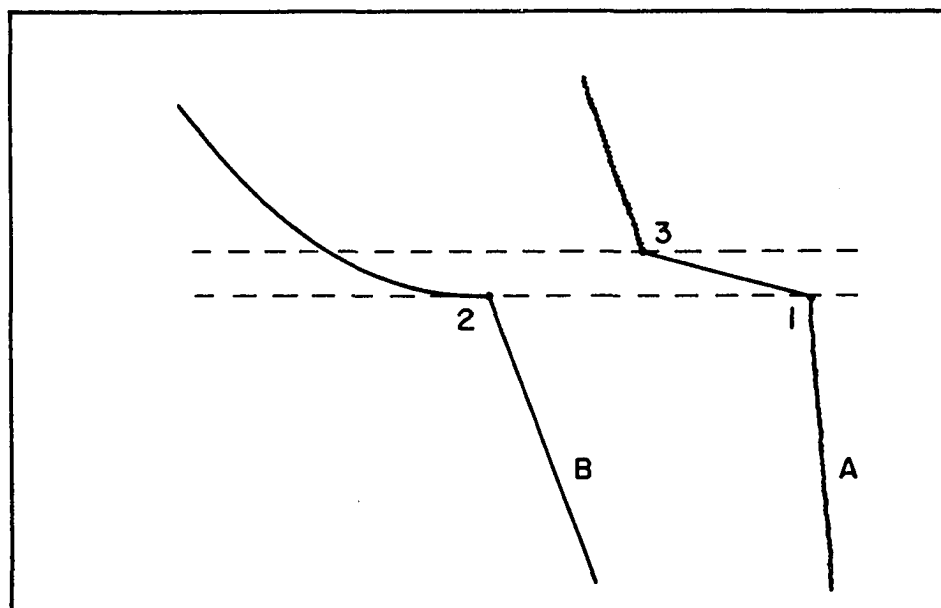


Figure C-3. Example Recorder Output for Reflectance Measurement. (A) Radiometer Output, (B) Thermocouple Output.

$$\rho_d = \frac{1477.5 V_s + 36 - (T_s/100)^4}{7379.2 H - (T_s/100)^4} \quad (C-7)$$

Equation C-7 is a rearranged form of Equation C-6 and the same units must be used.

To estimate the surface temperature rise during the short period of recorder time lag, the wood may be assumed to act as an inert semi-infinite solid that is initially at the temperature shown by thermocouple and has constant heat flux at the surface. If T_o denotes the temperature of thermocouple at exposure time and T gives the temperature thereafter, the heat transfer equation becomes

$$\alpha \frac{\partial^2 \Delta T}{\partial x^2} = \frac{\partial \Delta T}{\partial t} \quad (C-8)$$

where $\Delta T = T - T_o$. The initial and boundary conditions are

$$@ t = 0; \Delta T = 0 \quad (C-9)$$

$$t > 0; x = 0; -K \frac{\partial \Delta T}{\partial x} = H \quad (C-10)$$

$$x \rightarrow \infty; \frac{\partial \Delta T}{\partial x} = 0 \quad (C-11)$$

The solution to Equation C-8 with the described initial and boundary conditions is given by Carslaw and Jaeger (14, page 75). The temperature rise at the surface ($x = 0$) is given by

$$\Delta T_s = \frac{2H}{K} \left(\frac{\alpha t}{\pi} \right)^{\frac{1}{2}} \quad (C-12)$$

where H is the net absorbed radiant energy, considered to be constant for a short time. The temperature rise, calculated from Equation C-12 plus T_o , gives the temperature corresponding to Point 3 of Figure C-3. By substituting the resultant temperature into Equation C-7, the directional reflectance ρ_d is then estimated.

From thermodynamic equilibrium (33) it can be shown that the monochromatic directional emittance of a surface is given by

$$\epsilon_d = 1 - \rho_d \quad (C-13)$$

If wood surfaces are assumed to be "gray bodies" Equation C-13 will hold for entire range of infrared wavelengths. Although this expression was derived from thermodynamic equilibrium, it holds in general because the emittance and the reflectance are functions of the physical and chemical configuration of the surface (33).

In order to avoid interference with the weighing system, thermocouples could not be attached to the surface during normal ignition tests. A series of separate tests were carried out for the purpose of reflectance measurements. In doing so, two samples from each species were tested at

burner distances of 2, 4, 6, 8 and 10 inches. The uncharred samples then were exposed to flame radiation at a 2-inch distance to darken the surface quickly and without letting the charring to penetrate inside the sample. The purpose of this procedure was to make the use of the thermal conductivity of wood in the Equation C-12 justifiable. As mentioned in the literature, although the individual thermal properties of wood and charcoal are different, the thermal diffusivity may be considered to be constant. The same tests were carried out with charred samples. The results of calculations of ρ_d from Equation C-7 showed that some of the charred samples had a higher directional reflectance than uncharred wood. However the overall results showed that ρ_d for charred and uncharred samples were the same within the scatter of the experimental data. This behavior allowed the use of a single ρ_d throughout a test, from start of exposure to ignition point. Therefore, instead of using an average ρ_d for all samples of the same species and at the same burner distance, ρ_d was calculated for each individual test. The calculation was accomplished by using the initial temperature T_s (which is the thermocouple temperature T_o plus the surface temperature rise ΔT_s during the recorder time lag) and the initial radiometer output of every individual test. The following is an example for calculation of ρ_d .

The average thermocouple temperature T_o for oak samples at a burner distance of 6 inches was about 62°C at

the time when the sample was exposed (Point 2 in Figure C-3). The temperature rise, ΔT_s , during the recorder time lag was calculated from Equation C-12 and was about 14°C . Therefore the initial temperature corresponding to Point 3 in Figure C-3 was $62 + 14 = 76^\circ\text{C}$. The ignition test number 19 was carried out for 1/2-inch thick oak sample at a 6-inch burner distance. The initial radiometer output corresponding to Point 3 in Figure C-3 for this test was calculated to be $V_s = 0.3088$. From Equation C-7 the directional reflectance for this sample was calculated to be $\rho_d = 0.0998$. Applying this ρ_d , and the V_s at any time throughout the test number 19, the surface temperature was calculated from Equation C-6. The ignition temperature for test number 19, which was carried out with pilot and under the condition of two-sided heating, was calculated from Equation C-6 and was 298°C . Without consideration of ρ_d the ignition temperature would be about 330°C .

The values of ρ_d generally were higher for the smaller burner distance because the specular component of the reflection increased as the burner approached the sample. In some cases ρ_d at larger burner distance is higher than a smaller burner distance. This result was due to the surface condition of the samples which could reflect more than the other. The overall range of directional reflectances calculated with the above method ranged from 0.056 to 0.257. Generally mahogany had the highest, and redwood the lowest, range of directional reflectance.

APPENDIX D

SUMMARY OF IGNITION DATA FOR OVEN DRIED WOOD SAMPLES

A summary of ignition data for oven dried wood is given in Table D-1 of this appendix. The first column in this table gives the identification of each test, which consists of a combination of numerical and alphabetical characters. The first number gives the order in which the test was carried out. The letter that follows indicates the species used in that test. The letters used are: F for fir, M for mahogany, O for oak, P for pine, and R for redwood. The next letter, S or P, indicates whether ignition (if it occurred) was spontaneous or piloted, respectively. The last group, 1S or 2S, indicates whether the test was carried out under the condition of one-sided or two-sided heating, respectively.

The missing numbers in the column of ignition time and subsequent columns in Table D-1 indicate that samples did not ignite. As explained in Chapter IV, in some cases an upward change of curvature in the surface temperature curve and a rapid temperature rise which was the sign of glowing were followed by ignition. In other words, flaming

occurred after the surface, especially at the corners and edges of cracks, glowed. These tests are marked with an asterisk (*) in Table D-1.

The second column of Table D-1 gives the density of every test sample. The density of every sample was calculated from dividing its weight by the average volume of ten samples of the same size. The weight of the sample was taken as the initial weight as shown by weighing system. This procedure is discussed in Appendix B.

The thermal conductivity of each sample can be calculated from equation B-13 of Appendix B and the thermal diffusivity and specific heat given in Table B-2.

The values of heating rate reported in Table D-1 are measured experimentally by an asymptotic rapid response calorimeter called "pyrheliometer." The details of irradiance measurements are given in Appendix A.

Ignition temperature is the surface temperature at the instant that ignition occurred. The reported temperatures were measured by Barnes Engineering Industrial Radiometer Model R-4D1. The reported ignition temperatures are corrected for surface reflectance. The experimentally measured initial temperatures of the samples are also given in Table D-1. The details of temperature measurement are discussed in Appendix C.

The weight loss rate at ignition was obtained from measuring the slope of the weight loss curve at the point of ignition and dividing it by the total irradiated surface area.

TABLE D-1

SUMMARY OF IGNITION DATA FOR OVEN-DRIED WOOD SAMPLES

Run Number	Sample Density (gm/cm ³)	Sample Thickness (in)	Heating Rate (cal/cm ² sec)	Time to Ignition (sec)	Ignition Temperature T _s (°C)	Initial Temperature T _o (°C)	Ignition Energy (cal/cm ²)	Weight Loss Rate at Ignition (gm/cm ² sec x 10 ³)
1 O S 2S	0.772	0.500	0.577	273	408	67	159	2.17
2 O S 2S	0.754	0.500	0.531	--	--	--	--	--
3 O S 2S	0.753	0.500	0.487	--	--	--	--	--
4 O S 2S	0.756	0.500	0.668	89	337	71	59	1.13
5 O S 2S	0.781	0.500	0.771	66	328	75	51	1.23
7 O S 2S	0.748	0.625	0.668	93	360	71	62	0.95
8 O S 2S	0.807	0.625	0.771	86	331	75	66	1.06
9 O S 2S	0.718	0.625	0.577	--	--	--	--	--
10 O S 2S	0.743	0.625	0.577	225	334	67	130	1.51
11 O S 2S	0.814	0.625	0.531	--	--	--	--	--
12 O S 2S	0.788	0.750	0.771	99	336	75	76	1.15
13 O S 2S	0.786	0.750	0.668	141	322	71	94	1.14
14 O S 2S	0.758	0.750	0.577	--	--	--	--	--
15 O S 2S	0.775	0.750	0.577	--	--	--	--	--
16 O P 2S	0.752	0.500	0.771	143	--	--	110	--
17 O P 2S	0.780	0.500	0.668	155	319	71	104	1.06
18 O P 2S	0.781	0.500	0.577	207	310	67	119	1.14
19 O P 2S	0.747	0.500	0.487	213	298	62	104	0.90
20 O P 2S	0.774	0.500	0.419	261	303	58	109	0.99
21 O P 2S	0.765	0.500	0.373	305	304	53	114	0.95
22 O P 2S	0.754	0.500	0.337	378	281	49	127	1.03
23 O P 2S	0.774	0.500	0.303	400	272	45	121	0.69
24 O P 2S	0.771	0.500	0.275	496	262	40	136	0.80
25 O P 2S	0.743	0.625	0.487	246	324	62	120	0.98

TABLE D-1 (Continued)

Run Number	Sample Density (gm/cm ³)	Sample Thickness (in)	Heating Rate (cal/cm ² sec)	Time to Ignition (sec)	Ignition Temperature T _s (°C)	Initial Temperature T _o (°C)	Ignition Energy (cal/cm ²)	Weight Loss Rate at Ignition (gm/cm ² sec x 10 ³)
26 O P 2S	0.738	0.625	0.373	481	282	53	179	0.98
27 O P 2S	0.781	0.625	0.303	732	256	45	222	0.84
28 O P 2S	0.743	0.625	0.275	1080	266	40	297	0.60
29 O P 2S	0.762	0.750	0.487	351	362	62	171	1.08
30 O P 2S	0.759	0.750	0.373	535	331	53	200	1.26
31 O P 2S	0.770	0.750	0.303	743	294	45	225	1.21
32 O P 2S	0.763	0.750	0.275	957	297	40	263	1.02
34 O S 1S	0.760	0.750	0.740	--	--	--	--	--
35 O S 1S	0.760	0.750	0.740	--	--	--	--	--
36 O S 1S	0.751	0.750	0.827	59	358	80	49	0.33
37 O S 1S	0.760	0.750	0.784	123	430	78	96	1.19
38 O S 1S	0.760	0.750	0.762	--	--	--	--	--
39 O S 1S	0.751	0.750	0.774	--	--	--	--	--
40 O S 1S	0.754	0.750	0.774	150	479	77	116	1.26
41 O S 1S	0.738	0.625	0.784	138	475	78	108	1.19
42 O S 1S	0.750	0.625	0.827	57	362	80	47	0.79
43 O S 1S	0.732	0.625	0.805	71	360	79	57	1.01
44 O S 1S (*)	0.743	0.625	0.762	266	546	76	203	1.34
45 O S 1S	0.754	0.625	0.740	--	--	--	--	--
46 O S 1S	0.720	0.500	0.784	85	402	78	67	1.24
47 O S 1S	0.745	0.500	0.762	--	--	--	--	--
48 O P 1S	0.771	0.750	0.740	91	393	75	67	1.05
49 O P 1S	0.763	0.750	0.568	--	--	--	--	--
50 O P 1S (*)	0.754	0.750	0.568	468	555	67	266	1.13

* Surface partly glowed before ignition occurred.

TABLE D-1 (Continued)

Run Number	Sample Density (gm/cm ³)	Sample Thickness (in)	Heating Rate (cal/cm ² sec)	Time to Ignition (sec)	Ignition Temperature T _S (°C)	Initial Temperature T _O (°C)	Ignition Energy (cal/cm ²)	Weight Loss Rate at Ignition (gm/cm ² sec x 10 ³)
51 O P 1S	0.760	0.750	0.653	303	452	71	198	1.07
52 O P 1S (*)	0.760	0.750	0.653	375	535	71	245	1.04
53 O P 1S (*)	0.745	0.625	0.740	333	550	75	246	1.09
54 O P 1S (*)	0.865	0.625	0.653	336	519	71	219	1.05
55 O P 1S	0.861	0.625	0.568	180	356	67	102	0.65
56 O P 1S	0.855	0.625	0.484	311	352	62	151	0.51
57 O P 1S	0.883	0.625	0.399	--	--	--	--	--
58 O P 1S	0.884	0.500	0.740	93	373	57	69	1.21
59 O P 1S (*)	0.868	0.500	0.653	261	488	71	170	1.09
60 O P 1S	0.891	0.500	0.568	270	391	67	153	0.71
61 P S 2S	0.377	0.750	0.771	66	450	82	51	0.90
62 P S 2S	0.377	0.750	0.668	150	447	78	100	0.63
63 P S 2S	0.382	0.750	0.577	204	378	73	118	0.49
64 P S 2S	0.372	0.750	0.487	378	378	68	184	0.69
65 P S 2S	0.377	0.750	0.419	--	--	--	--	--
66 P S 2S	0.384	0.625	0.771	90	419	82	69	0.66
67 P S 2S	0.377	0.625	0.668	117	405	78	78	0.70
68 P S 2S (*)	0.367	0.625	0.577	291	437	73	168	0.85
69 P S 2S	0.374	0.625	0.487	--	--	--	--	0.85
70 P S 2S	0.381	0.500	0.771	96	--	--	74	1.11
71 P S 2S	0.391	0.500	0.668	105	388	78	72	0.70
72 P S 2S	0.392	0.500	0.577	201	379	73	116	0.94
73 P S 2S	0.393	0.500	0.487	--	--	--	--	--
74 P P 2S	0.404	0.750	0.771	40	344	82	31	0.42
75 P P 2S	0.381	0.750	0.577	127	361	73	73	0.27

* Surface partly glowed before ignition occurred.

TABLE D-1 (Continued)

Run Number	Sample Density (gm/cm ³)	Sample Thickness (in)	Heating Rate (cal/cm ² sec)	Time to Ignition (sec)	Ignition Temperature T _s (°C)	Initial Temperature T _o (°C)	Ignition Energy (cal/cm ²)	Weight Loss Rate at Ignition (gm/cm ² sec x 10 ³)
76 P P 2S	0.377	0.750	0.373	327	313	59	122	0.19
77 P P 2S	0.378	0.750	0.275	1027	317	45	282	0.22
78 P P 2S	0.383	0.625	0.771	38	379	82	29	0.37
79 P P 2S	0.382	0.625	0.577	119	348	73	69	0.39
80 P P 2S	0.373	0.625	0.373	480	350	59	179	0.59
81 P P 2S	0.368	0.625	0.275	--	--	--	--	--
82 P P 2S	0.393	0.500	0.771	35	330	92	27	0.20
83 P P 2S	0.380	0.500	0.577	125	312	73	72	0.37
84 P P 2S	0.387	0.500	0.373	390	309	59	145	0.52
85 P P 2S	0.382	0.500	0.275	--	--	--	--	--
86 P P 2S	0.386	0.500	0.487	210	322	68	102	0.49
87 P S 1S	0.380	0.750	0.740	--	--	--	--	--
88 P S 1S	0.379	0.750	0.827	37	382	87	31	0.40
89 P S 1S	0.377	0.750	0.784	88	470	85	69	0.98
90 P S 1S	0.377	0.750	0.762	--	--	--	--	--
91 P S 1S (*)	0.380	0.750	0.774	122	604	84	94	1.01
92 P S 1S	0.366	0.625	0.827	48	401	87	40	0.79
93 P S 1S	0.374	0.625	0.784	--	--	--	--	--
94 P S 1S	0.378	0.500	0.827	58	401	87	48	0.65
95 P S 1S	0.374	0.500	0.784	94	479	85	74	0.96
96 P S 1S	0.393	0.500	0.740	--	--	--	--	--
97 P P 1S	0.376	0.750	0.740	46	378	82	34	0.48
98 P P 1S (*)	0.375	0.750	0.653	159	474	78	104	0.66
99 P P 1S (*)	0.371	0.750	0.568	279	528	73	158	0.69
100 P P 1S	0.377	0.750	0.484	--	--	--	--	--

* Surface partly glowed before ignition occurred.

TABLE D-1 (Continued)

Run Number	Sample Density (gm/cm ³)	Sample Thickness (in)	Heating Rate (cal/cm ² sec)	Time to Ignition (sec)	Ignition Temperature T _g (°C)	Initial Temperature T _o (°C)	Ignition Energy (cal/cm ²)	Weight Loss Rate at Ignition (gm/cm ² sec x 10 ³)
101 P P 1S	0.386	0.625	0.740	62	388	82	46	0.67
102 P P 1S (*)	0.388	0.625	0.653	213	549	78	139	0.74
103 P P 1S (*)	0.382	0.625	0.568	330	574	73	184	0.60
104 P P 1S (*)	0.377	0.625	0.526	525	564	70	276	0.58
105 P P 1S	0.368	0.625	0.484	474	391	68	229	0.34
106 P P 1S (*)	0.371	0.625	0.442	715	447	66	316	0.35
107 P P 1S	0.388	0.625	0.399	--	--	--	--	--
108 P P 1S (*)	0.387	0.500	0.740	142	515	82	105	0.85
109 P P 1S (*)	0.404	0.500	0.653	243	589	78	159	0.81
110 P P 1S (*)	0.386	0.500	0.568	315	468	73	179	0.65
111 P P 1S (*)	0.386	0.500	0.484	650	567	68	315	0.49
112 P P 2S	0.395	0.750	0.487	153	320	68	75	0.23
113 P P 2S	0.399	0.750	0.419	237	305	63	99	0.19
114 P P 2S	0.393	0.750	0.303	--	--	--	--	--
115 P P 2S	0.387	0.625	0.337	--	--	--	--	--
116 P P 2S	0.371	0.625	0.487	306	367	68	149	0.58
117 P P 2S	0.385	0.500	0.487	247	322	68	120	0.60
118 P P 2S	0.393	0.500	0.337	--	--	--	--	--
119 M S 2S	0.564	0.750	0.771	93	391	78	72	0.85
120 M S 2S	0.563	0.750	0.668	154	397	73	103	0.48
121 M S 2S	0.549	0.750	0.577	198	376	69	114	0.64
122 M S 2S	0.550	0.750	0.487	417	386	65	203	0.94
123 M S 2S	0.546	0.750	0.419	--	--	--	--	--
124 M S 2S	0.583	0.625	0.771	88	367	78	68	0.78
125 M S 2S	0.562	0.625	0.668	117	359	73	78	0.73

* Surface partly glowed before ignition occurred.

TABLE D-1 (Continued)

Run Number	Sample Density (gm/cm ³)	Sample Thickness (in)	Heating Rate (cal/cm ² sec)	Time to Ignition (sec)	Ignition Temperature T _s (°C)	Initial Temperature T _o (°C)	Ignition Energy (cal/cm ²)	Weight Loss Rate at Ignition (gm/cm ² sec x 10 ³)
126 M S 2S	0.556	0.625	0.577	228	382	69	132	0.74
127 M S 2S	0.574	0.625	0.487	382	399	65	186	1.16
128 M S 2S(*)	0.545	0.625	0.419	646	447	60	271	0.52
129 M S 2S	0.576	0.500	0.771	63	370	78	49	0.95
130 M S 2S	0.579	0.500	0.668	100	362	73	67	0.86
131 M S 2S	0.601	0.500	0.577	160	349	69	92	0.89
132 M S 2S	0.563	0.500	0.487	258	365	65	126	1.42
133 M S 2S	0.560	0.500	0.419	--	--	--	--	--
134 M P 2S	0.551	0.750	0.771	45	304	78	35	0.31
135 M P 2S	0.558	0.750	0.577	120	327	69	69	0.44
136 M P 2S	0.550	0.750	0.419	467	337	60	196	0.78
137 M P 2S	0.558	0.750	0.337	652	305	51	220	0.71
138 M P 2S	0.551	0.750	0.275	--	--	--	--	--
139 M P 2S	0.561	0.625	0.771	54	328	78	42	0.56
140 M P 2S	0.545	0.625	0.577	192	324	69	111	0.73
141 M P 2S	0.588	0.625	0.419	404	287	60	169	0.63
142 M P 2S	0.589	0.625	0.337	620	293	51	209	0.74
143 M P 2S(*)	0.576	0.625	0.303	687	283	47	208	0.59
144 M P 2S	0.562	0.625	0.303	760	280	47	230	0.65
145 M P 2S	0.586	0.500	0.771	65	311	78	50	0.64
146 M P 2S	0.583	0.500	0.577	177	298	69	102	0.76
147 M P 2S	0.577	0.500	0.419	304	282	60	127	0.64
148 M P 2S	0.579	0.500	0.337	513	271	51	173	0.64
149 M P 2S	0.587	0.500	0.303	672	274	47	204	1.05
150 M S 1S	0.549	0.750	0.827	57	363	82	47	0.73

* Surface partly glowed before ignition occurred.

TABLE D-1 (Continued)

Run Number	Sample Density (gm/cm ³)	Sample Thickness (in)	Heating Rate (cal/cm ² sec)	Time to Ignition (sec)	Ignition Temperature T _s (°C)	Initial Temperature T _o (°C)	Ignition Energy (cal/cm ²)	Weight Loss Rate at Ignition (gm/cm ² sec x 10 ³)
151 M S 1S	0.550	0.750	0.740	--	--	--	--	--
152 M S 1S	0.552	0.750	0.784	129	463	80	101	1.08
153 M S 1S	0.550	0.625	0.827	54	331	82	45	0.88
154 M S 1S	0.562	0.625	0.740	--	--	--	--	--
155 M S 1S	0.568	0.500	0.827	65	332	82	54	0.91
156 M S 1S	0.592	0.500	0.784	176	462	80	133	1.09
157 M S 1S	0.596	0.500	0.740	--	--	--	--	--
158 M P 1S	0.549	0.750	0.827	43	301	82	36	0.53
159 M P 1S	0.549	0.750	0.740	90	341	78	67	0.59
160 M P 1S(*)	0.549	0.750	0.653	285	493	73	186	0.77
161 M P 1S	0.549	0.750	0.568	426	429	69	242	0.65
162 M P 1S	0.539	0.750	0.484	--	--	--	--	--
163 M P 1S	0.546	0.625	0.827	76	343	82	60	0.97
164 M P 1S	0.574	0.625	0.740	177	437	78	131	0.93
165 M P 1S(*)	0.591	0.625	0.653	274	451	73	179	0.72
166 M P 1S(*)	0.559	0.625	0.568	576	491	69	322	0.68
167 M P 1S(*)	0.583	0.625	0.526	702	459	67	369	0.52
168 M P 1S	0.581	0.500	0.827	106	350	82	83	0.91
169 M P 1S(*)	0.571	0.500	0.740	255	489	78	189	0.89
170 M P 1S	0.586	0.500	0.653	226	389	73	148	0.72
171 M P 1S	0.579	0.500	0.740	177	397	78	131	0.81
172 M P 1S(*)	0.577	0.500	0.568	675	512	69	383	0.60
173 M P 1S	0.568	0.500	0.827	64	330	82	50	0.78
174 M P 1S(*)	0.579	0.500	0.526	800	506	67	421	0.52
175 R S 2S	0.465	0.500	0.855	39	293	94	33	0.72

* Surface Partly glowed before ignition occurred.

TABLE D-1 (Continued)

Run Number	Sample Density (gm/cm ³)	Sample Thickness (in)	Heating Rate (cal/cm ² sec)	Time to Ignition (sec)	Ignition Temperature T _S (°C)	Initial Temperature T _O (°C)	Ignition Energy (cal/cm ²)	Weight Loss Rate at Ignition (gm/cm ² sec x 10 ³)
176 R S 2S	0.475	0.500	0.771	106	370	88	82	0.74
177 R S 2S	0.447	0.500	0.668	138	365	82	92	0.63
178 R S 2S	0.450	0.500	0.577	--	--	--	--	--
179 R S 2S	0.459	0.625	0.668	232	382	82	155	0.74
180 R S 2S	0.489	0.625	0.771	126	387	88	97	0.74
181 R S 2S	0.455	0.625	0.855	45	346	94	38	0.74
182 R S 2S	0.480	0.625	0.577	--	--	--	--	--
183 R S 2S	0.464	0.750	0.577	--	--	--	--	--
184 R S 2S	0.466	0.750	0.668	244	398	82	163	0.79
185 R S 2S	0.446	0.750	0.771	146	441	88	113	0.64
186 R S 2S	0.462	0.750	0.855	24	299	94	21	0.30
187 R P 2S	0.444	0.750	0.771	58	317	88	45	0.36
188 R P 2S	0.455	0.750	0.577	130	335	75	75	0.35
189 R P 2S	0.461	0.750	0.419	442	318	63	185	0.58
190 R P 2S	0.454	0.750	0.337	628	317	50	212	0.49
191 R P 2S	0.465	0.625	0.771	58	302	88	40	0.32
192 R P 2S	0.472	0.625	0.577	175	324	75	101	0.50
193 R P 2S	0.446	0.625	0.419	356	294	63	149	0.44
194 R P 2S	0.460	0.625	0.337	501	291	50	169	0.35
195 R P 2S(*)	0.467	0.625	0.275	1254	277	38	345	0.16
196 R P 2S	0.456	0.750	0.275	--	--	--	--	--
197 R P 2S	0.450	0.500	0.275	--	--	--	--	--
198 R P 2S	0.440	0.500	0.337	432	270	50	146	0.43
199 R P 2S	0.431	0.500	0.419	238	280	63	100	0.40
200 R P 2S	0.458	0.500	0.577	114	285	75	66	0.34

* Surface partly glowed before ignition occurred.

TABLE D-1 (Continued)

Run Number	Sample Density (gm/cm ³)	Sample Thickness (in)	Heating Rate (cal/cm ² sec)	Time to Ignition (sec)	Ignition Temperature T _s (°C)	Initial Temperature T _o (°C)	Ignition Energy (cal/cm ²)	Weight Loss Rate at Ignition (gm/cm ² sec x 10 ³)
201 R P 2S	0.440	0.500	0.771	42	302	88	32	0.41
202 R S 1S	0.451	0.750	0.827	48	353	94	40	0.70
203 R S 1S	0.465	0.750	0.784	--	--	--	--	--
204 R S 1S	0.480	0.625	0.827	58	362	94	48	0.76
205 R S 1S(*)	0.454	0.625	0.784	130	518	91	102	0.80
206 R S 1S	0.492	0.625	0.740	--	--	--	--	--
207 R S 1S(*)	0.439	0.500	0.827	108	466	94	89	0.80
208 R S 1S	0.451	0.500	0.784	--	--	--	--	--
209 R P 1S	0.456	0.500	0.827	39	321	94	32	0.47
210 R P 1S	0.446	0.500	0.740	54	317	88	40	0.49
211 R P 1S(*)	0.439	0.500	0.653	240	520	82	157	0.70
212 R P 1S(*)	0.435	0.500	0.568	400	428	75	227	0.46
213 R P 1S	0.450	0.500	0.484	--	--	--	--	--
214 R P 1S(*)	0.448	0.625	0.568	348	476	75	193	0.60
215 R P 1S(*)	0.491	0.625	0.653	306	485	82	200	0.63
216 R P 1S	0.489	0.625	0.740	60	335	88	44	0.55
217 R P 1S	0.457	0.625	0.827	40	320	94	33	0.57
218 R P 1S	0.454	0.750	0.827	52	345	94	43	0.73
219 R P 1S	0.463	0.750	0.740	54	325	88	40	0.68
220 R P 1S	0.469	0.750	0.653	197	407	82	129	0.49
221 R P 1S(*)	0.460	0.750	0.568	345	440	75	196	0.49
222 R P 1S	0.449	0.750	0.484	--	--	--	--	--
223 F S 2S	0.655	0.750	0.855	44	318	91	38	0.40
224 F S 2S	0.649	0.750	0.771	102	358	86	79	0.82
225 F S 2S	0.558	0.750	0.668	144	355	81	96	0.64

* Surface partly glowed before ignition occurred.

TABLE D-1 (Continued)

Run Number	Sample Density (gm/cm ³)	Sample Thickness (in)	Heating Rate (cal/cm ² sec)	Time to Ignition (sec)	Ignition Temperature T _s (°C)	Initial Temperature T _o (°C)	Ignition Energy (cal/cm ²)	Weight Loss Rate at Ignition (gm/cm ² sec x 10 ³)
226 F S 2S	0.561	0.750	0.577	294	366	76	170	0.69
227 F S 2S	0.550	0.750	0.487	--	--	--	--	--
228 F S 2S	0.549	0.625	0.855	40	329	91	34	0.56
229 F S 2S(*)	0.546	0.625	0.771	92	384	86	71	0.67
230 F S 2S	0.547	0.625	0.668	123	269	81	82	0.72
231 F S 2S	0.577	0.625	0.577	240	349	76	138	0.72
232 F S 2S	0.568	0.625	0.487	310	357	70	151	0.79
233 F S 2S	0.567	0.625	0.487	382	344	70	186	0.75
234 F S 2S	0.560	0.625	0.419	--	--	--	--	--
235 F S 2S	0.573	0.500	0.419	--	--	--	--	--
236 F S 2S	0.639	0.500	0.487	328	327	70	160	1.08
237 F S 2S	0.662	0.500	0.577	201	309	76	116	0.70
238 F S 2S	0.630	0.500	0.668	126	318	81	84	0.59
239 F S 2S	0.667	0.500	0.771	96	298	86	74	0.73
240 F P 2S	0.567	0.500	0.419	382	269	66	160	0.56
241 F P 2S	0.621	0.500	0.337	690	272	55	233	0.58
242 F S 2S	0.569	0.500	0.855	30	308	91	26	0.28
243 F P 2S	0.678	0.500	0.771	54	281	86	23	0.28
244 F P 2S	0.617	0.500	0.577	102	265	76	59	0.22
245 F P 2S	0.662	0.500	0.303	963	281	50	292	0.57
246 F P 2S	0.565	0.625	0.771	54	279	86	23	0.26
247 F P 2S	0.575	0.625	0.577	150	294	76	87	0.18
248 F P 2S(*)	0.546	0.625	0.419	825	302	66	327	0.57
249 F P 2S	0.563	0.625	0.337	966	289	55	326	0.51
250 F P 2S	0.656	0.750	0.771	54	272	86	23	0.28

* Surface partly glowed before ignition occurred.

TABLE D-1 (Continued)

Run Number	Sample Density (gm/cm ³)	Sample Thickness (in)	Heating Rate (cal/cm ² sec)	Time to Ignition (sec)	Ignition Temperature T _S (°C)	Initial Temperature T _O (°C)	Ignition Energy (cal/cm ²)	Weight Loss Rate at Ignition (gm/cm ² sec x 10 ³)
251 F P 2S	0.552	0.750	0.577	132	286	76	76	0.15
252 F P 2S	0.658	0.750	0.419	366	245	66	153	0.15
253 F P 2S	0.646	0.750	0.337	500	246	55	169	0.13
254 F P 2S	0.636	0.750	0.303	732	241	50	222	0.24
255 F S 1S	0.575	0.625	0.827	111	382	91	92	0.79
256 F S 1S	0.653	0.750	0.827	123	393	91	102	0.88
257 F S 1S	0.658	0.750	0.784	126	407	89	99	0.98
258 F S 1S	0.649	0.750	0.740	--	--	--	--	--
259 F S 1S	0.571	0.625	0.784	190	495	89	149	1.08
260 F S 1S	0.664	0.500	0.827	90	372	91	74	0.86
261 M P 2S	0.567	0.625	0.487	186	297	65	91	0.43
262 F S 1S	0.650	0.500	0.784	108	357	89	85	0.81
263 F P 1S	0.659	0.500	0.740	100	334	86	74	0.65
264 F P 1S	0.569	0.500	0.653	252	407	81	165	0.79
265 F P 1S	0.651	0.500	0.568	366	400	76	208	0.55
266 F P 1S	0.667	0.500	0.484	786	383	70	380	0.47
267 F P 1S	0.563	0.625	0.740	106	362	86	78	0.73
268 F P 1S	0.545	0.625	0.653	106	349	81	69	0.40
269 F P 1S	0.574	0.625	0.568	305	354	76	173	0.48
270 F P 1S	0.544	0.625	0.484	770	385	70	373	0.39
271 F P 1S	0.655	0.750	0.740	95	345	86	70	0.54
272 F P 1S	0.657	0.750	0.653	120	325	81	78	0.48
273 F P 1S	0.653	0.750	0.568	226	327	76	128	0.37
274 F P 1S	0.635	0.750	0.484	196	281	70	95	0.10
275 M S 2S	0.549	0.750	0.855	38	292	82	32	0.58

TABLE D-1 (Continued)

Run Number	Sample Density (gm/cm ³)	Sample Thickness (in)	Heating Rate (cal/cm ² sec)	Time to Ignition (sec)	Ignition Temperature T _s (°C)	Initial Temperature T _o (°C)	Ignition Energy (cal/cm ²)	Weight Loss Rate at Ignition (gm/cm ² sec x 10 ³)
276 M P 2S	0.545	0.750	0.668	72	301	73	48	0.25
277 M P 2S	0.551	0.750	0.487	174	286	65	85	0.20
278 O S 2S	0.768	0.750	0.855	48	315	80	41	0.59
279 O P 1S	0.803	0.750	0.827	72	317	80	60	1.09
280 O P 2S	0.811	0.750	0.577	174	287	67	100	0.44
281 R P 2S	0.453	0.750	0.855	35	303	94	30	0.50
282 R P 2S	0.455	0.750	0.668	50	294	82	33	0.41
283 R P 2S	0.457	0.750	0.487	186	296	69	91	0.37
284 R P 2S	0.461	0.750	0.373	282	266	56	105	0.26
285 R P 2S (*)	0.462	0.750	0.303	606	330	44	184	0.39
286 O P 2S	0.754	0.625	0.771	58	277	75	43	0.12
287 O P 2S	0.752	0.625	0.577	176	260	67	102	0.39
288 R P 2S	0.462	0.625	0.487	288	298	69	140	0.52

* Surface partly glowed before ignition occurred.

APPENDIX E

REFERENCES

1. Alvares, N. J., "Measurement of the Temperature of the Thermally Irradiated Surface of α -Cellulose," U.S. Naval Radiological Defense Lab., Tech. Rept., DASA 1467, USNRDL-TR-735 (1964).
2. Alvares, N. J., "The Effect of Oxygen Concentration on The Temperature of the Thermally Irradiated Surface of Blackened Alpha-Cellulose," U.S. Naval Radiological Defense Laboratory, San Francisco, California, Report No. WSCI 67-18 (1967).
3. Alvares, N. J., "Oxygen Concentration and Pressure Effects on the Ignition of Cellulosic Fuels by Thermal Radiation," U.S. Naval Radiological Defense Laboratory, San Francisco, California, Report No. USNRDL-TR-67-25, AD 650 622 (1967).
4. Arseneau, D. F., "The Differential Thermal Analysis of Wood," Can. J. Chem., 39, 1915-1919 (1961).
5. Bamford, C. H., J. Crank, and D. H. Malan, "The Combustion of Wood, Part I," Proc. of Cambridge Philos. Soc., 42, 166 (1946).
6. Boehringer, J.C. and R. J. Spindler, "Radiant Heating of Semi-Transparent Materials," AVCO Corporation, Technical Rept., RAD-TR-61-8 (1961).
7. Bowes, P. C., "Estimates of the Rate of Heat Evolution and of the Activation Energy for a Stage in the Ignition of Some Woods and Fiberboard," Fire Research Note No. 266, Joint Fire Research Organization, England (1956).
8. Bowes, P. C. and S. E. Townshend, "Ignition of Combustible Dusts on Hot Surfaces," Brit. J. of Appl. Phys., 13, 105-114 (1962).

9. Brown, C. R., "The Determination of Ignition Temperatures of Solid Materials," Fuel, 14, 14 (1935).
10. Browne, F. L., "Theories of the Combustion of Wood and its Control," USDA Forest Products Lab., Report No. 2136 (1958).
11. Bruce, H. D. and L. E. Downs, "Ignition of Newspaper by Radiation with Variations in Moisture Content and Pulse Time," USDA Forest Products Lab., Technical Rept. AFSWP-1099 (1958).
12. Buschman, A. J., Jr., "Ignition of Some Wood Exposed to Low Level Thermal Radiation," NBS Project No. 1002-11-10427, Tech. Rept. No. 1 (1961).
13. Butler, C. P., S. B. Martin and W. Lai, "Thermal Radiation Damage to Cellulosic Materials--Part II--Ignition of Alpha-Cellulose by Square Wave Exposure," U.S. Naval Radiological Defense Lab., Tech. Rept. USNRDL-TR-135, NS 081-001, AFSWP-906 (1956).
14. Carslaw, H. S. and J. C. Jaeger, Conduction of Heat in Solids, Oxford at the Clarendon Press, Second Edition, (1959).
15. Chung, P. K. and M. L. Jackson, "Thermal Diffusivity of Low Conductive Materials," Ind. & Eng. Chem., 46(12), 2563-6 (1954).
16. Delmonte, J. and M. A. Azam, "Ignition Points of Plastic Materials," Modern Plastics, 20, 88 (1943).
17. Fons, W. L., "Heating and Ignition of Small Wood Cylinders," Ind. & Eng. Chem., 42, 2130 (1950).
18. Francis, R. E., "The Experimental Determination of Reflectance Function for Type 302 Stainless Steel," Master of Engineering, Department of Aerospace and Mechanical Engineering, University of Oklahoma (1967).
19. Gardon, R., "An Instrument for the Direct Measurement of Intense Thermal Radiation," Rev. Sci. Inst. 24(5), 366-370 (1953).
20. Gardon, R., "Temperature Attained in Wood Exposed to High Intensity Thermal Radiation," Fuel Research Lab., MIT, Tech. Report No. 3 (1953).
21. Gray, P. and M. J. Harper, "The Thermal Theory of Induction Periods and Ignition Delays," Seventh International Symposium on Combustion, Butterworths, London, 425-430 (1959).

22. Gross, D. and A. F. Robertson, "Self-Ignition Temperature of Materials from Kinetic Reaction Data," Journal of Research of the NBS, 61(5), 413-417 (1958).
23. Hopkin, H. C., Jr., "The Study of Temperature in Flammable Solids Exposed to High-Intensity Thermal Radiation," M. S. Thesis, Chem. Eng., MIT (1952).
24. Hottel, H. C. and C. C. Williams III, "Transient Heat Flow in Organic Materials Exposed to High Intensity Thermal Radiation," Ind. & Eng. Chem., 47, 1136-1143 (1955).
25. Jakob, Max, Heat Transfer Vol. I PP. 275-278, John Wiley and Sons, Inc. (1949).
26. Jakob, Max and G. A. Hawkins, Elements of Heat Transfer P. 19, John Wiley and Sons, Inc., 3rd Ed. (1957).
27. Kilzer, F. J. and A. Broido, "Speculations on the Nature of Cellulose Pyrolysis," Pacific Southwest Forest and Range Experiment Station, Forest Service, USDA, Berkely, California, Report No. WSS/CI Paper 64-4 (1964).
28. Lawrence, E. K., "Analytical Study of Flame Initiation," S. M. Thesis, Chem. Eng., MIT (1952).
29. Lawson, D. I. and D. L. Simms, "The Ignition of Wood by Radiation," Brit. J. of Appl. Phys., 3, 288-292 (1952).
30. Lincoln, K. A. , "Flash Pyrolysis of Solid-Fuel Materials by Thermal Radiation," Western States Section Meeting of the Combustion Inst., Stanford, California, April (1964).
31. Lipska, A. E., "The Pyrolysis of Cellulosic and Synthetic Materials in a Fire Environment," U.S. Naval Radiological Defense Laboratory, USNRDL-TR-1113 (1966).
32. Lipska, A. E. and W. J. Parker, "Kinetics of the Pyrolysis of Cellulose over the Temperature Range 250-300°C," U.S. Naval Radiological Defense Laboratory, San Francisco, California, Report No. WSCI-66-22 (1966).
33. Love, T. J., Radiative Heat Transfer, to be published by Charles E. Merrill Book Co., Columbus, Ohio.

34. Maclean, J. D., "Relation of Wood Density to Rate of Temperature Change in Wood in Different Heating Medium," Am. Wood-Preservers' Assoc. Proceedings, 3, 220 (1940).
35. MacLean, J. D., "Thermal Conductivity of Wood," Transactions American Society of Heating and Ventilating Engineers, 47, (No. 1184), 323 (1941).
36. MacLean, J. D., "Rate of Disintegration of Wood under Different Heating Conditions," Am. Wood-Preservers' Assoc. Proceedings, 47, 155-169 (1951).
37. Martin, S. B., "The Mechanisms of Ignition of Cellulosic Materials by Intense Thermal Radiation," U.S. Naval Radiological Defense Lab., Tech. Report USNRDL-TR-102 NS 081-001, AFSWP-779 (1956).
38. Martin, S. B. and N. J. Alvares, "Critical Irradiance for Ignition of Cellulosic Fuels," U.S. Naval Radiological Defense Laboratory, San Francisco, California, Report No. WSCI-66-23 (1966).
39. Martin, S. B. and R. W. Ramstad, "Temperature Profile in Thermally Irradiated Cellulose Accompanying its Spontaneous Ignition," U.S. Naval Rad. Def. Lab., Tech. Rept. USNRDL-TR-353, NS 081-001, DASA-1142 (1959).
40. Martin, S. B. and R. W. Ramstad, "Stable Pyrolysis Products of Cellulose Exposed to Intense Thermal Radiation," U.S. Naval Radiological Defense Lab., DASA-1546, USNRDL-TR-810 (1965).
41. McAdams, W. H., Heat Transmission, McGraw Hill Book Co., Inc., Third Ed. (1954).
42. Mitchell, N. D., "New Light on Self Ignition," National Fire Protec. Assoc. Quarterly, 45, 165-172 (1951).
43. Mitchell, R. L., R. M. Seborg and M. A. Millett, "Effect of Heat on the Properties and Chemical Composition of Douglas Fir Wood and its Major Components," Journal of Forest Prod. Res. Soc., 3, 38-42, 72-73 (1953).
44. Pickard, R. W. and H. Wraight, "The Effect of Moisture on the Ignition and Flame Propagation of Thin Cellulosic Materials," Fire Research Note 450, Joint Fire Research Organization, England (1961).

45. Sauer, F. M., "The Charring of Wood during Exposure to Thermal Radiation: Correlation Analysis for Semi-infinite Solids," USDA Forest Service, California Forest and Range Experiment Station, Berkeley, Calif., Interim Tech. Rept. AFSWP-838, August (1956).
46. Schaffer, E. L., "An Approach to the Mathematical Prediction of Temperature Rise within a Semi-infinite Wood Slab Subjected to High Temperature Condition," Prepared for Presentation at the Western States Section Meeting of the Combustion Inst. at Stanford Univ., Stanford, Calif., April 27-28 (1964).
47. Schaffer, E. L., "Review of Information Related to the Charring Rate of Wood," U.S. Forest Service Research Note FPL-0145, November (1966).
48. Schoenborn, E. M. and D. S. Weaver, Jr., "Ignition Temperature of Rigid Plastics," ASTM Bulletin No. 146, 80 (1947).
49. Setchkin, N. P., "Discussion of Paper on the Ignition Temperature of Rigid Plastics," ASTM Bulletin, No. 151, 66 (1948).
50. Setchkin, N. P., "A Method and Apparatus for Determining the Ignition Characteristics of Plastics," Journal of Research, NBS, 43, 591-605 (1949).
51. Simms, D. L., "The Correlation of Ignition Time with the Physical Properties of Material, Part I, Spontaneous Ignition of Cellulosic Materials," Fire Research Note No. 319, Joint Fire Research Organization, England (1958).
52. Simms, D. L., "Ignition of Cellulosic Materials by Radiation," Combustion and Flame, 4(4), 293-300 (1960).
53. Simms, D. L., "Experiment on the Ignition of Cellulosic Materials by Thermal Radiation," Combustion and Flame, 5, 369-375 (1961).
54. Simms, D. L., "Damage to Cellulosic Solids by Thermal Radiation," Combustion and Flame, 6(4), 303-318 (1962).
55. Simms, D. L., "On the Pilot Ignition of Wood by Radiation," Combustion and Flame, 7, 253-261 (1963).

56. Simms, D. L., "On the Spontaneous Ignition of Cellulose Materials by Radiation," Fire Research Note No. 573, Joint Fire Research Organization, England (1964).
57. Simms, D. L., M. Law, P. L. Hinkley, and R. W. Pickard, "The Effect of Size of Irradiated Area on the Spontaneous Ignition of Materials, Part I, The Effect on Ignition Time," Fire Research Note No. 307, Joint Fire Research Organization, England (1957).
58. Simms, D. L. and V. E. Roberts, "Effect of Prolonged Heating on the Subsequent Spontaneous Ignition of Oak," Journal of the Institute of Wood Science, 5, 29-37 (1960).
59. Squire, W. and C. Foster, "A Mathematical Study of the Mechanism of Wood Burning," Southwestern Research Institute, NBS Contract CST-362, Tech. Progress Rept. No. 1 (1961).
60. Stamm, A. J., "Thermal Degradation of Wood and Cellulose," Ind. & Eng. Chem., 48, 413-417 (1956).
61. Stemple, F. C. and D. L. Rall, "Applications and Advancements in the Field of Direct Heat Transfer Measurements," Instrument Society of America, 18th Annual ISA Conference and Exhibit, Chicago, September 9-12 (1963).
62. Stout, H. P., "Ignition of Wood by Radiation," Brit. J. of Appl. Phys. 3, 394 (1952).
63. Thomas, P. H., D. L. Simms, and M. Law, "The Effect of Moisture Content on the Spontaneous Ignition of Wood by Radiation," Fire Research Note No. 280, Joint Fire Research Organization, England (1956).
64. Weatherford, W. D., Jr., "Mathematical Study of Wood-Burning Mechanisms," Southwest Research Institute, NBS Contract CST-362 (1962).
65. Weatherford, W. D., Jr. and D. M. Sheppard, "Basic Studies of the Mechanism of Ignition of Cellulosic Material," Southwestern Research Institute, NBS Contract CST-1102, Tech. Rept. No. 2, Prepared for Publication in the Tenth Symposium (International) on Comb., July (1964).
66. Weatherford, W. D., Jr., D. M. Sheppard, and M. L. Valtierra, "An Experimental and Mathematical Study of the Mechanism of Wood Ignition," Southwest Research Inst., San Antonio, Texas, NBS Contract CST-1102 Final Report, November (1965).

67. Westwater, J. W. and M. G. DeFries, "Discussion of Paper on Ignition Temperatures of Rigid Plastics," ASTM Bulletin No. 148, 86 (1947).
68. Williams, C. C., "Damage Initiation in Organic Materials Exposed to High-Intensity Thermal Radiation," Sc. D. Thesis, Chem. Eng., MIT (1953).
69. Wright, R. H. and A. M. Hayward, "Kinetics of Thermal Decomposition of Wood," Canadian Journal of Technology, 29 (12), 503-510 (1951).

APPENDIX F

NOMENCLATURE

A	= area	cm ²
c	= heat capacity	cal/gm°C
c	= velocity of light (C-2) = 2.9979×10^{10}	cm/sec
c _g	= heat capacity of gaseous products at constant pressure	cal/gm°C
c _p	= heat capacity of air at constant pressure	cal/gm°C
d	= depth of char	cm
E	= activation energy	cal/gm mole
E	= radiant energy (C-1)	watts/cm ²
E _{bλ}	= monochromatic emissive power of black body (C-2)	erg/cm ³ sec
F	= Fourier modulus, $\alpha t/L^2$	dimensionless
F _i	= fraction of total incident flux H characterized by absorption coefficient γ_i	dimensionless
f	= frequency factor	sec ⁻¹
H	= irradiance	cal/cm ² sec
H _o	= critical irradiance	cal/cm ² sec
H _p	= critical irradiance for pilot ignition	cal/cm ² sec

H'_p	= irradiance of time varying pulse at peak	$\text{cal/cm}^2\text{sec}$
H_s	= critical irradiance for spontaneous ignition	$\text{cal/cm}^2\text{sec}$
H_s	= flux of unreflected radiation	$\text{cal/cm}^2\text{sec}$
H'_s	= initial incident flux of unreflected radiation	$\text{cal/cm}^2\text{sec}$
H_x	= radiation flux at a distance x from surface	$\text{cal/cm}^2\text{sec}$
h	= overall surface heat transfer coefficient	$\text{cal/cm}^2\text{sec}^\circ\text{C}$
h	= Plank's constant (C-2) = 6.6236×10^{-27}	erg/sec
h_c	= heat transfer coefficient due to convection	$\text{cal/cm}^2\text{sec}^\circ\text{C}$
h^*_{ρ}	= equivalent heat transfer coefficient due to surface reflection (IV-24)	$\text{cal/cm}^2\text{sec}^\circ\text{C}$
h_r	= equivalent heat transfer coefficient due to net radiation (IV-31)	$\text{cal/cm}^2\text{sec}^\circ\text{C}$
h^*_r	= equivalent heat transfer coefficient due to surface radiation to surrounding (IV-23)	$\text{cal/cm}^2\text{sec}^\circ\text{C}$
K	= thermal conductivity	$\text{cal/cm}^2\text{sec}^\circ\text{C/cm}$
k	= reaction rate constant	sec^{-1}
k	= Boltzmann constant (C-2) = 1.3802×10^{-16}	$\text{erg}/^\circ\text{K}$
k	= system constant (C-4)	dimensionless
L	= sample thickness in one-sided heating and half thickness in symmetrical heating	cm
l	= vertical height of sample (IV-25)	cm
M	= moisture content	percent
Q	= heat of reaction	cal/gm

q_c	= heat loss due to surface convection (IV-21)	cal/cm ² sec
q_r	= heat loss due to radiation from surface to surroundings (IV-21)	cal/cm ² sec
q_p	= heat loss due to surface reflection (IV-21)	cal/cm ² sec
q''	= heat supplied as a plane source (II-66)	cal/cm ² sec
r	= radial distance from cylinder axis	cm
R	= gas constant	cal/gm mole°K
R	= radius of cylinder	cm
T	= temperature	°K, °C
T_a	= ambient temperature	°K, °C
T_f	= flame temperature	°K, °C
T_o	= initial temperature	°K, °C
T_s	= surface temperature	°K, °C
ΔT	= temperature rise, $T - T_o$	°C
ΔT_m	= mean temperature rise, $T_m - T_o$	°C
ΔT_s	= surface temperature rise, $T_s - T_o$	°C
t	= time	sec
t_p	= time to reach the peak of a pulse	sec
x, y, z	= spatial distance	cm
V	= free stream air velocity (IV-25)	cm/sec
V_s	= radiometer output signal voltage (C-4)	rms volts
v	= velocity (II-60)	cm/sec
<u>Greek</u>		
α	= thermal diffusivity, $K/\rho c$	cm ² /sec
α	= surface absorbtance	dimensionless

β	= cooling modulus, $h\sqrt{t}/\sqrt{k\rho c}$	dimensionless
γ	= Lambert's law absorption coefficient	cm^{-1}
ϵ	= emittance	dimensionless
ϵ_d	= directional emittance	dimensionless
ζ	= constant	sec^{-1}
κ	= modifying factor (IV-39)	dimensionless
λ	= wavelength	cm
λ	= shape factor	dimensionless
μ	= viscosity	gm/cm sec
ξ	= x/L	dimensionless
ξ	= spatial distance (II-60)	cm
ρ	= density	gm/cm^3
ρ	= reflectance	dimensionless
ρ_d	= directional reflectance	dimensionless
σ	= Stefan-Boltzmann constant = 1.356×10^{-12}	$\text{cal/cm}^2 \text{sec}^\circ \text{K}^4$
τ	= ft	dimensionless
Φ	= RT/E	dimensionless
Φ	= function of geometry (II-62)	--
Φ_o	= RT_o/E	dimensionless
ω	= weight of volatile products of pyrolysis	gm
ω_o	= initial weight of volatiles present in a sample	gm
$\Delta\omega$	= $\omega - \omega_o$	gm