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A Survey of Literature on the Pyrolysis of Wood and Other Cellulosic Solids

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A SURVEY OF LITERATURE ON THE PYROLYSIS OF WOOD AND OTHER CELLULOSIC SOLIDS

A Thesis
Presented to the
Department of Mechanical Engineering Science
Brigham Young University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Kenneth P. Sasine
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Typed by Katherine Shepherd

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NOMENCLATURE

Symbol	Name	Units
T	Temperature	°C
t	Time	sec.
I	Intensity or heating rate	cal/cm^2-sec.
	Thermal diffusivity	cm^2/sec.
L	Length	cm, in.
x, r	Position, radius	cm, in.
w	Weight	gm
	Density	gm/cm^3
h	Convective heat transfer coefficient	cal/sec. cm^2 °C
K	Thermal conductivity	cal/sec cm °C
c	Specific heat	cal /gm °C
E	Activation energy	cal/mole
A	Arrhenius rate constant	1/sec
q	Heat of reaction	cal/gm
R	Gas constant	$\frac{\text{Atm liter}}{\text{gm-mole } ^{o}\text{K}}$
	Stefan-Boltzman constant	BTU/hr ft^2 ^{o}R^4
a	Absorbtivity	Dimensionless
e	Emittance	Dimensionless

Symbol	Name	Units
F_o	Fourier number	Dimensionless
Re	Reynolds number	Dimensionless
Nu	Nusselt number	Dimensionless
Bi	Biot number	Dimensionless

SUBSCRIPTS

Symbol	Name
o	Initial
f	Final
x	At a depth, x
c	Center
s	Surface
ig	Ignition
m	Maximum
TGA	Temperature of reactive sample in TGA test
DTA	Weight of reactive sample in DTA test

Occasionally subscripts will be used in combination for purposes of clarity. For example, the symbol T with the subscripts ig_c (T_{ig_c}) would be interpreted "ignition temperature measured at the center of the test specimen."

INTRODUCTION

The study of the ignition of wood and other cellulosic materials has resulted in the publication of a large amount of literature. As an aid in the planning and interpretation of future research, it was felt that a survey of a representative body of literature should be made. With this as its motivation, the present work was initiated.

The survey presented here is not intended to provide an exhaustive outline of all the work which has been done to date on the ignition of wood, but rather to review a representative sample of the work which has been done in recent years by those most noted in the field. The period of time covered by the survey is 1950-1969; however, the larger portion of the material was published in the interval 1960-1968.

It is estimated that of the total amount of literature (published in the last twenty years) directly related to the ignition of wood, the articles considered in this survey represent perhaps 5 to 10 per cent. This estimate was arrived at by noting that in the bibliographies given in each article, there are listed the titles of at least five references dealing with the ignition of wood. Multiplied by the number of articles in the primary and related references, this results in a total of over three hundred. The previous estimate was placed at 5 to 10 per cent by dividing the number of primary references (thirty-six) by the previously-mentioned total of over three hundred.

The study of wood ignition, and the modeling of the ignition process of cellulosic materials in general, has important application in several areas. Building and forest fire prevention, flame-retardant evaluation, and the study of flame weapon effectiveness are all topics in which an understanding of the ignition process is basic.

While it is apparent in the literature that there are as many specific approaches to the ignition problem as there are researchers, there are generalities which may be made with regard to the basic method of analysis used by the researcher in gathering the data. These are:

1. The analysis is performed by measurement of temperature versus time data; i.e., the measurement of a particular temperature of interest (surface, ambient surrounding, or at a specified depth below the surface) over a particular time interval. Data obtained in this manner are given in many of the articles surveyed.

2. The time to ignition at a given rate of heating is measured. In this type of analysis, samples are heated at various intensity levels, and the time required to ignite a particular specimen is measured.

3. Investigation is made by Thermogravimetric Analysis and Differential Thermal Analysis (see Appendixes for explanation of TGA and DTA). Papers of this type approach the problem from the chemical-rate point of view, and give results in terms of Activation Energy E, rate constant

A, and reaction order n (assumed in most cases to be equal to 1).

4. Analysis is made of the products of combustion with regard to identification of the type and relative amounts of compounds present. Articles of this type are more appropriate and useful in the consideration of the combustion process as opposed to the ignition process, but they are included in this survey because they represent a body of research which does have a limited bearing upon the nature of the problem to which this survey is directed.

5. There are articles which deal primarily with the mathematical modeling of the ignition process. The bulk of papers of this category use the heat-conduction equation in some form, depending upon the assumptions made and the coordinate system chosen.

The survey is organized in what shall be called "columnar form." It is felt that by arranging the information under separate column headings it will be easily accessible and readily usable. The following list is given in partial explanation of the column headings to be used in the body of the survey. A more complete explanation of the method of data presentation will be given later in the report.

1. Reference number, author, and date of publication.
2. Method of analysis.
3. General results.
4. Correlation parameters.
5. Tables and graphs.
6. Math models used.
7. Ignition data and conditions.
8. Author's conclusions.

In addition to the information supplied in columnar form, the survey will draw attention to what are felt to be significant results and conclusions given in the literature. Emphasis will be placed upon the comparison of points of contrast and similarity in the data, and in the conclusions drawn by each author regarding his work.

PART I

RESEARCH METHODS

CHAPTER I

METHOD OF ANALYSIS

Several general types of experimental methods of analysis were mentioned earlier. The purpose of the present chapter is to review in closer detail the specific method of analysis used in several of the articles.

Basic to the method of analysis is the choice of material upon which the tests are to be conducted. The two test materials most commonly found in this survey are wood, for which no accurate chemical formula has been proposed, and alpha-cellulose, having the composition $(C_6H_{10}O_5)_n$, indicating that as found in nature it is usually highly polymerized.

The two shapes most commonly found in the literature are the cylinder and the rectangular slab. These in turn, from a heat-transfer point of view, have been regarded as either "thin," or "semi-infinite," the major criterion used to differentiate between the two configurations being the time taken for that part of the sample not being heated to undergo a temperature change. A slab may be considered semi-infinite until that time when the unheated surface begins to react to the imposition of heat.

The following papers, identified by reference number and author, report work done on cylindrical specimens: Akita (1), Eickner (4), Fons (5), Blackshear (14), Murty (15), Roberts (17), and Roberts (22).

The articles listed below report experimental work done on slabs (either thin or semi-infinite): Gardon (6), Lawson (9), Schaffer (23), Smith (29, 30, 31), Simms (24, 25, 26, 27, 28), and Weatherford (34).

The following papers report work done on wood-sawdust either in pressed or in loose, natural form: Bowes (2), Brown (3), Roberts (20, 21).

The following articles report work done on specimens of paper, thin sheets of alpha-cellulose, cloth, or other material: Lincoln (10), Lipska (11), Martin (14), and Smith (30).

Another factor of importance in the interpretation of research considered in this survey is the surface temperature and heating rate at which the various tests were conducted. Generally speaking, the most useful temperature for correlation purposes is the surface temperature. Most of the researchers included this temperature in their analyses; however, there are exceptions worthy of mention:

1. Simms (25) measured the temperature in the volatile stream as a function of height above the specimen, as well as the surface temperature. This technique is unique to this paper.

2. The following papers report either the temperature in the center of the furnace in which the sample was heated, or the temperature at the center of the test specimen. In both cases, the temperatures reported are difficult to correlate with surface temperature data given in other papers. It has been suggested that where the sample is heated in a furnace, this situation may be compared to tests in which the specimen is ignited in the presence

of a pilot flame: Akita (1), Bowes (2), Brown (3), Eickner (4), Kilzer (7), Lipska (11), and Roberts (19, 21, 22).

Also of importance in the correlation of experimental data is the intensity level of the thermal energy to which the sample was subjected. For the most part, the experimental work reported in the literature was conducted at intensities of from 1 to 3 cal/cm^2-sec. The important exceptions are as follows:

1. The lowest level of intensity used was by Weatherford and Valtierra (34). Their work was conducted at levels varying from 0.06 to 0.10 cal/cm^2-sec.

2. The highest intensity used in the work reported was that used by Lincoln (10). His work was conducted with a helical Zenon flash tube which in short (less that thirty milliseconds) pulses yielded intensities of up to 3000 cal/cm^2-sec.

3. The following papers report work done at very high rates (over 100 cal/cm^2-sec.) of heating: Lincoln (10), and Martin (13, 14).

4. Unique not so much for its heating rate, but for its method of heating is the experimental work reported by Murty (16). The test specimens were cylindrical, and were heated by being inserted into a hollow copper cylinder of about twice the diameter of the sample. The copper cylinder-specimen unit was then heated from beneath by a flat-flame bunsen burner. In this manner, the specimen was touched only by heated air in the annulus between it and the copper cylinder.

Also worthy of mention is work done with the intent of evaluating the effectiveness of flame-retardant materials. The following papers are of this type: Akita (1), Brown (3), and Eickner (4). The fire-retardant salts used in the above tests were applied by immersing the wood to be tested in a solution of the salt. The salt content was measured by noting the weight of the sample before and after immersion.

CHAPTER II

MATH MODELS

In order to predict ignition characteristics it is necessary to formulate a mathematical model that permits correlation of ignition data. Equations which completely describe the ignition of thermally irradiated solids are so complex that analytic solution is impractical. The pyrolysis of combustible solids involves chemical reactions that act as sources and sinks of energy. At a given depth in the sample, pyrolysis depends not only upon the temperature at that depth, but also upon the length of time at that temperature. Even if it is assumed that properties of the solid are independent of temperature, the equation describing the process is a non-linear partial differential equation. If the effects of phase change, internal convection of gaseous volatile products and moisture, diathermancy, and self-heating are considered, the solution to the problem becomes extremely complex. For this reason, attempts have been made by various authors to correlate ignition data with highly simplified mathematical models. Some of these models, especially those that include the effect of chemical reactions, are solved by numerical methods. Only a few simplified models are capable of analytic solution, and these are used extensively in the literature. They are discussed below:

Model one

One-dimensional heating of a semi-infinite, opaque, inert solid (no chemical or phase change). In this model, the material is assumed to be irradiated at the surface with heat losses at the surface expressed by Newtonian cooling. The equation describing model one is:

$$\alpha \frac{\partial^2 \Delta T}{\partial x^2} = \frac{\partial \Delta T}{\partial t} \tag{1}$$

The initial and boundary conditions are:

$$t = 0; \quad \Delta T = 0 \tag{2}$$

$$t > 0; \; x = 0: \quad -K\frac{\partial \Delta T}{\partial x} = I - h\Delta T_s \tag{3}$$

$$x \to \infty \quad ; \; \Delta T = 0 \tag{4}$$

The solution to equation 1 with the initial and boundary conditions 2 through 4 is given by Carslaw and Jaeger (5 RR)* as:

$$\frac{\Delta T}{I/h} = \operatorname{erfc}\frac{x}{2(\alpha t)^{1/2}} - \exp\left(\frac{hx}{K} + \frac{h^2 \alpha t}{K^2}\right) \operatorname{erfc}\left(\frac{x}{2(\alpha t)^{1/2}} + \frac{h(\alpha t)^{1/2}}{K}\right) \tag{5}$$

At the surface (x = 0), equation 5 may be written as:

---

*RR refers to the list of related references.

$$\frac{I\sqrt{t}}{T_S\sqrt{K\rho c}} = \frac{\beta}{1 - \exp\beta^2 \operatorname{erfc}\beta} \qquad (6)$$

Where $\beta = h(\alpha t)^{1/2}/K = h\sqrt{t}/\sqrt{K\rho c}$ = cooling modulus.

Simms (24), (25), (26), (27), (28) correlated his data with the dimensionless groups of equation 6. Estimating the value of the heat transfer coefficient, h, to be .0008 cal/cm^2 sec. $^{\circ}$C, he adjusted ΔT_S such that the theoretical curve of equation 6 gave the best fit (within ± 30 per cent) through his experimental data. This adjusted surface temperature was found to be 525°C.

While it may be observed that the temperature at ignition is predictable within certain limits, other researchers contend that the constant surface temperature criterion is not adequate.

Model two

Another approach to the modeling process would be to recognize that once certain rather drastic assumptions are made (such as assuming the solid to be inert), it is reasonable to ignore all unknown parameters. The reason for this is that in trying to describe all cooling losses (including those due to chemical reactions) by means of Newtonian-type cooling, one might possibly make the correlation of results more difficult. Model 2, in a completely simplified approach, considers the wood to be an infinite slab of thickness L, irradiated at the surface ($x = 0$). The solid is assumed to be opaque and inert. The heat losses from the surface are completely ignored. The differential equation is again given by:

$$\alpha \frac{\partial^2 \Delta T}{\partial x^2} = \frac{\partial \Delta T}{\partial t} \tag{1}$$

The initial and boundary conditions are:

$$@\ t = 0;\ 0 \leq x \leq L;\ \Delta T = 0 \tag{7}$$

$$t > 0;\ x = 0;\ -K\frac{\partial \Delta T}{\partial x} = I \tag{8}$$

$$t > 0;\ x = L;\ \frac{\partial \Delta T}{\partial x} = 0 \tag{9}$$

The same model and boundary conditions apply to the case where heating is two-sided, with L then being the half-thickness when only half of the sample is considered at a time. The surface temperature rise for this case is given by Carslaw and Jaeger (5 RR) as:

$$\frac{\Delta T_s K}{IL} = Fo + \frac{1}{3} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2\pi^2 Fo) \tag{10}$$

Where $Fo = \alpha t/L^2$ = Fourier modulus. Of all the literature surveyed, only the article by Koohyar (8) employed this sample model. Koohyar modified the surface boundary condition to read $-K\partial \Delta T/\partial x = \eta I$, where η is a numerical parameter which is thought to be a function of time and other yet unknown variables.

Model three

This model is similar to model one (semi-infinite, opaque, inert solid), except that no heat losses are assumed for the surface boundary. In this case, equations 1, 2, and 4 hold, but equation 3, which defines the surface boundary condition, becomes similar to equation 8. The surface temperature rise in this case is given by Carslaw and Jaeger (5 RR) by:

$$\Delta T_S = \frac{2I}{K}\left(\frac{\alpha t}{\pi}\right)^{1/2} \tag{11}$$

It should be noted that in the semi-infinite solid case, the thickness L does not appear in the solution. For the comparison of models two and three, both sides of equation 11 are multiplied by K/HL to obtain:

$$\frac{\Delta T_S K}{IL} = \frac{2\sqrt{Fo}}{\sqrt{\pi}} = 1.1284\sqrt{Fo} \tag{12}$$

in which L may be thought of as a characteristic distance from the surface.

Both equations 10 and 12 suggest the correlation of data in terms of the energy modulus $IL/\Delta T_S K$, the Fourier modulus, or the dimensionless time variable $(\alpha t/L^2)^{1/2}$. It may be noticed that in plotting the irradiance modulus $IL/\Delta T_S K$ versus dimensionless time, $(\alpha t/L^2)^{1/2}$, for $(\alpha t/L^2)^{1/2}$ less than .6 the presumed models two and three behave alike, indicating that the sample is thick enough to be considered semi-infinite.

Model four

The last model to be considered describes the burning of a reactive, semi-infinite solid. It is assumed that the burning surface is consumed at a constant rate, and moves into the solid at a rate v. The differential equation is again:

$$\alpha \frac{\partial^2 \Delta T}{\partial x^2} = \frac{\partial \Delta T}{\partial t} \tag{1}$$

The transformation of variables

$$z = x - vt \tag{13}$$

places the origin on the moving surface. The original partial differential equation 1 now becomes an ordinary differential equation;

$$\frac{d^2T}{dz^2} = -\frac{v}{\alpha}\frac{dT}{dz} \tag{14}$$

Equation 14 has the general solution

$$T = c_1 + c_2 \exp\left(\frac{-vz}{\alpha}\right) \tag{15}$$

Applying the boundary conditions:

$$T = T_s \quad @ \quad z = 0 \tag{16}$$

$$T = T_i \quad @ \quad z = \infty \tag{17}$$

the final solution becomes

$$\frac{T - T_i}{T_\delta - T_i} = \exp\left(\frac{-vz}{\alpha}\right) \tag{18}$$

Model four is used in the analysis of combustion rather than ignition, and for this reason occurs less frequently in this survey than any of the other three considered in this chapter.

It will be found that each author employs at least the basic ideas of one or more of the models. Modifications in the approach taken in using each model vary with each article, but the equations discussed above remain the foundation for the work considered by this survey.

In the columnar review of each article presented in the following chapter, the models described are referred to by number. Where a particular author uses an equation felt to contribute significantly in a manner not expressed or implied by any of the four math models, it will be included in the column entitled "Math Models."

Highly specialized equations which do not fall into one of the categories mentioned in the preceding two paragraphs will be omitted. Where such is the case, the word "omitted" will be written in the math model column.

PART II

SURVEY AND DISCUSSION

CHAPTER III

REVIEW OF ARTICLES SURVEYED IN COLUMNAR FORM

On the following page, an explanatory article is given which will aid the reader in the interpretation of the material presented in this chapter. By reference to the article, no difficulty should be experienced in obtaining any of the information contained therein. The information contained in each article surveyed was categorized in each of several areas. These were then arranged into columns, one for each of the areas into which the articles were divided.

In compiling the contents of this chapter, effort was made to preserve as much of the exact wording of each article as possible. No additions were made except as necessary to piece together sections paraphrased or condensed from the work of a particular author.

Reference Number, Author, and Date	
	This column contains the number of the article as listed in the Bibliography, the name of the first author, and the year in which the article was published.
Author's Conclusions	The conclusions drawn by the author are presented in this column. No interpretation of the conclusions drawn by the author(s) is made at this point.
Ignition Data and Conditions	This column summarizes information concerning the actual testing of the sample. The information is presented in the following order: a) Radiant or convective source b) Self or pilot ignition c) Pressure (in atmosphere) at which the test was conducted d) The atmosphere surroundings of the test e) Temperature and time of ignition* f) Method of flux measurement* g) Method of temperature measurement* h) Orientation, size, and shape of
Math Models Used	This column contains the number of the math model (as described in Chapter Two) used by the author. Where the model is highly specialized or not related to one of the math models discussed, the word "Omitted" will be written.
Tables and Graphs	This column lists the graphs and tables presented by the author. Wherever possible, the contents will be indicated with the symbols used or described in the "Correlation Parameters" column.
Correlation Parameters	The parameters used in the gathering of data and its interpretation are presented in this column. Parameters common to most of the articles will be represented only by the symbols given in the list contained under "Nomenclature," where a complete definition may be found.
General Results	This column summarizes what the authors found out in the course of their work. Also given are a few of the author's preliminary conclusions regarding the interpretation of results.
Method of Analysis	In this column, a brief explanation is given of what is done, and how it is accomplished. A brief statement as to the scope of coverage is also given.

Reference Number, Author, and Date	
Author's Conclusions	
Ignition Data and Conditions	the sample* i) Ignition-detection criteria. *If reported.
Math Models Used	
Tables and Graphs	
Correlation Parameters	Parameters used only infrequently, and those which are peculiar to a single article, will be defined in this column but not under "Nomenclature."
General Results	
Method of Analysis	

Reference Number, Author, and Date

(1) Akita 1967

Author's Conclusions	Activation energy "undoubtedly" independent of the heating rate. The theory developed is reliable in the temperature range studied. The pyrolysis rate is accelerated by the addition of flame retardants. Activation energy is lowered by the addition of chemical retardants.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure: 1 atm. d) Air, nitrogen e) A thermocouple is located in the center of the body of the cylinder h) The cylinder is heated (radially inward) uniformly over its whole surface. Powdered samples of α-cellulose are from 100-200 mg in weight.
Math Models Used	Omitted
Tables and Graphs	Table of the kinetic parameters of cellulose (A, n, E, ω/ω_m). Graph of T_{TGA} vs Γ_s for various samples in air, nitrogen, and partial vacuum.
Correlation Parameters	t: T_s: T_{TGA}: ω; weight: n; reaction order
General Results	Average values of E, A, and n are: E = 53.5 kcal/mole; A = $10^{18.8}$/min for α-cellulose, and F = 32 kcal/mole; A = 10^{12}/min; n = 1 for modified cellulose. A deep endotherm is found in the DTA and TGA curves in the range of 300°-350°C for the samples pyrolyzed in the vacuum and N_2. DTA and TGA curves obtained for tests in air show only a slight endotherm masked by a sharp exotherm due to the oxidation of the volatile products.
Method of Analysis	α-cellulose and cellulose modified with dihydrogen ammonium phosphate are examined by Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) to obtain data regarding activation energy E, pre-exponential factor A, and reaction order n. Fire retardant properties of the salt (di-hydrogen ammonium phosphate) used to modify the cellulose are discussed. The authors propose a theory that the peak value of the DTA curve coincides with the maximum rate of action.

Reference Number, Author, and Date	(2) Bowes 1966
Author's Conclusions	The higher ignition temperature observed in samples having undergone one ignition-extinction cycle is concluded to be a result of: a) chemical change producing a higher activation energy (possibly 10% higher); b) physical changes including an increase in porosity and an accompanying decrease in thermal conductivity. More work on ignitions and re-ignition after extinction needs to be done to verify the above conclusions.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure: 1 atm. d) Oxygen, nitrogen e) T_{ig_c} = 230°C g) A thermocouple is located in the center of the cubes h) The cube is heated on all sides by being suspended in the center of an oven. The sawdust cube size varies from 2.5 cm to 10.2 cm on a side.
Math Models Used	Omitted
Tables and Graphs	Cube center and furnace ambient temperature vs time. Oxygen concentration vs rate of heat evolution. Table of minimum ignition temperature vs cube size and oxygen concentration.
Correlation Parameters	T: t: $\%O_2$: $\%N_2$: M; oxygen consumption rate: ρ_o; density of oxygen: D; diffusion coefficient: P; porosity: A; Arrhenius pre-exponential factor
General Results	Temperature vs time plots show an inflection point occurring at about t=1 hr. and T_c = 220° C. The authors state that ignition occurs at about 10°-20°C above the point of inflection, with the later and higher temperature ignitions occurring at the lower oxygen concentrations. Smaller cubes in general have higher ignition temperatures. Calculation of a mean activation energy results in E = 22.8 kcal/mole. A 2/3 power relationship is seen to exist between heat evolution and oxygen concentration.
Method of Analysis	Pressed sawdust cubes are suspended in the center of an oven. Atmosphere within the oven is varied by blowing in oxygen or nitrogen at a controlled rate. Tests are conducted to establish minimum ignition temperature for a given size cube and a given oxygen concentration. Temperature is monitored with a thermocouple in the center of the cube. In each test, furnace temperature is increased until ignition occurs, then decreased until extinction is attained.

Reference Number, Author, and Date

(3) Brown 1962

Author's Conclusions	In general, flame-retardant salts lower the temperature at which pyrolysis begins, and increase the amount of weight loss occurring below 340°C. The most effective salts decrease the amount of decomposition in direct proportion to their initial concentration. Salts are decomposed and almost wholly volatilized before pyrolysis of the wood is complete. DTA analysis reveals exthothermic peaks at 340° and 440°C with an endothermic well between. The most effective retardant is sodium tetraborate, the least effective sodium chloride.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure: 1 atm.; partial vacuum d) Nitrogen e) The lower threshold ignition temperature is 150°-220°C, depending upon what salt was used. (220°C is for untreated wood.) g) A thermocouple was located near the center of the sample h) Pine shavings .16 x 46 x 77 mm were heated in a furnace.
Math Models Used	Omitted
Tables and Graphs	Weight of char vs temperature. Table of salts used vs effect on weight loss for different temperature levels. Table of activation energy for wood impregnated with retardant salts. T_{DTA} vs T_S for treated and untreated wood.
Correlation Parameters	ω: T_S: T_{DTA}
General Results	TGA curves obtained in a vacuum are very closely approximated by TGA curves obtained in Nitrogen in 1 atmosphere (for wood shavings). For thick samples (wood dowels) pyrolysis occurred faster and yields less char in a vacuum than in Nitrogen at 1 atmosphere. Salts are classified in four groups according to their effectiveness in reducing level of decomposition. α-cellulose decomposes much more rapidly than lignin in the same temperature surroundings.
Method of Analysis	DTA and TGA are performed on specimens of wood dust and shavings to determine the effects of fire retardant salts on pyrolysis. Comparison of graphs thus obtained yield changes in rate constant, activation energy, and threshold temperature for active pyrolysis brought about by the addition of retardant chemicals. Also tested are specimens of α-cellulose and lignin.

Reference Number, Author, and Date

(4) Eickner 1962

Author's Conclusions	Once pyrolysis is begun, cellulose is volatilized nearly completely and mostly endothermally before 400°C is reached. Flame retardant salts lower the activation energy. Some salts lower the heat of combustion of the volatile products of the treated wood during the initial stages of the pyrolysis as compared to untreated wood. Salts in general lower the threshold temperature for decomposition, increase the weight loss occurring below 250°C, and exert an endothermic effect on the temperature at the point of greatest weight loss.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure 1 atm. d) Air, oxygen, nitrogen d) $T_{igs} \cong 150$-220°C depending upon which salt is used as the retardant g) A thermocouple is located below the sample. In this position it is claimed that the thermocouple reads within 3°C the actual surface temperature of the sample. h) The samples are heated in a furnace. The samples are veneers from .005 to .125 inch thick and dowels from .250 to .50 inch in diameter.
Math Models Used	Omitted
Tables and Graphs	$A_{vs} \frac{1}{T}$ vs T_S for treated and untreated samples. Tables of activation energy for treated and non-treated samples are given. Table of extent of decomposition observed with each retardant.
Correlation Parameters	A: T_{DTA}: T_S: ω
General Results	The author gives the most "logical" solution to the fire-retardation mechanism as: Fire-retardant chemicals lower the temperature at which pyrolysis starts, and thus direct the decomposition to less flammable gases and tars, and more charcoal and water. The promotion at lower temperatures may also cause the temperature at which the reaction becomes exothermic to be slightly increased. The author gives detailed explanations of experimental procedures.
Method of Analysis	Ponderosa pine cylinders and veneers are heated in a furnace at various temperatures. Thermogravimetric and differential thermal analyses of the samples are performed. Data thus obtained is used to evaluate the change in activation energy E and the rate constant A. Comparison of seven different fire-retardant salts is given with respect to individual affects of activation energy and amount of decomposition. The physical mechanism of fire retardation is discussed, with seven possible mechanisms offered as possible solutions.

Reference Number, Author, and Date

(5) Fons 1950

Author's Conclusions	No exothermic reaction occurs in the wood before ignition. The increase in ignition time caused by moisture content is greater than can be accounted for by the increase in the specific heat of the moisture alone. The author concludes that the presence of water vapor in the gaseous plume extends the time required for the volatiles to become a combustible mixture. Specimens below 235°C will glow, but not support flaming combustion.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure: 1 atm. d) Air g) A thermocouple is placed at various radial depths h) The samples are heated in a furnace. Specimens are dowels 5-1/8 inches in length, with diameters of 3/32, 1/8, 5/32, 3/16, 1/4, and 1/2 inches. i) Visual observation is made of the event. When flame first appears, material has undergone ignition.
Math Models Used	Model one
Tables and Graphs	Furnace temperature vs ignition time (for each size specimen). T_s vs t.
Correlation Parameters	t: T_s: r/r_o: F_o: 1/Bi
General Results	Initial temperatures of up to 150°C as the sample was introduced into the furnace had no effect on ignition time. For dowels of diameter $\geq$ 3/8", diameter size had no effect on ignition time. Ignition time increases with moisture content.
Method of Analysis	Ponderosa pine cylinders of 3/32" to 1/2" in diameter were irradiated at high rates in an electric furnace. Data was taken to provide time to ignition vs furnace temperature for specimens of varying size and moisture content.

Reference Number, Author, and Date

(6) Gardon 1953

Author's Conclusions	Under intense radiation the absorbtivity of natural colored wood appears to increase slightly, while that of pre-blackened wood seems to decrease slightly. The discrepancy in absorbtivity noted above is accompanied by values of measured absorbtivity of up to 25% less than expected. It is concluded that this difference may be accounted for by the reflecting, scattering, and re-radiation of the incident radiation by the smoke plume emitted by the target. Blackened samples behave as opaque solids with results following theory closely.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure 1 atm. d) Air f) A silver-disk calorimeter is used to measure flux intensity of up to 5 cal/cm^2-sec. g) Surface temperature and interior temperatures up to a depth of 5 mm are measured by means of thermocouples h) A 2-1/4" diameter circular area was irradiated perpendicular to the grain, with the sample lying horizontally. Wood samples are 2-1/2" x 2-1/2" x 1/2". i) Visual observation is made of the ignition process.
Math Models Used	Model one
Tables and Graphs	T_S vs t, ${}_L$ vs F_O, ${}_L$ vs , ${}_L$ vs F_O on log-log plots, with x/L and γ x included. This shows the relation between finite slabs, semi-infinite solids, and diathermanous materials.
Correlation Parameters	$\theta_L = \frac{\Delta T K}{I_0 L}$; dimensionless temperature rise): F_O: r = x/L; (dimensionless position: $\phi = \frac{x}{\sqrt{dt}}$; modified depth below surface).
General Results	Temperature distribution in finite slabs and in semi-infinite solids is reported for both opaque and diathermanous objects. Apparatus discussed: 1) solar furnace, 2) silver disk calorimeter, 3) circular foil radiometer, 4) thermocouples, 5) circular foil radiometer. An interesting observation is that the surface temperature of a pre-blackened samples rises smoothly to 500°C ± 50°C and then has a sharp break-point, dropping 20°C to 100°C.
Method of Analysis	Finite and semi-infinite slabs, some pre-blackened, some natural-color, are irradiated. Effective intensity and time to ignition are measured. Surface temperature and temperature distributions are measured. Various species of wood, including masonite, are used as samples. Percentage of moisture, content, color, and grain orientation are noted for each sample.

Reference Number, Author, and Date

(6) Gardon 1953

Author's Conclusions	The diathermancy of natural colored wood has a diminishing effect as time of irradiation increases.
Ignition Data and Conditions	
Math Models Used	
Tables and Graphs	
Correlation Parameters	
General Results	
Method of Analysis	The majority of the work is devoted to the semi-infinite dry solid, with consideration of variation in actual intensity of absorbed radiation vs intensity of radiation emitted by the source.

Reference Number, Author, and Date

(7) Kilzer 1965

Author's Conclusions	The pyrolytic decomposition of cellulose involves at least three processes, each having one or more reactions: a) A slightly endothermic reaction with loss of water to form "dehydrocellulose." b) An endothermic reaction competing with (a) forming levoglucosan (the major constituent of the tar). c) An exothermic reaction in which the "dehydrocellulose" experiences carbon-carbon and carbon-oxygen bond ruptures and hydride-ion transfers to produce volatile carbon-containing
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure 1 atm. d) Nitrogen, Helium
Math Models Used	Omitted
Tables and Graphs	T_S vs T_{DTA}
Correlation Parameters	T_S: T_{DTA}
General Results	Several possible explanations of the steps in the chemical breakdown of α-cellulose are given, with supporting evidence for each. Generalizations applicable to each possible explanation are given. The rate and heat of decomposition are strongly dependent on the concentration of inorganic impurities.
Method of Analysis	The authors speculatively interpret the results of mass-spectrographic, thermogravimetric, and differential thermal analysis of the products of cellulose pyrolysis. Consideration is given to the heat character of each step in the reaction, i.e., whether the step is endo- or exo-thermic.

Reference Number, Author, and Date

(7) Kilzer 1965

Author's Conclusions	compounds and hydrogen, and intermolecular condensations to produce char.
Ignition Data and Conditions	
Math Models Used	
Tables and Graphs	
Correlation Parameters	
General Results	
Method of Analysis	

Reference Number, Author, and Date

(8) Koohyar 1968

Author's Conclusions	An ignition criteria based only on the rate of weight loss is not adequate. The simplified model given (Model 2) agrees with experimental data. Since the physical properties of the samples appear in the dimensionless groups, the deviation of the data for different species shows that the rate and/or the mechanisms of pyrolysis reactions are dependent also upon the density and grain structure.
Ignition Data and Conditions	a) Convective source b) Self and pilot ignition c) Pressure 1 atm. d) Air h) Test specimens were heated over a 3.9 inch square area. Buoyancy effects must be considered.
Math Models Used	Model two
Tables and Graphs	$(F_o)^{1/2}$ vs IL/T_sK for pilot and self ignition for one and two-sided heating.
Correlation Parameters	T_s: t: F_o: η ; A numerical correction factor: IL/T_sK; A modified irradiance modulus: I; the net heat gained by the sample rather than the intensity with which it is irradiated.
General Results	The experimental work of this study is compared to the constant surface temperature criterion arrived at by Simms (24) and the conclusion is drawn that this criterion is not accurate over the range studied. The author proposes a simplified model, which, after the application of a numerical correction factor, agrees favorably with experimental data.
Method of Analysis	Wood samples of 5 different species are heated by being exposed to the buoyant diffusion flame from a liquid pool. Intensity level varies from .275 to .855 cal/cm^2-sec. Temperature and weight of the specimen is continuously recorded. Tests are conducted under both one-sided and two-sided heating conditions.

	Reference Number, Author, and Date (9) Lawson 1952
Author's Conclusions	Pilot ignition $(I-I_{cp})t^{2/3} = .025 \cdot 10^6 \cdot (kpc + 68 \cdot 10^{-6})$ Self-ignition $(I-I_{cs})t^{4/5} = .05 \cdot 10^6 \cdot (kpc + 35 \cdot 10^{-6})$ For a given species of wood, pilot ignition always occurs before self-ignition.
Ignition Data and Conditions	a) Convective source b) Pilot and self ignition c) Pressure 1 atm. d) Air f) Intensity as seen by the wood surface is measured with a radiation pyrometer h) The samples are irradiated perpendicular to the grain. The samples are placed in front of the gas-fired panel, so that bouyancy-effects may not be neglected. Wood samples are 2 inches square x 3/4 inches thick.
Math Models Used	Model one
Tables and Graphs	Log $(I-I_{cp})$ vs Log (time) Log $(I-I_{cs})$ vs Log (time) t_{ig} vs I for various species
Correlation Parameters	I_c; critical intensity: t_{ig} Subscripts p; pilot: s; self
General Results	Minimum intensities of irradiation for pilot and self ignition of wood are given. Empirical expressions are given for ignition time, intensity, and density for both pilot and self ignition. About 30% by weight of most species is liberated in the volatile plume. From log-log plots of $(I-I_c)$ vs time, empirical relationships are obtained.
Method of Analysis	Seven types of dry wood are tested. The specimens are irradiated with intensities ranging from 0.15 to 1.5 cal/cm²sec by varying the distance from source to specimen.

Reference Number, Author, and Date

(10) Lincoln 1965

Author's Conclusions	Flash heated α-cellulose will not decompose until its temperature is over 600°C. The heating rate has a significant effect on the type of volatiles produced. CO/CO_2 ratio increases with heating rate. The amount of char produced relative to other volatiles (especially CO) decreases with heating rate. High rates of heating breaks polymers into smaller constituents.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure 1 atm. d) Partial vacuum, Helium f) flux levels are measured with a calorimeter placed at the center of the helical flash tube h) The samples are irradiated by being placed in a cylindrical tube which is encircled by a helical flash tube. The sample is irradiated on all sides simultaneously. The samples are black α-cellulose sheets .002 inches thick x 1/2 inches thick.
Math Models Used	Omitted
Tables and Graphs	Time vs Kilo-volts Radiant energy vs Joules (input) Table of results of mass spectrometry
Correlation Parameters	Flash duration time: Radiant energy (cal/cm^2): Electrical input (Joules)
General Results	Results of mass spectrometry are given for various intensities and times irradiation. The results show the general break-down of the products of pyrolysis.
Method of Analysis	A helical zenon flash tube is used to irradiate black α-cellulose papers with high (3000 cal/cm^2-sec.) intensity pulses ($\leq$ .001 sec.). Products of combustion are immediately fed through a mass spectrometer.

Reference Number, Author, and Date

(11) Lipska 1965

Author's Conclusions	The three-phase explanation given for the physical mechanism of pyrolysis is correct. The initial weight loss in phase (a) is due to the decomposition of cellulose rather than simply a loss in adsorbed water. The pyrolysis of cellulose of both paper and cotton is kinetically similar whether performed in Nitrogen or in a partial vacuum. An understanding of the high rates of pyrolysis during the transient (b) phase is desirable in order to correlate TGA and DTA measurements with isothermal pyrolysis data and ignition studies where very high rates of heating are used.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure 1 atm.; partial vacuum d) Nitrogen, Oxygen g) The temperature inside the test chamber is controlled and measured with a thermocouple h) The samples are heated in a chamber through which Nitrogen or Oxygen is being passed. The samples are α-cellulose disks 2.0 cm x .030 in. thick.
Math Models Used	Omitted
Tables and Graphs	Table of temperature, time, weight, and residual weight of cellulose in the samples vs final weight of sample is given. Graph of log A vs $1/T_S$. Graph of percentage of weight loss vs oxygen content of surroundings. Graph of percentage of glucosan loss and weight loss vs time.
Correlation Parameters	Results t: T_S: A
General Results	Results indicate three chronological phases of pyrolysis at each temperature: (a) a rapid decomposition and weight loss period, (b) a zero-order decomposition and weight loss period, (c) a first-order weight loss period resulting in the char which does not undergo further pyrolysis. The decomposition and volatilization rate occurring during the zero-order phase increases with increasing temperature. Activation energy was found to be 42 kcal/mole.
Method of Analysis	Pure α-cellulose samples are pyrolyzed at constant temperatures ranging from 250-298°C. Results are reported in terms of weight loss and decomposition (glucosan loss). Samples tested are pre-dried. Measures are taken to insure against oxidation of the volatiles.

Reference Number, Author, and Date

(12) Madorsky 1963

Author's Conclusions	The identity of chromatograms taken of samples in oxidizing and non-oxidizing atmospheres suggests that the mechanism of degredation of cellulose is non-oxidative, being rather of a thermal nature.
Ignition Data and Conditions	a) Radiant and convective source b) Self ignition c) Pressure 1 atm. d) Air, Nitrogen, Helium h) The samples were heated in constant temperature surroundings monitored by thermocouples.
Math Models Used	Omitted
Tables and Graphs	v vs v/min. A table is given which shows twenty of the thirty-seven compounds the author says are indicated.
Correlation Parameters	Rate of volatilization; v/min.: v; percentage volatized.
General Results	Analysis of the volatiles indicates the presence of thirty-seven compounds. Chromatograms of the volatile products obtained from pyrolysis in neutral or oxidizing atmosphere and at different rates of degredation are found to be identical.
Method of Analysis	The author surveys six individual sources of literature from which are cited procedures used in preparation of samples for pyrolysis. The samples which are the subject of this paper were pyrolyzed in a furnace in tests designed to establish the effects of an oxidizing vs an inert atmosphere. The volatile products were analyzed by mass spectrometry, infrared absorbtion spectroscopy, and microcryoscopy.

Reference Number, Author, and Date	(13) Martin 1964
Author's Conclusions	Most investigators agree that above 250°C there are two methods of cellulose decomposition: (a) a depolymerization to levoglucosan. About 75% of the cellulose will be in the tar fraction, 80% of which is levoglucosan; (b) char formation as a result of drastic changes in molecular structure. The exposed surface is a site for secondary reactions. Hydrogen, Methane, Ethane, and Ethylene are triggered by secondary reactions in the char layer just prior to ignition--if the temperature profile is established at this time (of triggering), ignition will occur.
Ignition Data and Conditions	Due to the general nature of the survey, specific items in this area were omitted.
Math Models Used	Omitted
Tables and Graphs	
Correlation Parameters	T_s: t: I
General Results	Chemical changes in the cellulose are discussed: There are several competitive routes by which cellulose decomposes, each with its own temperature regime, i.e., when heated slowly, a large fraction of the original weight remains as char. Also with slow heating, the volatile plume is rich in oxygenated products such as H_2O and CO_2. Rapid heating leaves little or no char, and the volatile products are richer in carbon.
Method of Analysis	The author reviews and discusses methods and work being done by other researchers; he includes: Sauer; Butler, Martin, and Lai; Alvares; Hottel; Siddons; NASL, and NRDL.

Reference Number, Author, and Date

(14) Martin 1965

Author's Conclusions	The energy required for ignition is inversely proportional to irradiance level and independent of thickness. The steady-state ablation rate is directly proportional to intensity, while the amount ablated is directly proportional to the total radiant exposure (It). For short, high intensity pulses, persistent flaming ignition is not dependent upon exposure time.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure 1 atm. d) Air e) From his previous work, the author gives $T_{igs} \cong 600^{o}C$ f) A radiation calorimeter is used to measure flux levels h) The specimens are irradiated from the side, so that buoyancy effects may not be neglected. The samples were black α-cellulose disks, .005 in. to .031 in. thick.
Math Models Used	Omitted
Tables and Graphs	I vs I_t
Correlation Parameters	I: I_t
General Results	The ablation rate at 100 cal/cm^2-sec incident radiation is about 2 mm/sec. No reporting of surface temperature vs time was attempted. At high intensity levels (≥50 cal/cm^{2}sec) mechanical-thermal stresses were visible in the sample. The author suggests that structural damage would occur in buildings exposed to short thermal pulses of greater than 10,000 cal/cm^2-sec.
Method of Analysis	A parabolic mirror and carbon arc are used to irradiate a circular sample of 3/8" diameter at high values of intensity for short times, i.e., 50, 75, and 100 cal/cm^2-sec for times of about 30 milliseconds.

Reference Number, Author, and Date	(15) Murty 1966
Author's Conclusions	E increases with radius. This is concluded to be a result of the "incubation" of the inner layers for a longer period than the outer layers, initiating a change in structure making final decomposition easier in the inner layers--hence the lower E at the center. E increases with temperature. The "rearrangement" of cellulose which releases water and forms "dehydro-cellulose" occurs prior to the onset of decomposition. The math-model postulated gives satisfactory results for: E = 13 to 22 kcal/mole; A = 10^4 to 10^7 sec^{-1}. The above parameters are functions of size and heating rate.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure: 1 atm. d) Air g) The temperature of the sample is measured by thermocouples placed at various radial depths h) The specimens were placed horizontally inside a rotating copper tube. The tube was heated from beneath by a bunsen burner, such that in the 3/4 cm annulus surrounding the sample there was turbulent Couette flow.
Math Models Used	Omitted
Tables and Graphs	T_x vs time for various radial depths. Density vs radius. T_x vs density for various radial depths. E vs radius. E vs T_x.
Correlation Parameters	T_x: t: ρ: E: A
General Results	At about 357°C, the temperature vs time plot lags, indicating an energy "sink." Above 400°C the temperature-time response steepens, indicating a source of energy. The two "sinks" are assumed to be approximate boiling points of the migrant volatiles. The formation of "dehydrocellulose" postulated by Kilzer and Broido is supported.
Method of Analysis	α-cellulose cylinders are heated in a rotating hollow copper cylinder which is heated from beneath by a flat flame bunsen burner. During heating, temperature profiles are measured with thermocouples while density is measured with x-ray photography. Specimens are pre-dried, so that any water formed is due to the decomposition of the cellulose.

Reference Number, Author, and Date

(16) Murty 1966

Author's Conclusions	Heat of combustion is negative (endothermic reaction) in the specimen where the temperature is below 350°C. The strong exothermic reaction occurring in the surface char-layer is a result of: (a) "cracking" reactions in the out-flowing products; (b) an oxidation process in which the out-flowing products react with oxygen that diffuses into the char-layer from the surroundings. The reaction rate plateau evidenced by the endothermic well in differential thermal analysis curves is possibly the result of the vaporization of the migrant condensates. Activation energy will vary with size of sample as well as with depth below the char-layer.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure 1 atm. d) Air e) T_{ig} is estimated by results of DTA to be in the range 350°-450°C g) The temperature was measured with thermocouples h) The samples were heated uniformly in a furnace.
Math Models Used	Omitted
Tables and Graphs	Density distribution as a function of time and radius. Volatile mass flow rate as a function of time and radius. Char thickness and temperature vs time. A space-time map shows regions and processes controlling heat and mass evolution and transfer.
Correlation Parameters	ρ: t: x: F_o
General Results	A strong endothermic process occurs near 300°C. The controlling reactions appear to take place just beneath the char layer. Mass flow rate near the surface is fairly constant due to high porosity and cracks in the char. The thermal diffusivity is approximately three times larger in a direction parallel to the grain, than in a direction perpendicular to the grain.
Method of Analysis	Local temperature and density in a pyrolyzing α-cellulose cylinder are used to: (a) estimate the heat of reaction as a function of space and time, (b) correlate the heat of reaction with density changes to obtain volumetric heat sources or sinks, (c) map the position and time distribution of the regions in which various processes are important.

	Reference Number, Author, and Date (17) Persson 1964
Author's Conclusions	For the tube heated from within, the model gives the best results near the inner wall, and becomes poorer toward the outer wall. The model correctly describes the temperature distribution in semi-infinite slabs for low Biot number.
Ignition Data and Conditions	No experimental work was performed.
Math Models Used	Omitted
Tables and Graphs	E vs t* η vs t* F vs η
Correlation Parameters	F_o: Bi: $\eta = \frac{T(x,t)}{T_o}$: $t^* = \frac{dh^2t}{k^2}$
General Results	The authors assume the temperature profile may be represented by a fourth-order polynomial for t(x, t).
Method of Analysis	The paper is a review of the mathematical technique used to obtain an integral solution to the problem of calculating the temperature distribution in a convectively heated body: a slab and cylinder are considered.

Reference Number, Author, and Date

(18) Rein 1968

Author's Conclusions	The differences in the constants for the four equations are due to the effective reflectances for the various combinations of sample color and radiation sources. The steeper slopes of the curves for the pre-blackened specimens indicates a nearly constant reflectance throghout the irradiation period. Ignition time increases with sample thickness. In general, plastics take longer to ignite than wood heated at the same rate.
Ignition Data and Conditions	a) Convective source b) Pilot ignition c) Pressure 1 atm. d) Air h) Samples were 10.1 cm square, and varied in thickness from .2 to 1.9 cm. Buoyancy effects must be considered i) Ignition was defined as the first appearance of flame.
Math Models Used	The equation used in correlation of the data is of the form $t_{ig} = f[\rho, I, \text{erf}\,(1/2\ F_o{}^{1/2})]$, in which the time to piloted ignition is predicted as a function of the irradiance level I, the density ρ, and the Fourier number F_o.
Tables and Graphs	t_{ig} vs I for each specimen. t_{ig} vs $I^{1/3}$ - [erf (1/4 $F_o{}^{1/2}$)] F (view factor) vs the different geometries used in the tests.
Correlation Parameters	t_{ig}: T_s: I: F; the dimensionless view factor: Fo
General Results	Ignition times for natural and blackened, dried wood samples were correlated as a function of sample thickness, incident irradiance, density, and thermal diffusity for both flame and Tungsten lamp radiation. A dimensionless view factor F is used in determining the amount of heat transferred from the flame to the target.
Method of Analysis	Fourteen types of wood and fourteen types of plastic are subjected to both flame and Tungsten-lamp radiation in pilot ignition tests. Ignition-time is measured at various levels of irradiance. The data obtained in the experimental work is tested for correlation using a model adapted from an equation used in a previous report. Sample thickness is considered for its effect on ignition time.

Reference Number, Author, and Date	(19) Roberts and Clough 1963
Author's Conclusions	Weight loss is dependent on heating rate conditions. q decreases radially inward.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure 1 atm. d) Nitrogen e) T_{ig} is estimated by results of thermocouple data to be in the range $350\text{-}450^{\circ}C$ g) The temperature at various depths was measured by thermocouples h) The specimens were heated uniformly on all surfaces in a furnace. Beech wood cylinders 15 cm x 2 cm diameter.
Math Models Used	Omitted
Tables and Graphs	w vs t q vs r/r_o T vs r/r_o T_r vs t
Correlation Parameters	t: w: x: q
General Results	Samples are in a furnace to a pre-selected temperature at a rate of $20^{\circ}C/min$. The reaction kinetics are analyzed assuming: (a) first-order reaction, (b) heat released by exothermic reactions is proportional to weight-loss rate. Equations are given by which weight loss and reaction rate are related.
Method of Analysis	Beech cylinders are heated in a furnace through which Nitrogen is pumped. Radial temperature variation is measured with thermocouples, and the weight continuously measured. The equations for heat generation by a first-order reaction and heat conduction in a solid are solved by a finite difference method. The values of activation energy and heat of reaction which give the best agreement between experimental and calculated values are determined.

Reference Number, Author, and Date

(20) Roberts 1964

Author's Conclusions	The calorific value of the evolved volatile matter is concluded to be constant throughout the decomposition process at 3.96 kcal/gm. The calorific value of the unheated wood is found to be 4.66 kcal/gm. The combustion of the charcoal accounts for 30% of the heat released by the combustion of undecomposed wood.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure 1 atm. d) Air
Math Models Used	Omitted
Tables and Graphs	
Correlation Parameters	q: w: T
General Results	Wood decomposition reactions are influenced by pressure, rate of heating, and size as primary factors.
Method of Analysis	The calorific values of seven wood samples in varying degrees of decomposition are determined so that the calorific value of the evolved volatile matter can be estimated by a difference method. Tests are performed using a bomb-calorimeter in which wood dust in varying states of decomposition is exploded.

Reference Number, Author, and Date

(21) Roberts 1964

Author's Conclusions	The average composition of the evolved volatiles is constant throughout the decomposition process. The mean molecular formulas of the specimens are: Unheated wood: $(CH_{1.5}O_{.7})_n$ Volatiles: $(CH_2O)_n$ Charcoal: $(CH_{.2}O_{.02})_n$
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure 1 atm. d) Air g) Furnace temperature is monitored with thermocouples.
Math Models Used	Omitted
Tables and Graphs	Tables: Ultimate analysis for varying degrees of decomposition. Average composition and theoretical air requirements for wood, volatiles, and charcoal.
Correlation Parameters	w: T
General Results	A mass-balance equation is used to test the hypothesis that the composition of the volatiles is constant throughout the entire decomposition process.
Method of Analysis	Ultimate analysis is made of seven wood samples in varying states of decomposition. The ultimate analysis of the volatile products is made by a method of differences.

Reference Number, Author, and Date

(22) Roberts 1967

Author's Conclusions	The heat of combustion of the volatile products varies substantially with degree of decomposition.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure 1 atm. d) Air
Math Models Used	Omitted
Tables and Graphs	Table of ΔH vs furnace temperature.
Correlation Parameters	w: ΔH; heat of combustion
General Results	The heat of combustion of volatile products varies almost linearly in direct proportion to w/w_a, the weight loss fraction. ΔH varies from 2100 to 4000 cal/gm.
Method of Analysis	Pine cylinders 1" x 1/4" diameter are heated in a furnace. Weight-change is measured after pyrolysis. Bomb calorimeter measurement of the heat of combustion of the specimen is made before and after pyrolysis.

Reference Number, Author, and Date	(23) Schaffer 1965
Author's Conclusions	Exothermic and endothermic reactions in wood may be neglected below 300°C. The equation given as the solution (see math model column) applies to a quasi-steady state process which may be said to exist after the formation of the first 1/2" of char. The solution gives results within 10% of experimental data for char depths to 1-1/2". Temperature effects on thermal properties are compensated for in part by the effect of moisture movement within the wood, so that the overall effect might lead to the conclusion that thermal properties remain unchanged.
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure 1 atm. d) Air e) The temperature at base of char averages 288°C for most species g) The specimens are heated in a furnace.
Math Models Used	Model four
Tables and Graphs	T_X vs t. Temperature gradient for various times.
Correlation Parameters	T_X: t: x
General Results	The two assumptions allow the system to be modeled as a semi-infinite slab being approached by a moving, constant temperature, plane heat source, representing the moving gase of the char layer. The author gives temperature at char base $\approx 288^{\circ}$C for five species of wood. For 2" x 8" fir laminates, the char base moves at 1.54 in./hr. The char-base speed is constant for moisture content up to 16% of dry weight.
Method of Analysis	By assuming that: (a) a constant temperature is developed at the base of the char zone, and (b) char penetration occurs at a constant rate for a given specie, the author derives an equation to predict the temperature-time behavior of wood specimens. By this method and the two assumptions, the temperature rise of the wood beneath the char layer is modeled, with the char layer itself neglected.

Reference Number, Author, and Date

(24) Simms 1960

Author's Conclusions	Ignition is thwarted if volatiles are exhausted before surface temperature rises to T_{ig}. This is to say that under certain conditions and levels of flux intensity it is possible for the specimen to achieve a temperature distribution sufficient to cause the emission of volatiles without the occurrence of ignition. Minimum intensity for ignition increases as the area being irradiated decreases. Minimum intensity for ignition increases with increasing moisture content. Ignition occurs in gas phase, at turbulent point. Turbulence is a necessary factor, but not sufficient always to permit ignition.
Ignition Data and Conditions	a) Radiant and convective source b) Self ignition c) Pressure (1) d) A e) $T_{ig} \approx 525^{o}C$
Math Models Used	Models one and two
Tables and Graphs	a vs t t_{ig} vs a and I "E" vs "C" Fo vs Bi
Correlation Parameters	"E"; $I_t/2L\rho c T_m$ (energy received / heat content at ignition): "C"; $ht/\rho c L$ (energy lost / heat content)
General Results	The effect of absorbtivity is obtained by ignition time and intensity comparison of duplicate specimens, one pre-blackened. The flame first appears in volatile stream, at the point where the stream becomes turbulent.
Method of Analysis	Specimens of varying thickness* ($.02 < T < 1$ cm) are irradiated at different intensities and the time to ignition measured. *i.e., both thin slabs and semi-infinite solids are modeled.

Reference Number, Author, and Date

(25) Simms 1961

Author's Conclusions	If turbulence does not occur, ignition will not take place even though the temperature at the surface and in the volatile stream are the same as when ignition does occur. Small areas emit small volatile plumes which become turbulent farther away from the surface. Longer heating time is required for the plume to reach ignition temperature and hence small areas require longer heating times. Superimposing a turbulent draught on an already turbulent stream will not shorten ignition time any further.
Ignition Data and Conditions	a) Radiant and convective source b) Self ignition c) Pressure 1 atm. d) A e) Rates of heating are greater than 3.0 cal/cm^2-sec. T_{ig_s} = 525°C g) Surface temperature was measured with a thermocouple h) Experimental apparatus was arranged so that buoyancy effects could be eliminated or included.
Math Models Used	Model one
Tables and Graphs	Temperature in volatile stream vs height above surface. t_{ig} vs I t_{ig} vs T_s
Correlation Parameters	T: I: t
General Results	Flame first appears in the volatile stream. Flame appears at the point of turbulence in the volatile stream. The radiant source required higher intensity for ignition than the convective source for both pilot and self ignition. Temperature distribution in the volatile stream appears to be the same regardless of whether or not ignition occurs.
Method of Analysis	Oak, cedar, and fibre insulating board are irradiated with radiant and convective sources to determine the effect of turbulence upon ignition time and intensity. Experiments are done with pre-blackened specimens, so that diathermancy is ignored. The temperature distribution in the volatile stream is measured by placing a thermocouple in the stream at various heights above the sample. Specimens were dry.

Reference Number, Author, and Date	(26) Simms 1962
Author's Conclusions	The temperature at which a given amount of damage occurs with the intensity or rate of heating. The internal convection of volatiles is close to zero before charring occurs. It may be neglected in cases where ignition occurs before or at the first sign of char. Volatiles issued at the interface of the sample with its surroundings are produced very near the surface of the specimen. Only during very high or low rates of heating does the heat transferred by the internal convection of the volatile gases become significant.
Ignition Data and Conditions	a) Convective source b) Self ignition c) Pressure: 1 atm. d) A e) $T_{ig} = 525^{\circ}C$
Math Models Used	Model one
Tables and Graphs	"E" vs "C" for both thin slabs and semi-infinite solids.
Correlation Parameters	$\text{"E"} = \frac{It}{2\rho LcT}$; $\text{"C"} = \frac{ht}{\rho CL}$
General Results	The following methods are suggested as ways to solve the equation: a) Assume ignition or charring occurs at a given surface temperature, made non-dimensional by using RT/E. b) Assume a critical rate of volatile issue. c) Assume that charring occurs when the volatile content falls to a critical level. d) Assume a critical weight loss criterion.
Method of Analysis	The author begins with the one-dimentional energy-balance differential equation in a form which includes diathermancy effects. The equation is non-dimensionalized after which the terms which make solution difficult are removed. The simplified equation is applied to the thin slab and the semi-infinite solid.

Reference Number, Author, and Date	(27) Simms 1963
Author's Conclusions	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 occurs will increase the minimum ignition intensity. The quantitative production rate of the volatile gases controls the ignition process in connection with the surface temperature.
Ignition Data and Conditions	a) Convective source b) Pilot ignition c) Pressure, 1 atm. d) Air e) $T_{igs} = 525^{\circ}C$ h) Buoyancy-effect must be considered. The specimens are 5 cm. square x 1.9 cm. thick.
Math Models Used	Model one
Tables and Graphs	"E" vs "C" for both pilot and self ignition. t_{ig} vs I for various woods. t_{ig} vs position of pilot flame above surface of sample.
Correlation Parameters	$\text{"E"} = \frac{I_t}{2\rho LcT}$: $\text{"C"} = \frac{ht}{\rho CL}$
General Results	Time to ignition varies with position of pilot flame at a given intensity. The boundary layer thickness of the volatile stream is calculated. It is found that when the volatile stream becomes turbulent, the position of the pilot flame ceases to be a critical factor. The equation used to calculate the thickness of the boundary layer is given. Denser woods appear to ignite at lower temperatures than lighter woods.
Method of Analysis	This paper reviews earlier work on pilot ignition, and discusses original experimental tests. The tests are conducted to determine ignition time vs intensity for various woods.

Reference Number, Author, and Date

(28) Simms) 1967

Author's Conclusions	Moisture increases the total energy required for ignition. The additional energy used is manifested in the longer ignition times required for the moisture-bearing wood. The ignition temperature remains about the same as for dry wood. The increase in ignition time for the wet wood is accounted for satisfactorily by using the values of the thermal properties appropriate to the different moisture contents, and allowing for the effect of the heat of wetting and latent heat of vaporization in the equation given for the specific heat.
Ignition Data and Conditions	a) Convective source b) Self and pilot ignition c) Pressure, 1 atm. d) Air e) $I_{min} = .31$ cal/cm^2-sec. T_{ig} (pilot) = 360°C. T_{ig} (self) = 525°C f) I was measured with a Thwing-type pyrometer h) Buoyancy effects must be considered. Wood specimens were 7.6 cm square x 1.9 cm thick.
Math Models Used	The following equations are given to correct c and k for the amount of moisture content: $c_m = c_o + [W + 0.01 (L + T_{100}) M] / T_s$ $k_m = 10^{-4} [\rho_o (4178 + 10.2 m) + 0.57]$
Tables and Graphs	"E" vs "C" for each wood species for both self and pilot ignition, and for varying moisture contents. Graph of minimum intensity vs moisture content for each specie. A table is given containing moisture content, density, and ignition time data for each sample.
Correlation Parameters	"E" = $\frac{I_t}{2\rho LcT}$: "C" = $\frac{ht}{\rho cL}$: M; percentage of moisture content: W; heat of wetting: L; latent heat of steam: T_{100}; temperature rise from ambient to 100°C.
General Results	Ignition time increases with moisture content. Total energy for ignition, and minimum intensity for both pilot and self ignition, also increase with moisture content. A plateau on the temperature versus time graphs shows the apparent correlation at 100°C of the time lag caused by the vaporization of the water and the longer ignition time observed.
Method of Analysis	The test specimens are dried and then wetted with water to given percentages of water content. They are then heated and the intensity versus ignition time plotted. Five different woods are tested in this manner.

Reference Number, Author, and Date

(29) Smith 1965

Author's Conclusions	The "dip" is due to an endothermic decomposition or "destructive distillation" of the wood, which advances like a wave from the surface inward, leaving char behind. Charring is closely associated with the appearance of the dip, although only part of this effect can be attributed to changes in reflectivity due to charring. Transient flow calculations or extrapolations of temperature within the solid to surface conditions ignore the decomposition layer, and, if inertness is assumed, give low surface temperature for ignition. Rubber, sappy wood, and treated canvas would be difficult to ignite by radiation from hydrocarbon fires alone. Conversely, cardboard, low-sap wood, cotton uniform material and paper may be
Ignition Data and Conditions	a) Radiant source b) Self ignition c) Pressure 1 atm. d) Air e) The ignition temperature is measured in the range of 670-1200°C f) Flux is measured with a copper slug calorimeter g) The temperature is measured with a thermo-dot TD-6 infrared pyrometer h) The sample is nearly vertically below the fresnel lens, so that bouyancy-effects may be neglected. Specimens were 3" x 3" square. Thickness varied from sample to sample.
Math Models Used	Omitted
Tables and Graphs	T_s vs t. Table of "dip" temperatures for various target materials including pine of varying sap content. Author's schematic drawing of conditions present during ignition of wood illustrates a hypothetical mechanism.
Correlation Parameters	T_s: t
General Results	Copper slug calorimeter measurements of the flux incident on the target give a value of about 1 cal/cm^2-sec. On temperature time curves for each specimen, there is a pronounced "dip" just prior to ignition. Estimate is made that with errors "lumped," the maximum error in temperature would be 16°C low. The author suggests a possible explanation of the events leading up to ignition: As the volatile gas diffuses through the char layer it is super-heated. It then expands and loses
Method of Analysis	Various cellulose and wood specimens are ignited with the use of solar radiation magnified through a fresnel lens. Surface temperature rise versus time to ignition is recorded for each specimen. Surface temperature is measured with a recording infrared pyrometer.

Reference Number, Author, and Date

(29) Smith 1965

Author's Conclusions	easily ignited by the radiation. Important questions for further work: 1) What is the relation between heat flux and the "dip" in temperature? 2) What is the rate of destructive distillation at various temperatures? 3) How does the temperature, turbulence and composition of the surrounding atmosphere affect the ignition process? 4) What are surface temperature ranges in which ignition may be initiated by a spark?
Ignition Data and Conditions	i) Visual observation is made of the sample. When flame first appears, the observer calls "fire," upon which event the other observer would mark a pencil-dot on the time-strip chart.
Math Models Used	
Tables and Graphs	
Correlation Parameters	
General Results	temperature as it crosses the thermal boundary layer. Ignition must depend on the degree of super-heat attained being of a magnitude such that after cooling in the boundary layer, it is still hot enough to ignite once it achieves a suitable mixture with the surrounding air. Locally violent convection currents may carry eddies of combustible mixture near the surface, thus complicating the ignition process.
Method of Analysis	

Reference Number, Author, and Date

(30) Smith 1968

Author's Conclusions	Due to convective cooling, re-radiation, and reflective losses, even blackened specimens have available only a fraction of the total incident flux to raise their temperatures. This fraction varies with temperature and is smaller for thermally thin than thick specimens. The difference in ignition time for radiant versus convective sources is due more to the sensitivity of ignition time to heat flux than to large differences in absorbed flux at less than 1.0 cal/cm^2-sec.
Ignition Data and Conditions	a) Convective and radiant source b) Self ignition c) Pressure 1 atm. d) Air f) Flux is measured with a copper slug calorimeter g) An Ircon Infrared Pyrometer is used to measure the specimen temperature. h) Pine, cardboard, and cloth specimens are tested. The specimens are approximately 2" x 2" square, and of various thicknesses.
Math Models Used	Omitted
Tables and Graphs	T_s vs t. I vs T_s to 200°C. Blackened vs natural colored specimens compared. Spectral distribution vs radiant (quartz) source
Correlation Parameters	T: t: I: wavelength
General Results	Surface temperature history of blackened versus natural specimens is devised for making approximation of reflectance and retained heat flux during ignition tests.
Method of Analysis	Both natural and pre-blackened specimens of four cellulosic materials are irradiated at I = 1 cal/cm^2-sec., and the temperature rise versus time of the surface noted. Primary consideration is given to observing and comparing differences in temperature rise-time response to radiation from radiant versus convective sources, with the intent of observing and generalizing the effects of reflectivity upon data from radiant versus convective source. No attempt is made to dry the test samples.

Reference Number, Author, and Date

(31) Smith 1968

Author's Conclusions	This being an interim report, no specific conclusions are drawn.
Ignition Data and Conditions	a) Radiant source b) Self and pilot ignition c) Pressure 1 atm. d) Air e) Minimum ignition time particular to each sample is given in tables in appendix of article f) A Hy-Cal Engineering Co. calorimeter of the water-cooled Gardon-type was used to measure flux.
Math Models Used	Omitted
Tables and Graphs	Table of each target sample ignited in each iso-damage zone. Bar-graph of I_m observed in each zone. T vs t at various flux levels for "standard" ignition. Iso-damage zone lines plotted on drop zone. Curves of heat flux vs time to flaming ignition obtained with quartz-lamp for several materials.
Correlation Parameters	T_s: t: I
General Results	Temperature versus time data is taken from chromel-alumel thermocouples mounted on blackened steel plates. The fire-bomb attack is monitored remotely via the thermocouple response. Roughly elliptical "iso-damage" zones are drawn around ground zero. Fluxes of up to 5.0 cal/cm^2-sec are measured near ground zero.
Method of Analysis	Ignition times at various flux levels are measured for several target materials subjected to radiation from a quartz-lamp radiant heat source. Data obtained in this matter are corrected to represent ignition by a convective source, by applying a time correction factor. An ignition chart is constructed. The chart is used to predict what specific target material will ignite within a particular zone surrounding the site of a fire-bomb explosion, thus giving a means of evaluating fire-bomb effectiveness.

Reference Number, Author, and Date

(32) Smith 1969

Author's Conclusions	As a natural colored specimen of wood is heated at a constant rate, the surface temperature climbs at a decreasing rate towards an equilibrium temperature that is a balance between heat input and heat losses. Ignition will occur only if this equilibrium temperature is high enough to ignite the pyrolysis gases issuing from the surface. When the surface temperature reaches 425°C, at heat fluxes of from 1.0 - 2.5 cal/cm^2-sec the volatile gases are evolved at a rate great enough to provide a flammable mixture. Flaming combustion will occur at this point if a pilot igniter is present and is in the correct position. Small "hot-spots" form on the surface of the specimen, as char forms at different times over the surface. This makes temperature measurement subject to additional error, and
Ignition Data and Conditions	a) Radiant source b) Self and pilot ignition c) Pressure 1 atm. d) Air e) T_{igs} is generally between 340-425°C. t_{ig} varies inversely with I f) Flux is measured with a Hy-Cal Engineering water-cooled Gardon gauge type calorimeter. The flux varies from .125 to 2.5 cal/cm^{2}sec. g) Temperature is measured by sighting an Ircon-radiation pyrometer model 710 between the two banks of quartz-lamps h) The samples tested are irradiated on
Math Models Used	Omitted
Tables and Graphs	T_{igs} vs I T_s vs t for both piloted and self-ignition of several types of samples. Table of average surface temperatures at ignition.
Correlation Parameters	T_s: t: I
General Results	Temperature rise is rapid at first, decreasing in slope with time. The slope becomes constant between 230 and 260°C where scorching and charring begin. Above 315°C the slope tends to increase slightly and then again decreases above 480°C until ignition occurs. Specimens heated with .75 cal/cm^2-sec using a pilot-igniter ignite at much higher surface temperatures than those subjected to higher heat fluxes. At .5 cal/cm^2-sec, no flame occurs, due to the volatiles being driven off before the surface temperature had risen to the 340-425°C necessary for ignition, with slower heating ($I = .5$ cal/cm^2-sec), ignition does not occur.
Method of Analysis	Wood, cloth, cardboard, and other samples, including non-cellulosic types of material, are subjected to a radiant quartz-lamp source in pilot and self-ignition tests. A radiation pyrometer is used to measure the surface temperature of the specimen. The sensitivity range is that reflected radiation (which is in the range less than 3.5 micron) such that it is not seen, thus eliminating all but the correction for emissivity necessary for accurate surface temperature measurement.

Reference Number, Author, and Date (32) Smith 1969	
Author's Conclusions	since the pyrometer can only see a 1/8" x 1/8" area, the measured temperatures may be on the low side. Unpiloted ignition will occur when the surface temperature rises to above 370°C when charring and surface oxidation allow certain parts of the surface to glow and make self-ignition possible.
Ignition Data and Conditions	a three-inch square area. Buoyancy effects must be considered. i) Ignition is detected by the first appearance of flame.
Math Models Used	
Tables and Graphs	
Correlation Parameters	
General Results	
Method of Analysis	

Reference Number, Author, and Date (33) Squire 1963	
Author's Conclusions	The approximate analytical solution shows ± 20% agreement with data obtained experimentally.
Ignition Data and Conditions	a) Radiant and convective source b) Self ignition c) Pressure 1 atm. d) Air
Math Models Used	Model three
Tables and Graphs	The author's numerical solution (trapezoidal method) is plotted against experimental data obtained by other researchers. The experimental data were obtained from temperature-time plots of the ignition of sawdust spheres.
Correlation Parameters	T_s: t: I
General Results	Application of the non-steady theory allows the partial differential equation to become an ordinary differential equation by using the time variation of an average temperature and composition. The differential equations are approximated by an integral equation which is subsequently solved by the trapezoidal method.
Method of Analysis	The method is an approximate analytical-numerical solution of the equation governing a non-steady explosion. The method assumes: a) Constant thermophysical properties. b) First-order Arrhenius reaction rate. c) Rate of escape of volatiles is measured by rate of formation rather than by diffusion.

Reference Number, Author, and Date

(34) Weatherford 1966

Author's Conclusions	A fixed fuel-generation rate criterion must be satisfied to achieve sustained pilot ignition in the presence of a heat source. Lower ignition temperatures for slabs heated on one side only indicate a lower heat-loss rate for the one-sided heating case, which will lead to a shorter ignition time than slabs heated on both sides, where heat is lost from both surfaces.
Ignition Data and Conditions	a) Convective source b) Pilot ignition c) Pressure 1 atm. d) Air h) Compacted cotton slabs 15 cm square are heated on an area 15 cm by 12 cm.
Math Models Used	Omitted
Tables and Graphs	hl vs $\frac{h^2t}{pc}$ $\frac{h^2t}{pc}$ vs ψ_s The above are given for two cases: (a) heating on one side only, (b) heating on both sides simultaneously.
Correlation Parameters	hl: $h^2t/\rho c$: $h^2t/\rho ck$; a dimensionless fuel generation rate: $\psi_s = (T_s - T_x)/(T_\infty - T_s)$, the dimensionless temperature: Nu: Fo
General Results	Small variations from sample of density and thickness have significant influence on ignition time. It is reasonable to model the sustained ignition in the presence of the heat source as being controlled by a fixed fuel generation rate.
Method of Analysis	Compacted cotton slabs (.1, .3, 1.0 and 3.0 cm thick) are heated at rates varying from .06 to .10 cal/cm^2-sec with time to ignition measured and moisture content carefully noted.

Reference Number, Author, and Date

(35) Welker 1968

Author's Conclusions	The correlation-equation for ignition time, intensity, and density is satisfactory in predicting the ignition-behavior for eleven species of wood with densities ranging from .3 to .7 gm/cm^3 for intensities of .5 to 2.5 $cal/cm^2 sec$. Radiation from clean, smokeless flames produces ignition-data of essentially the same character as that obtained using rich, sooty flames. It is concluded that wood absorbs radiation from equal-intensity flames at a rate independent of the nature of the flame.
Ignition Data and Conditions	a) Convective source b) Pilot ignition c) Pressure 1 atm. d) Air e) I varies from .5 to 3 cal/cm^2-sec. h) Buoyancy effects must be included. Specimens are 10.1 cm square.
Math Models Used	The least-squares analysis resulted in the equation: $t_{ig} = 80\rho/I^3$.
Tables and Graphs	t_{igs} vs $I^{(-.33)}$ t_{igs} vs I for various specimens
Correlation Parameters	t: T: I: K, a, b are numerical constants.
General Results	A least-squares curve-fit on the ignition time versus intensity data, with a proposed equation of the form $t_{ig} = KI^a\rho^b$, is used to predict ignition time at a given intensity and for wood of a certain density. Of the three kinds of specimens, the plastic takes longest to ignite at a given intensity. Blackened samples ignite sooner than natural colored samples.
Method of Analysis	Wood, cardboard, and plastic samples are tested in piloted ignition experiments at intensities of .5 to 3 cal/cm^2-sec. Ignition is accomplished by subjecting the sample to a buoyant diffusion flame produced from a pool of burning acetone or benzene. Heating rate is adjusted by varying the distance between the specimen and the flame.

Reference Number, Author, and Date

(36) Welker 1969

Author's Conclusions	For future research, it is important to measure the values of the reflectivity and transmissivity of the target for each applicable wave-length, as well as function of wave-length for both target and source. The proposed single correlation of material ignition times as a function of the intensity appears to correctly represent the ignition behavior whether specimens are heated with a convective or radiant source.
Ignition Data and Conditions	a) Convective source b) Pilot and self ignition c) Pressure 1 atm. d) Air h) Buoyancy effects must be considered i) Ignition was described as the occurrence of flaming or glowing.
Math Models Used	Omitted
Tables and Graphs	E vs wavelength. a vs wavelength. I vs t.
Correlation Parameters	I: t: C: a
General Results	Evidence is obtained proving that ignition behavior of a material not acting as a black body is strongly dependent upon the spectral absorbtivity of the target and the emissive power of the irradiating source. Ignition by flame radiation occurs in about one-third the time as ignition by the Tungsten filament source.
Method of Analysis	The effect of spectral quality on ignition behavior is studied. Two sources, one a Tungsten lamp, the other a vertical diffusion flame, are used to determine the ignition response of specimens subjected to flux of the same intensity from each source. White and black α-cellulose is tested.

CHAPTER IV

GRAPHS AND TABLES

Reference to Figures 1 through 4 will point out the influence on the ignition time of the type of source used to heat the specimen, the type of ignition (spontaneous or pilot), and the color of the sample.

It is apparent from these figures that in general, ignition time at a given intensity will be shortest for a sample being heated by a convective source, using pilot ignition, and which has been blackened prior to testing. Where one or more of these conditions are missing, the time required for ignition will be correspondingly longer.

On Figure 1, the two points in the upper left and lower right corners are difficult to correlate with the majority of the other sources of data. It is possible that if the curves of the more "average" data were extrapolated to extreme values in both directions, the point indicated at 3000 cal/cm^2-sec., .0001 sec., might possibly lie on or near one of the extrapolated curves, indicating that at high rates of heating the material responds to the thermal energy in a more rapid, but nevertheless predictable manner. On the other hand, the point shown in the lower right-hand corner at .06 cal/cm^2-sec., 1700 sec. (reported by Weatherford and Valtierra, 35), does not appear to be in a position that would lie on one of the extrapolated curves mentioned earlier.

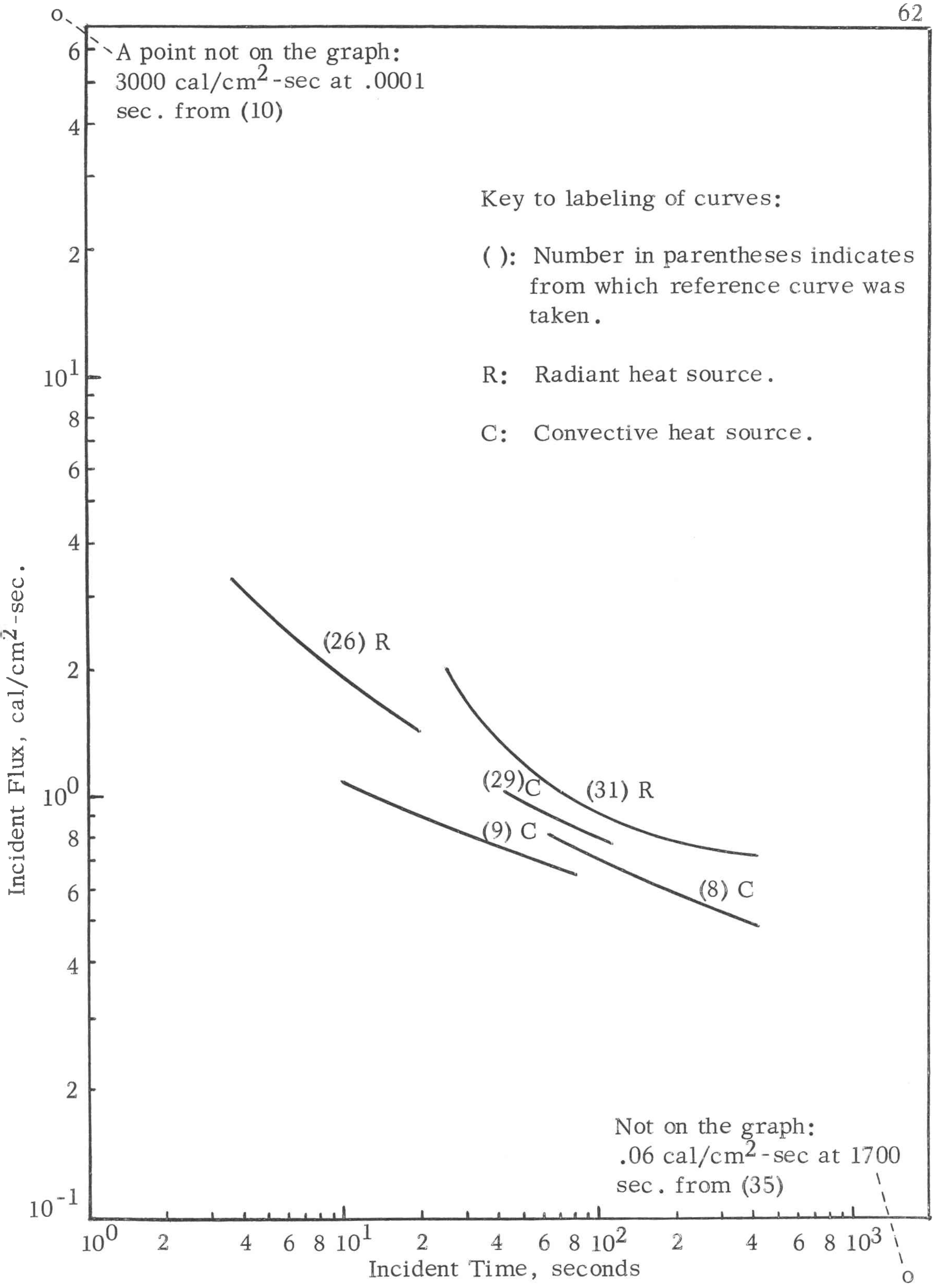

Fig. 1.--Incident flux vs ignition time for spontaneous ignition of natural colored wood.

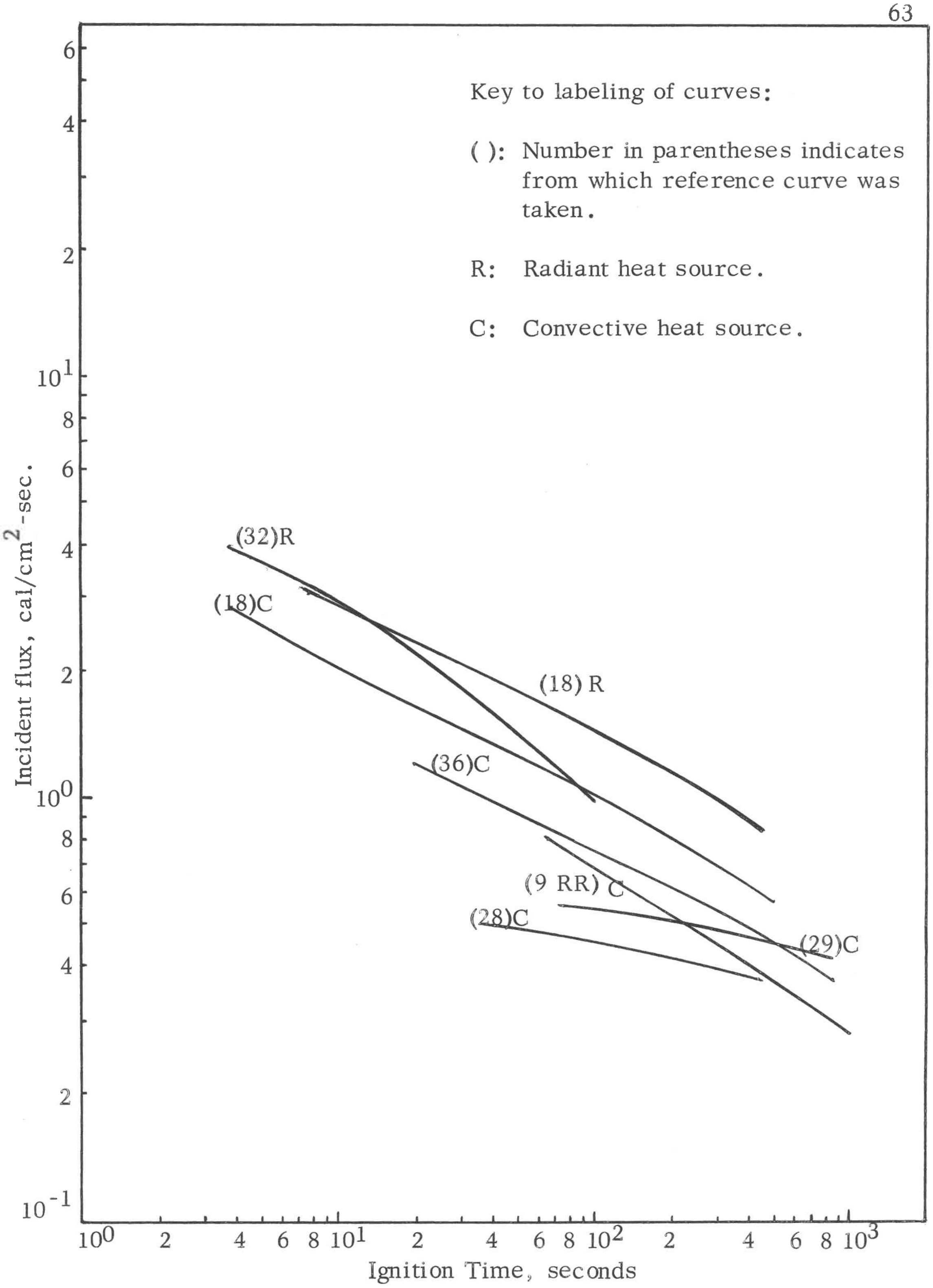

Figure 2.--Incident flux versus ignition time for pilot ignition of natural colored wood.

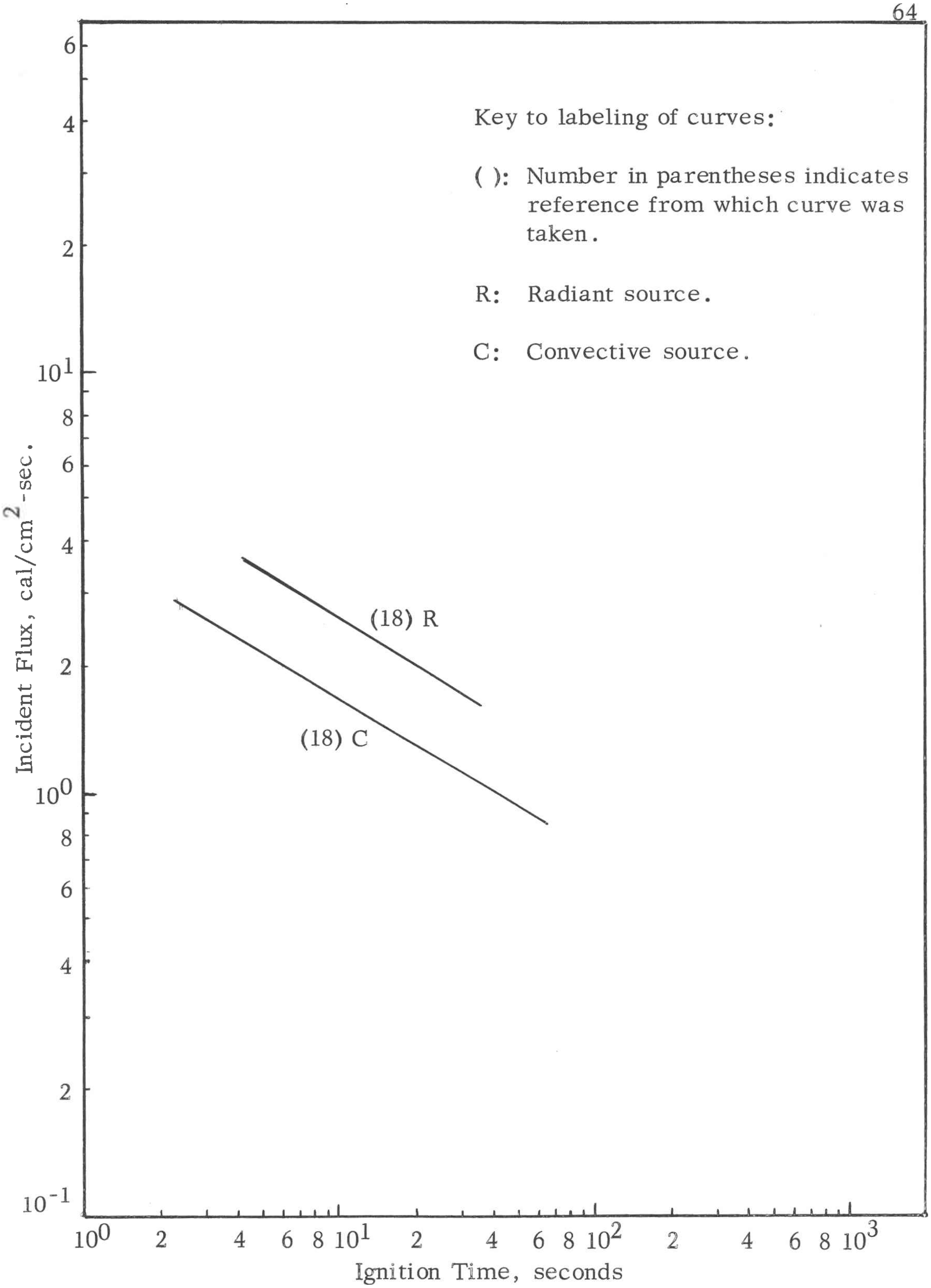

Figure 3.--Incident flux versus ignition time for pilot ignition of pre-blackened wood.

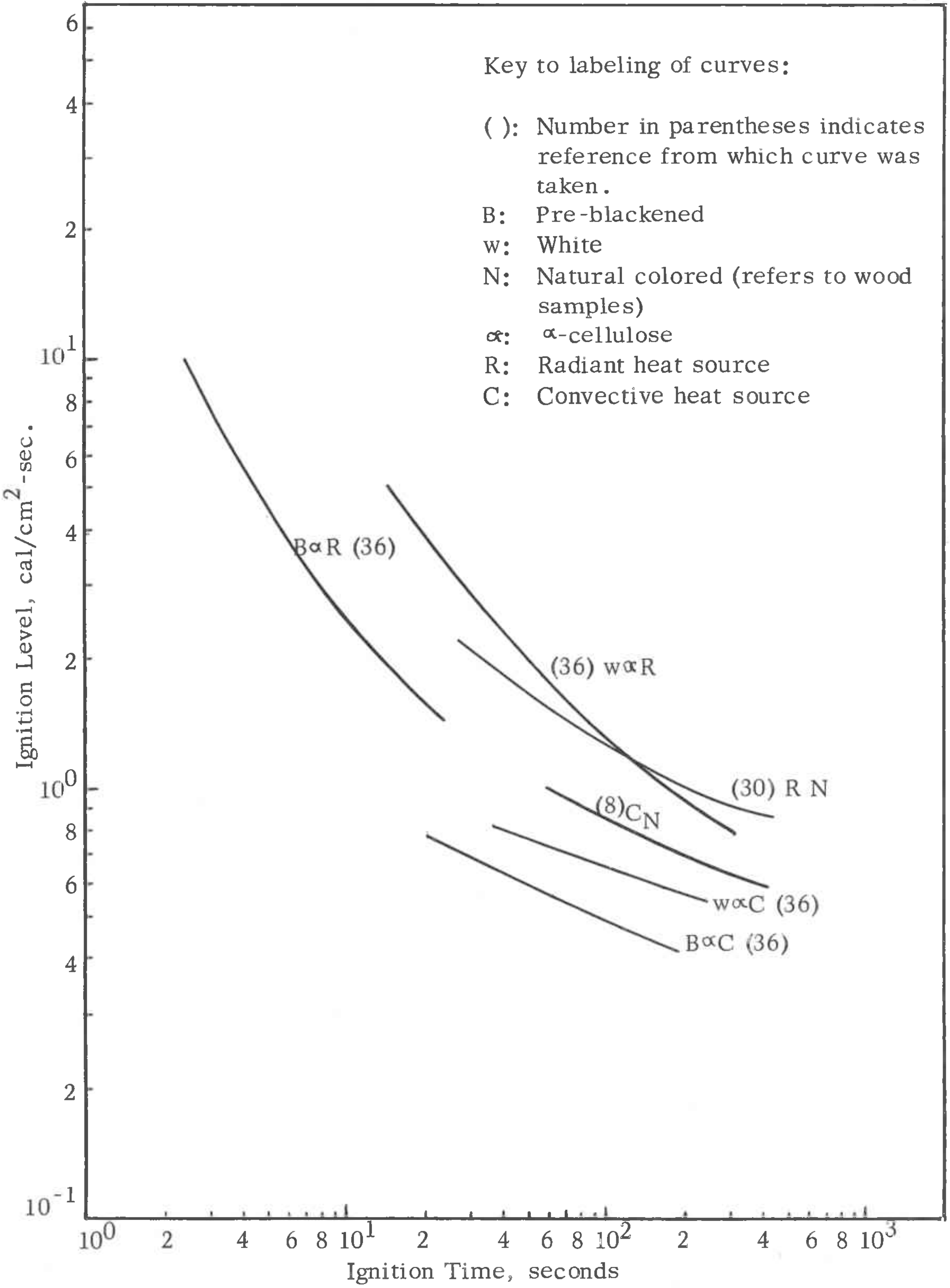

Figure 4.--Intensity versus ignition time for spontaneous ignition of α-cellulose and wood specimens.

The heating rate used in this case is approximately three times the solar constant. It is possible that at very low rates of heating, the ignition process is influenced by parameters other than those which are currently thought to be most important. In any event, without further experimental verification, it would be difficult to determine from presently available data whether or not the few instances of ignition reported at extreme values of time or flux intensity are entirely representative of the ignition process at such levels.

Figures 5 and 6 show the surface temperature history of wood specimens during the heating process. The data of Figure 6 may be compared to Figure 5 to show the influence of the rate of heating. Note that at a given rate of heating, the black-painted specimens experience a more rapid rise in surface temperature. Also of interest is that at high heating rates there is an abrupt drop in temperature with a subsequent sharp temperature rise in the 450^{o}-550^{o}C range. Similar behavior has been noted by several other researchers who have used the technique of Differential Thermal Analysis to study the ignition process. Akita (1), Brown (3), and Kilzer (7) were among those who reported an endothermic "well" in the DTA curves, i.e., a depression followed by a sharp rise in temperature. The range of temperature in these latter cases was 350^{o}-550^{o}C, wider than shown on the figures, but nevertheless within limits that could be accounted for by sample texture, size, color, or other possible differences.

Figure 7 shows the temperature profile within the stream of volatiles above a heated specimen of wood. The data are taken from the work of

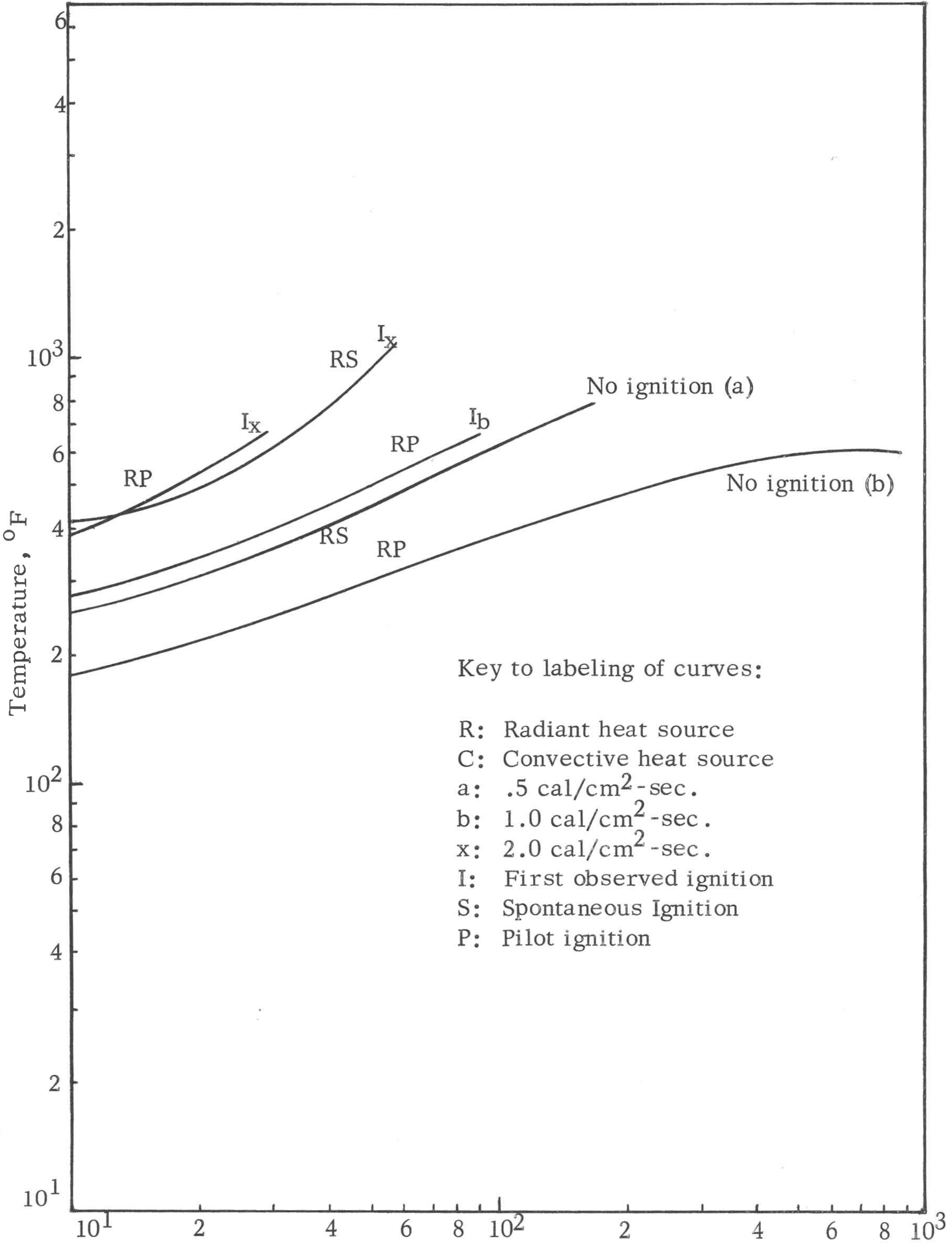

Figure 5.--Surface temperature of natural colored wood heated to first occurrence of ignition (after Smith, 32).

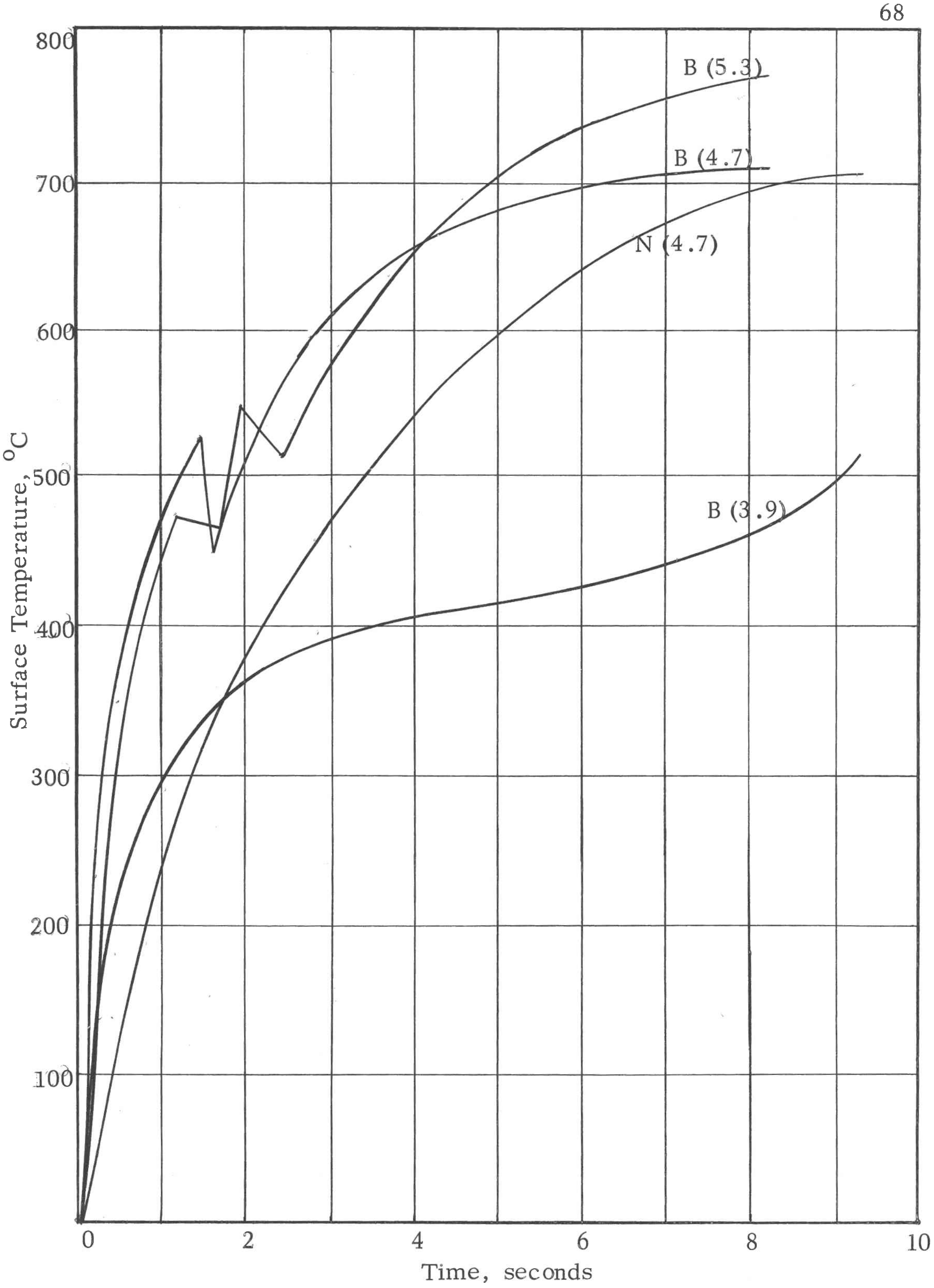

Figure 6.--Surface temperature versus time for natural and preblackened wood at various intensities (after Gardon and Hottel, 6).

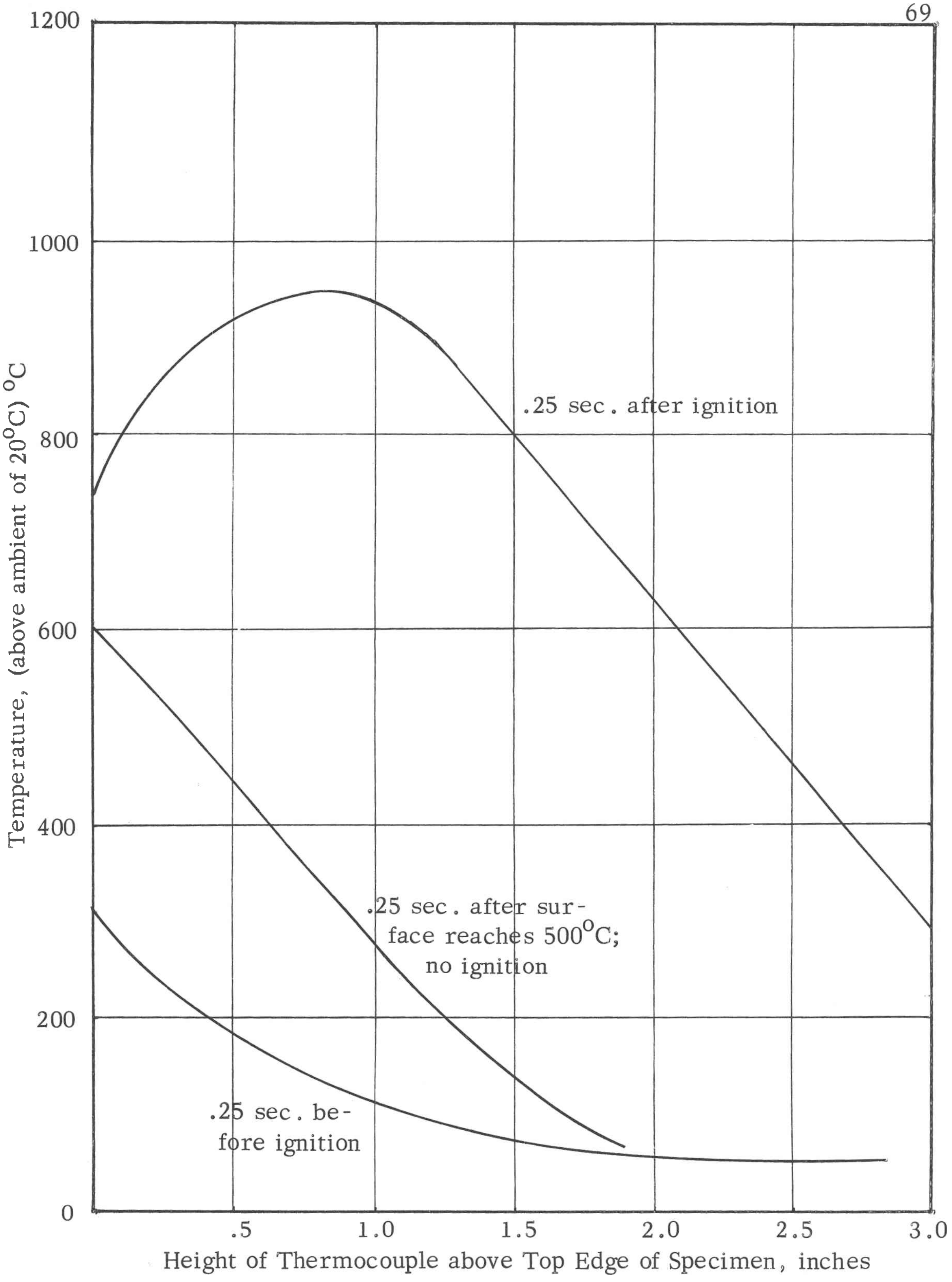

Figure 7.--Temperature profile in volatile stream at various times: before ignition, after ignition, and when no ignition occurred (after Simms, 25).

Simms (26). In this particular study, Simms used a gas-fired panel to heat the sample being tested. Thermocouples were placed at various heights above the wood so that the temperature at each of the several points could be read simultaneously. Of interest is the point at which each of the curves becomes approximately linear. For the data shown on the figure, this point is at about one and one-half inches above the top edge of the specimen. The fact that all three curves (before, after, and when no ignition occurred) seem to become linear at about the same point might indicate that the overall heat-transfer mechanism at a certain distance above the sample is the same regardless of whether or not ignition occurs. Simms pointed out that ignition occurs at the point in the volatile stream at which the flow becomes turbulent. It would be of interest to determine in future experiments if there is any correspondence between the turbulent point and the point at which the temperature profile becomes linear. In such experimental work, it would be necessary to verify the behavior illustrated in Figure 7, and examine the degree to which the temperature profile is affected by the heating rate, orientation, and distance between the sample and heat source.

Three of the four math models discussed earlier result in parameters which are plotted together on Figure 8. The graph shows the range of values for which the models give similar results.

Each axis of the figure has two labels. It is intended that the labels be read in pairs, i.e., energy modulus vs cooling modulus, and irradiance modulus vs (Fourier modulus)$^{1/2}$.

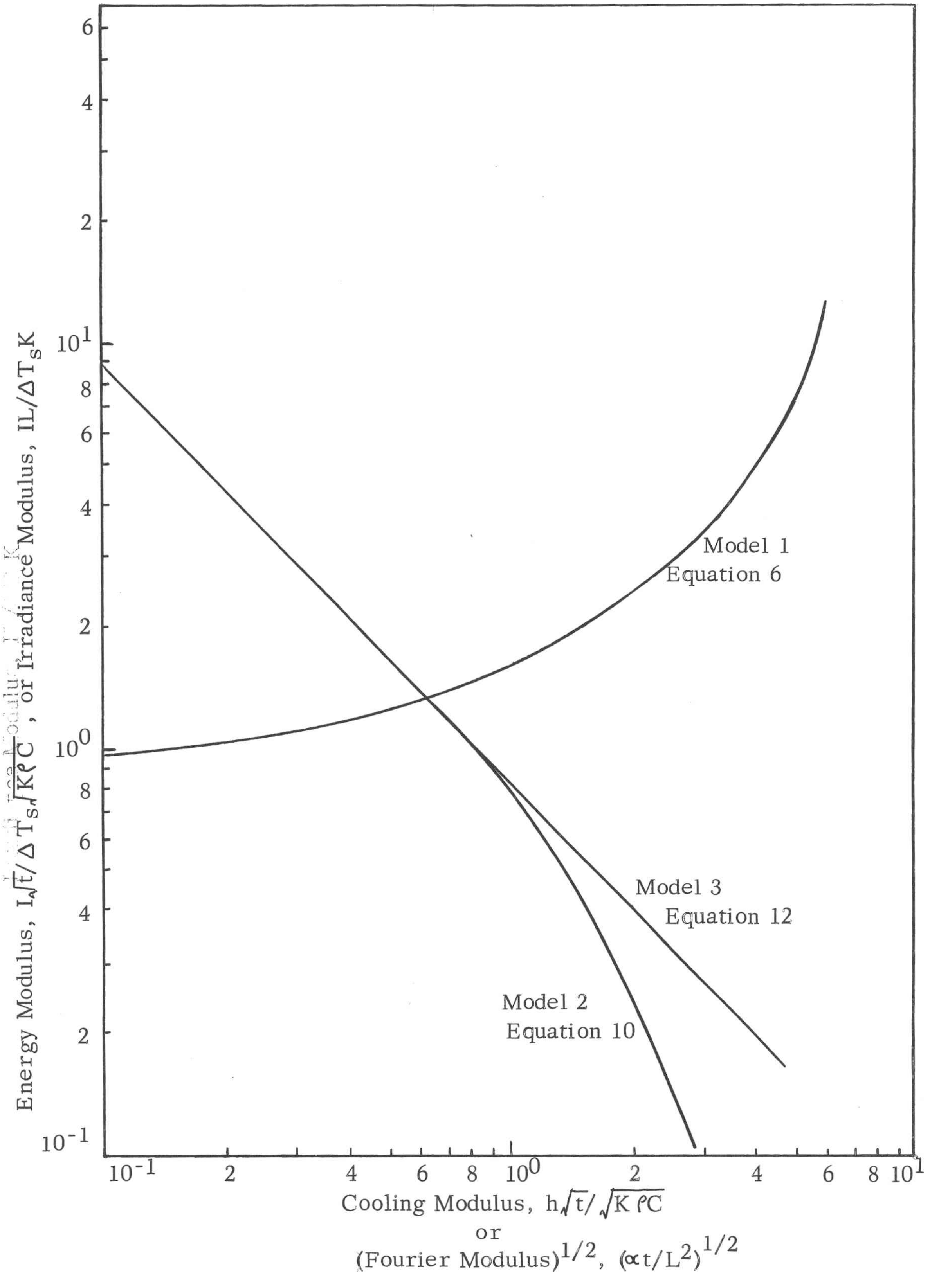

Figure 8.--Theoretical curves of equations 6, 10, and 12

With reference to the first pair of axis labels, the curves may be thought of as representing the locus of energy balance combinations for which the math models predict ignition will occur.

The second pair of axis labels represent the dimensionless flux intensity vs the dimensionless ignition time, i.e., the time required to obtain ignition of a specimen being irradiated at a given intensity of heat flux. Note that for (Fourier modulus)$^{1/2}$ or cooling modulus in the range of 0.6 all three models give approximately the same results, but for large values of these parameters the curves representing each model become increasingly divergent.

The fourth math model is not shown on Figure 8 because it is a model of the combustion process rather than the ignition process, and as such is not capable of being correlated with the other three models as discussed above.

Figure 9 shows the variation of ignition time as the size of the area being heated is changed. This data, taken from Simms (25), show that as the area being heated is made larger, the ignition time at a given rate of heating becomes shorter. The curves have been extrapolated downward to meet the abscissa at a point which for each intensity level or heating rate is the time which would be required to ignite a specimen of infinite area.

The curves also point out that for heating at high rates, the size area being irradiated becomes less and less an important factor. This is illustrated by the curve plotted in which the rate of heating was 10.0 cal/cm^2-sec. Note that this curve is nearly vertical, indicating that large changes in area size will have little effect on ignition time.

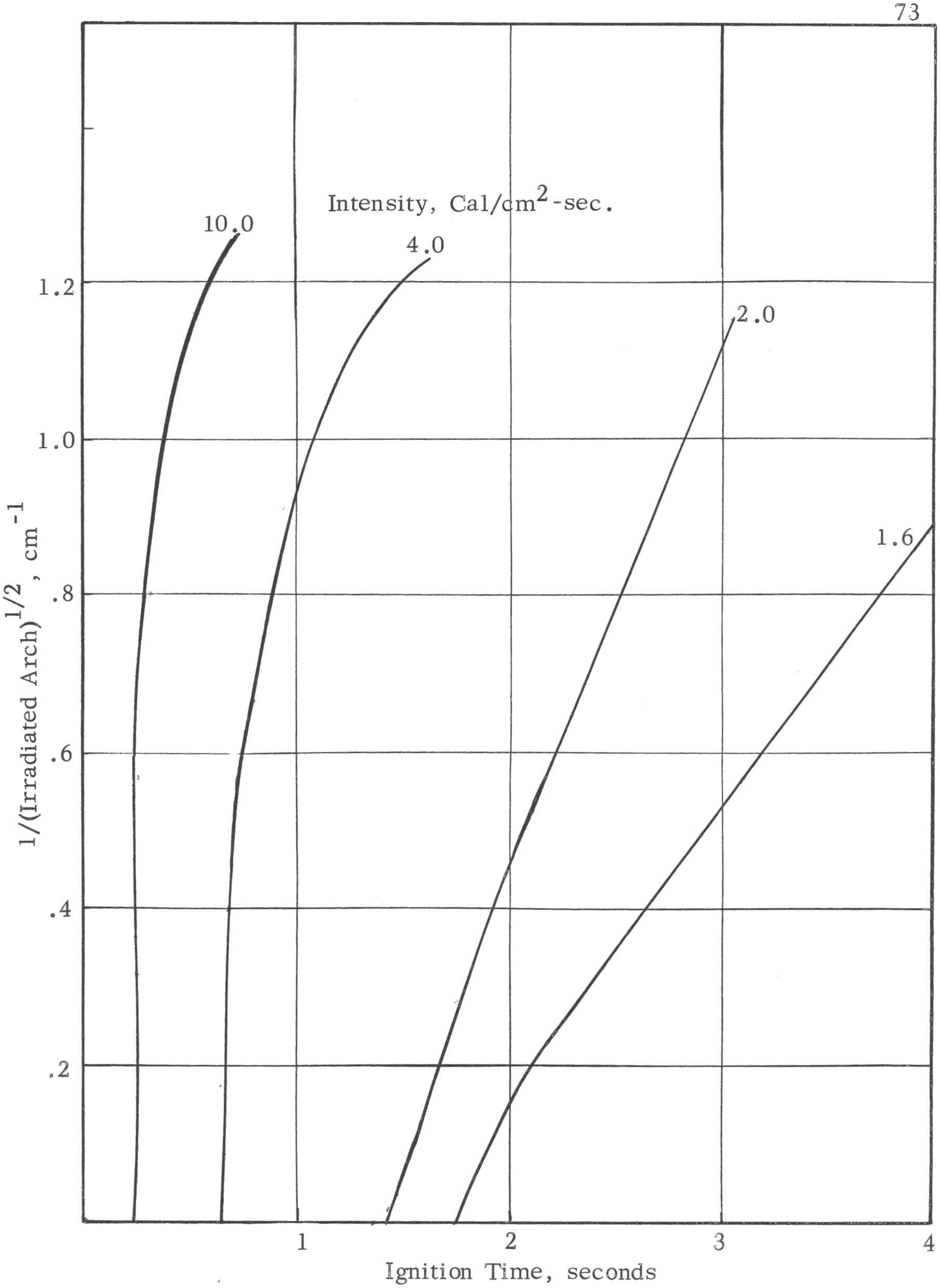

Figure 9.--Variation of ignition time with irradiated area for various intensity levels (after Simms, 24).

Figures 10 and 11 show the variation of minimum intensity for ignition with varying moisture content and density respectively. It is shown that as density and moisture content increase, the minimum intensity required for ignition also increases.

With regard to moisture content, Simms was able to account for the increase in minimum ignition intensity and in the correspondingly longer time required to obtain ignition with the use of an equation which corrects the thermal properties for changing values of moisture content. In doing so, Simms implies that all changes in the ignition process which may be caused by the addition of moisture to the test specimen are predictable by making appropriate changes in the values of the thermal properties.

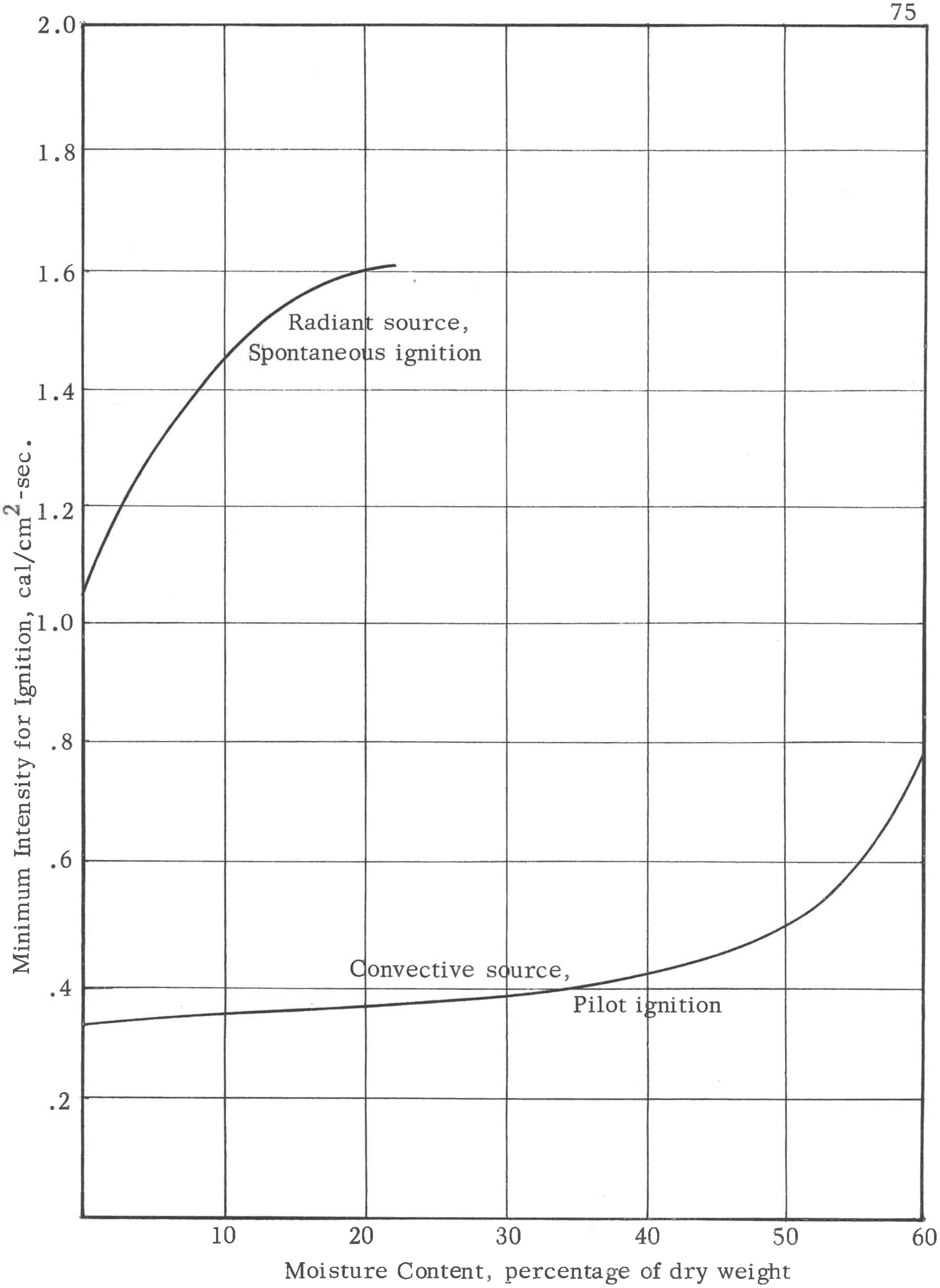

Figure 10.--Minimum intensity for ignition of wood with varying moisture content (after Simms, 24, 28).

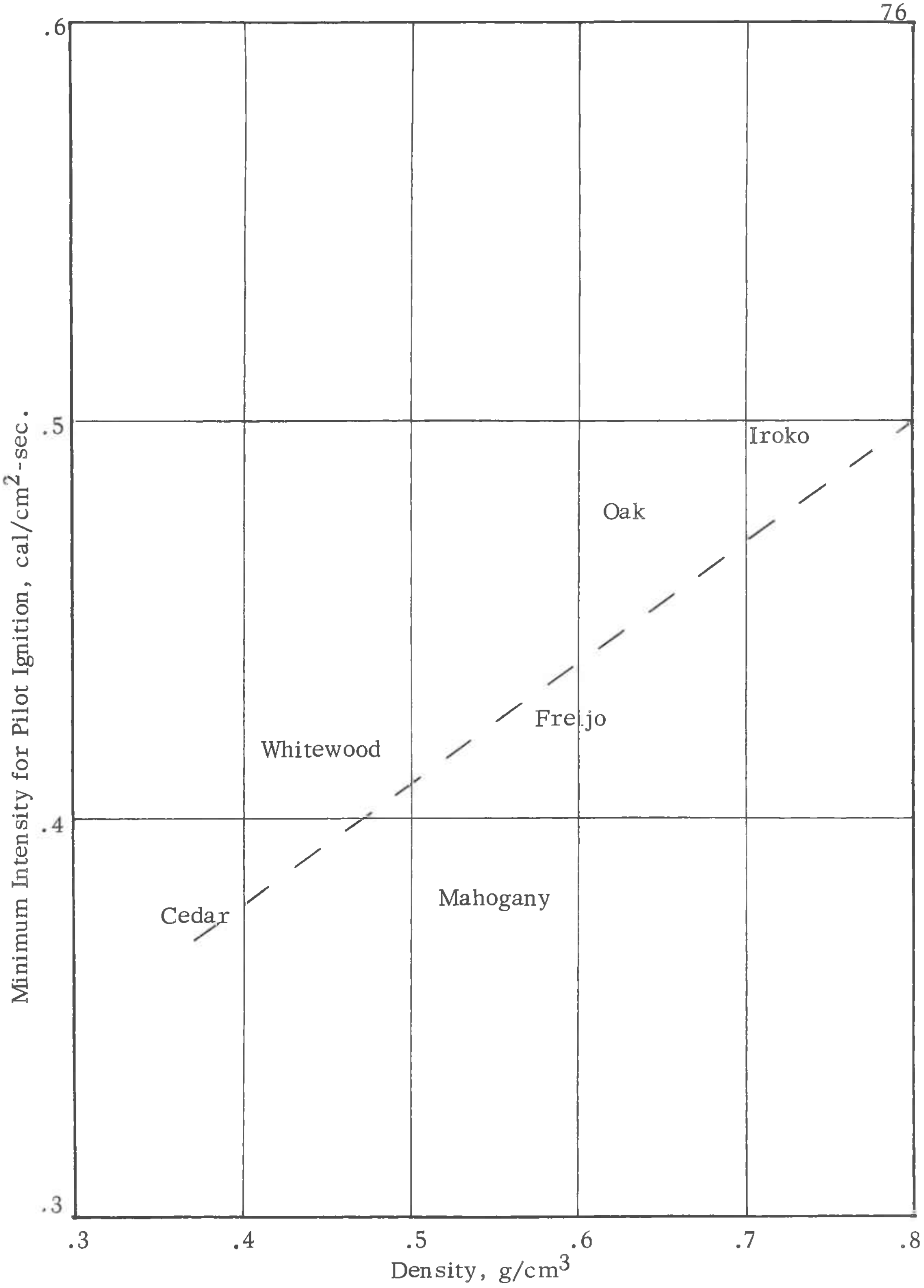

Figure 11.--Variation of minimum intensity for pilot ignition with density, after Simms (27).

Reference Number	E; kcal/mole	Wood	α-cellulose
1	53.5		X
2	22.8	X	
10	42.0		X
16	17.0		X
19	25.0 15.0	X	

Figure 12.--Values of activation energy reported for wood and α-cellulose.

TABLE 1

GAS-LIQUID CHROMATOGRAPHIC ANALYSIS OF THE PYROLYZATE FROM PYROLYSIS OF COTTON CELLULOSE*

Compound	Identification**
Volatile Gases; CO, CO_2	P
Formaldehyde	P
Acetaldehyde	P
Acrolein	P
Propionaldehyde	P
n-Butyraldehyde	T
Glyoxal	P
Furfural	P
5-Hydroxymethyl Furfural	P
Acetone	P
Methyl Ethyl Ketone	P
Methanol	T
Formic Acid	T
Acetic Acid	P
Lactic Acid	P
Water	P
Levoglucosan	T

*Taken from reference number 11.

**P = Positive identification; T = Tentative identification.

CHAPTER V

DISCUSSION OF RESULTS

In order that the material presented in this survey be viewed in proper perspective, it is felt necessary to provide answers to several questions raised when attempting to correlate results from different authors. The questions are as follows:

1. Are differences in ignition temperature reported by the several authors connected in any way with the method used to measure this temperature?

2. Are any of the ignition parameters influenced by the orientation of the test specimen relative to the source of heat and/or the force of gravity?

3. Is the size sample or area being irradiated a controlling parameter?

4. Does there exist a generally-accepted set of ignition criteria?

5. Are there areas of contradiction between the authors of the literature surveyed?

The answers to the above questions will be discussed in the following pages in the order given above.

Temperature measurement effects

Examination of the ignition temperatures reported in the literature lead to the following generalization with respect to methods of temperature measurement:

Three overlapping levels of ignition temperatures are apparent;

1. The highest, in which surface ignition temperatures are reported in the range of 750°C - 500°C.

2. The middle range, in which surface ignition temperatures are reported in the range 500°C - 300°C.

3. The low range, in which temperature at the center of a body was measured in the range 300°C - 175°C.

It is important to note the qualification given to the low range above. The temperatures reported in this range were from experimental work performed in a furnace, and with cubical, cylindrical, or spherical specimens whose body-center temperature was being measured by a thermocouple. Under these circumstances it is difficult to make any generalizations about the temperature-measurement method.

The temperatures in the high range (#1 above) were reported for the ignition of samples by flame and quartz-lamp radiation, and were measured with optical methods, in most cases a radiation-pyrometer.

The temperatures reported in the middle range (#2 above) were reported for the ignition of samples by flame and quartz-lamp radiation, and were measured by means of thermocouples placed both on the surface and at known depths below it. For the latter case, the temperature at the surface was extrapolated from the temperature at the known positions beneath the surface.

From the graphs related to the question being presently discussed (Figures 1 through 5), it may be observed that the three temperature ranges discussed are not well defined, but rather are somewhat overlapping.

In answer to the question of temperature measurement method and its relation to the temperature observed at ignition, it must be said that there does seem to be a correlation between the two; however, at this point it is difficult to determine how interdependent the two are. It is interesting to notice that in those cases where the temperature was measured optically and resulted in the ignition temperature falling in the low range (300° - 175° C), in nearly every case the test was for piloted ignition. This seems to suggest that piloted ignition may be analogous to the test in which the sample is heated in a furnace at a pre-determined rate. Subject to further verification, the correlation spoken of earlier suggests that ignition tests in which the surface temperature is measured with an optical device will result in the observation of higher surface temperatures than similar tests in which the surface temperature is measured with thermocouples. Furthermore, both of the above methods when compared to tests in which the specimen is heated in a furnace yield high values of ignition temperature. This does not necessarily imply that the differences in ignition temperature noted above are a result only of the method of temperature measurement. It will be pointed out later that such differences are attributable to many other factors, among them the heating rate and type of source used to provide the heat.

Orientation effects

Of the several possible experimental configurations of sample and heat source, the following three occur with about equal frequency in the literature:

1. Sample and heat source located on the same horizontal plane, so that the radiant energy travels horizontally to the target. The volatile plume issues forth from the target and forms a free-convection boundary layer as buoyancy effects propel the volatiles upward along the target surface.

2. Sample and heat source located on the same vertical plane, so that the radiant energy travels downward to the target. The volatile plume issues forth from the target and rises vertically and perpendicularly away from the target surface. In this test configuration no external boundary layer (supported by buoyancy and free convection) affects the ignition process.

3. Sample is heated at a pre-determined rate or at a constant temperature in a furnace. In this configuration, the sample is surrounded completely by the hot gases within the furnace. Boundary-layer effects are thought to be a minimum in this type of heating.

The effect of sample-heat source orientation is difficult to measure. This particular phenomenon is not specifically dealt with by any of the literature surveyed, although it is felt to have a measurable influence over one or more of the ignition parameters. One reference which offers an insight into this problem is that work reported by Simms (27): Simms investigated the effect of turbulence upon the ignition process. Orientation of the sample with respect to the heat source and to the force of gravity may influence the location of the point of turbulence. For this reason, the following conclusions drawn by Simms (27) are presented.

1. Turbulence imposed on a previously laminar volatile stream will permit ignition to occur where the sample would normally not have ignited.

2. Given two tests in which the surface temperature and temperature gradient in the volatile stream are the same, ignition will occur, if at all, in that specimen which has, in addition to the above, a turbulent volatile stream.

3. Small surface areas emit small volatile plumes which by nature become turbulent farther from the irradiated surface than a large sample being heated at the same rate. The small area will take longer to ignite due to the additional time required for its volatile stream to become combustible.

These observations by Simms suggest that one controlling parameter in the ignition process is the point at which the volatile stream becomes turbulent. With this premise, it is logical to assume that if the turbulent point can be affected by the orientation of the sample with respect to the heat source, this orientation effect may to some degree control the process leading to ignition. Further support is given to this idea by a statement made by Simms (29). He pointed out that from his measurements of the temperature in the volatile stream, it appeared that the temperature distribution in the stream is the same regardless of whether or not ignition occurs in a particular test. If this truly is the case, then the location of the point of turbulence in relation to the irradiated surface may well be the deciding factor in determining the occurrence of ignition. For heating at a given rate, the parameters most likely to be influenced by the sample orientation are the ignition temperature at the surface and the ignition time, as discussed below.

The reasons for this will be discussed in detail later, but for the present it is sufficient to say that the sample-heat source orientation can affect the surface temperature by its influence on the formation of a boundary layer along the interface between the sample and its surroundings. The presuence of a boundary layer may also influence the time taken for the surface of the specimen to reach a temperature at which ignition can occur.

When the sample is below the heat source, the boundary layer will be almost negligible because the volatile plume rises vertically away from the target surface. However, when the sample is being heated from the side, the volatiles are carried upward along the surface and form a boundary layer which can affect the temperature distribution over the surface and potentially influence both ignition temperature and ignition time.

No work has been done to specifically determine the magnitude of any effects caused by differences in sample-heat orientation. It is difficult to isolate this effect by comparing the work of two or more authors because of the differences in experimental apparatus.

Reference to the ignition temperature data will reveal that for a particular heating rate, ignition temperature has been reported with a variation of as much as 200°C by different authors (see Brown, 3, and Smith, 30). It is almost certain that a portion of the reported differences in ignition temperature are due to orientation effects. In the orientation referred to in which the sample and source are on the same horizontal plane, it is quite conceivable that as the boundary layer builds up along the target surface, because this layer is composed of hot gases it will cause the temperature at the upper edge of the target to be higher than the temperature at the lower edge. If this is the case, then thermocouples placed on the surface would measure different ignition temperatures. It is also possible that for a duplicate experiment using the same thermocouples with the second orientation (sample and source in the same vertical plane), in the absence of the boundary layer, still a different temperature range for ignition would be measured. For measurement with an optical device, this same problem would exist because the device "sees" only a very small area and no tests were reported in which the surface was "scanned." With reference now to the time required for ignition to occur, it would be impossible to say with confidence which of the two configurations would lead to consistently shorter ignition times without experimental verification. The location of the point of turbulence is different in both cases, and this conceivably could make a difference in the ignition time. In the first case, the point of turbulence (at low rates of heating) is above the level of the plane along which the radiant energy passes to arrive at the target surface. The tendency for the laminar boundary layer which is present in this case to prevent the proper mixing of the volatiles with the surrounding air may prolong the time required for ignition to occur. On the other hand, the hot volatiles issuing from the bottom of the target surface may actually heat the upper part of the surface (as discussed earlier) and hasten the ignition process. In the second orientation (sample and source in the same vertical plane), it is conceivable that because the volatiles are rising up and directly away from the target surface that the point of turbulence would occur farther away from the sample and thereby prolong the ignition time. Conversely, the absence of a boundary layer may permit the oxygen-bearing surrounding atmosphere to mix more effectively with the volatiles and accelerate the occurrence of ignition.

Finally, it must be added that although much of the preceding discussion concerned the orientation of the specimen relative to the gaseous plume of volatiles, it is difficult to obtain a mental picture of the experimental apparatus without mentioning the location of the source.

Area effects

Although only a few of the articles surveyed considered this question, those that did (Simms, 24, 25, 26, 27, 28) were in agreement as to the fact that for a given flux level, specimens being irradiated on a small area require longer exposure (at the same heating rate) for ignition than do large areas. The size areas in question are considered small if under 5 cm on a side, and large if over this size (the largest size areas encountered were about 10 cm square). Of the theories offered in explanation of this behavior, the most common proposes that since ignition first occurs in the volatile plume, the size of the plume will determine to a large extent the time required for a combustible mixture to be found somewhere within the gases which make up the plume. This being the case, it follows that the larger the size of the volatile column, the more likely it is that its gases will combine with the surrounding atmosphere to form a combustible mixture. Because of this greater likelihood, the large exposed surface will generally ignite in shorter time than the small surface. In general, the size of the heated area is only slightly smaller (less than 10 per cent) than the whole surface in question.

In answer to the question originally posed, the size of the area being irradiated *is* a controlling parameter to the extent that the time required for large areas to ignite will generally be shorter than that for small areas. Other parameters which may be affected by area are the ignition temperature and the mass rate of flow of the volatiles. No comments regarding these last two parameters with regard to area effect were found in the literature.

Ignition criteria

The complexity of the process leading to ignition is such that of all the models described in the literature, no single solution or set of equations has been proposed which gives a complete picture of the entire ignition process.

In one sense, then, it is true that no one set of parameters combined in an equation is accepted by all authors as the one solution to the ignition process. In fact, it is apparent that each researcher believes his approach to the problem gives the best overall picture of what is taking place.

It is true, however, that there are specific criteria which occur regularly in the literature and seem to be the basis of most attempts to correlate ignition data. These are: The surface temperature at ignition, T_{ig}; the critical rate of weight loss at ignition, w_c; the time taken for the specimen to ignite, t_{ig}; the intensity (or heating rate) to which the specimen is subjected, I; the activation energy, E; and the reaction rate constant, k. As mentioned earlier, there is no agreement as to which criteria truly govern the ignition process. There is a group, most notable of whom is Simms, that adhere to a fixed ignition-temperature criteria as being descriptive of the ignition process. Another school of thought suggests that a critical weight loss rate is a better criteria. Still another group holds that there is a numerical correlation between the ignition time required and a given heating rate. And finally, it is proposed by some that by using combined differential thermal analysis and thermogravimetric analysis, that the ignition response may be predicted from the slopes of curves obtained in the above methods. In addition, there are authors whose work incorporates the use of more than one of the above-mentioned methods of approach.

Areas of contradiction

In the discussion immediately preceding, it was pointed out that several schools of thought have been proposed, all of which are claimed to successfully model the ignition process. To the extent that they cannot all be 100 per cent correct, they may be said to be self-contradictory. For the moment, however, it is not these differences in acceptance of ignition criteria which will be discussed. The purpose of the present discussion is to point out other differences of opinion as expressed either as a result or a conclusion by the authors concerned.

Activation energy.--Akita (1) states that "activation energy is undoubtedly independent of the heating rate," while Murty and Blackshear (15) (16) contend that the activation energy is a function of radius, with E at the center of the specimen being lower than at the surface. This is perhaps not an obvious contradiction, but if it is remembered that the inner parts of a particular sample do actually heat at different rates than the surface, the statement that E is a function of radius is equivalent to saying that E is a function of the heating rate, which is in direct opposition to the previous statement by Akita (1). Of further interest is the fact that on several other points the authors cite information which is in close agreement. Both articles used TGA and DTA as the method of approach to the problem, thus making the one contradictive point seem more out of place.

Activation energy.--With further reference to the activation energy, Murty and Blackshear (15) state that activation energy increases with temperature of the sample, while Roberts and Clough (19) claim their work shows a decrease in E with temperature. Again the method of analysis used in both articles was TGA and DTA.

Moisture content.--With reference now to the effect of moisture content upon the ignition process, it is agreed by those researchers who considered moisture effects that wood which is dampened will require additional energy to ignite as compared with dry wood. The extra energy required is manifested by the longer time taken for the dampened specimen to ignite. The point upon which there is a difference of opinion is whether or not the longer ignition times required by the moisture-bearing samples may be reconciled by the application of a correction factor to the specific heat and thermal conductivity, or if there exists some valid equation relating the moisture content M to the specific heat and thermal conductivity. Simms (27) states that it is possible to correlate the longer ignition times of moisture-bearing wood with changes in the thermal properties caused by water. Fons (5) concludes from his work that such a correlation is not possible. It must be pointed out that the equations used in these two articles to arrive at these conclusions were quite different.

Heat of reaction.--Roberts (20, 21), claims that the heat of reaction is essentially constant throughout the decomposition process, but in a later article (22) reverses his thinking and concludes that the heat of reaction varies during decomposition.

Thickness effect.--Smith (31) concludes that due to convective cooling, re-radiation, and reflective losses, the fraction of the total incident flux actually available to raise the temperature of the specimen is small. This fraction is said to vary with temperature and is smaller for thermally thin specimens than for those which are thermally thick. Martin (14) states that the energy required for ignition is independent of thickness. It is significant that Martin's work was done on samples of black alpha-cellulose ranging in thickness from .005 to .031 inches, while Smith tested samples which were .026 to .75 inches thick. This might suggest that there is a range in which thickness is not a significant parameter. It should be mentioned, however, that Martin used a very high rate of heating (100 cal/cm^2-sec.) as compared with Smith (.5 to 2.5 cal/cm^2-sec.) and this difference might override any other conclusions drawn by comparing these two articles.

CHAPTER VI

CONCLUDING RECOMMENDATIONS

By its very nature, that is, unsupported by any original experimental work, a literature survey is limited with regard to the conclusions which may be drawn. Rather than report any new discovery which proposes to be a solution to a particular problem, the survey can only review and compare, or analyze and discuss what from the literature are taken to be significant contributions to the overall objective. That objective is, in this case, the modeling of the process by which wood, and other materials whose structure is basically cellulose, is heated and eventually ignited by exposure to a source of thermal energy. Finally, the survey can point out areas in which no research has been done. Such voids in the experimental investigation of a particular subject could hold the key to greater understanding of the entire question. In such cases, the survey can make recommendations for research to be done to fill any existing gaps in present knowledge.

A first conclusion coming out of the literature is that each author, if judged only in the light of his own data, is correct is his description of the ignition process with its according model; i.e., each author thinks his approach is most correct. It is important, therefore, not to assume that any one individual or team of individuals is correct without first examining a few of the basic differences in approach taken and in results obtained. As was pointed out earlier, examination of this kind resulted in the bringing to light of contradictions in both method of approach and results obtained by several of the authors.

Since no one model of the ignition process has been shown or accepted by any of the authors to be the complete solution of the ignition problem, it may be valuable for future researchers to consider the following points:

1. The failure of any of the simplified mathematical models to accurately describe the ignition process suggests that the simple model is the wrong choice. The effects of chemical reactions within the solid, change of properties with temperature, surface cooling by other than Newtonian methods, and convection of mass within the solid might actually dominate the process. If this is the case, then, by eliminating them in the initial assumptions, the final solution is made inaccessible.

2. The problem of orientation-effects on the ignition process has not been adequately resolved. Further study should include the consideration of this effect. One means of doing this would be to run two independent series of tests, with the method of flux and temperature measurement exactly the same on each, in which identical specimens were tested in each of the two most commonly used orientations (described earlier in the paper). Any major differences in the results of such tests would indicate that the orientation of the sample does indeed exert a strong influence on the ignition process.

3. The three temperature ranges mentioned in an earlier chapter,

which seem to be a result of the method of temperature measurement used by the various authors, introduce the possibility that differences between optical and electrical methods of temperature measurement are significant. To further investigate this possibility, a sample on whose surface was attached several thermocouples could be heated while the surface temperature in the vicinity of each thermocouple was measured with a radiation pyrometer sensitive in a range which would eliminate the possibility of "seeing" any energy of the same wave-length as that produced by the heat source. This type of test should aid in the determination of the magnitude of the effect of temperature measurement, and perhaps account for part of the wide variation of reported ignition temperatures.

4. Mentioned only briefly by Smith (31), the possibility exists that reported flux levels have been measured by improperly calibrated instruments (this would also apply to methods of temperature measurement). Smith reported that of four calorimeters tested, there was a maximum variation of 22 per cent when measuring flux of 1 cal/cm^2-sec. Errors such as this could be magnified if the instruments of one author measured high and another's measured low. The low slope of the intensity versus time to ignition curves (Figures 1 through 4) illustrates that at moderate rates of heating (1 to 3 cal/cm^2-sec.), small changes in the value of the heating rate will produce large variation in the ignition time. If even a 15 per cent difference in the value of the heating rate was attributable to errors in measurement, it would appear as a large difference in the time required for ignition, and

perhaps lead to the making of invalid conclusions with regard to the ignition process. There does not appear to be any immediate solution to this problem. Its influence is potentially great and deserves future consideration.

In addition to the above, it is important to consider the following points upon which agreement was reached by most of the authors surveyed:

5. Ignition time at a given intensity level is shorter for targets subjected to a flame-type (convective) source than for those heated by a radiant source. Various explanations were offered as to the reason, but that which predominated claimed that the turbulence induced by the convective source was the deciding factor.

6. Ignition temperature, while not always constant, nevertheless lies within a predictable range. The range varied with the experimental method of approach and math model used.

7. Ignition time is shorter for tests in which the sample is heated in the presence of a pilot igniter than for those in which the sample is required to ignite spontaneously.

8. The addition of flame retardant salts to wood has the effect of lowering the activation energy, and lowering the temperature at which active pyrolysis begins. The pyrolysis process in general is accelerated so that the damage occurs at temperatures below that at which damage would occur in untreated wood. The amount of damage to the treated wood is much less, and seems to be related to the concentration of fire retardant present in the specimen.

9. The total energy required for ignition of a given sample is proportional to the sample size and thickness, and inversely proportional to the size area which is subjected to the thermal energy.

10. Of the total energy available to a test specimen, only a fraction of this total is used to actually raise the temperature of the specimen. This fraction increases as the specimen chars and begins to turn black.

11. The following three parameters exhibit behavior which supports the contention that they are mutually dependent: I, T_{ig}, and t_{ig}.

Finally, it is observed that no work was done on natural (green) fresh-cut wood or tree bark. Such a study would fill a void in the literature, and provide for further understanding of the ignition process.

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APPENDIX

THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric Analysis (TGA) is a process in which the sample is heated at constant temperature while its weight is recorded as a function of time. Such analysis makes possible the calculation of basic reaction-rate constants.

Assuming the reaction to be first order, the reaction rate constant is the slope of the plot of the log of the residual weight versus time. This can be written as: $K = -\ln (1-w/w_d)/t$ where w_d = the weight loss at the end of the pyrolysis at constant temperature and w = the weight loss at any time t.

The thermal stability or activation energy can be obtained by performing the TGA at each of a series of constant temperatures. The activation energy is a measure of the amount of energy required to activate the material to the state of reaction. By applying the arrhenius equation, the activation energy E has the following relationship to the reaction rate constant, K: $E = -RT \ln K + CT$, where R = gas constant, T = absolute temperature, and C = constant. E therefore can be computed from the slope of the logarithmic plot of the reaction rate constants for a given series of temperatures versus the reciprocal of the absolute temperature.

More detailed information on the application of TGA is available in reference number twelve of the related references section of the bibliography.

DIFFERENTIAL THERMAL ANALYSIS

Differential Thermal Analysis (DTA) involves the continuous measurement of the temperature difference between a small sample (usually 10 to 75 mg) and a thermally inert reference material, as a function of sample or reference material are heated at a pre-determined rate. Such analysis reveals the occurrence of endothermic and exothermic reactions at various levels of temperature, and gives a rough estimate of the amount of heat envolved or absorbed in the reaction. When a reaction occurs, changes in the heat content and in the thermal properties of the sample are indicated by a deflection or peak which shows on the graphic record. If the reaction proceeds at a rate varying with temperature (i.e., possesses an activation energy), the position of the peak varies with the heating rate, providing that other experimental conditions are maintained fixed.

Detailed information on the application of DTA is available in reference number twelve in the related references section of the bibliography.

A SURVEY OF LITERATURE ON THE PYROLYSIS OF WOOD AND OTHER CELLULOSIC SOLIDS

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ABSTRACT

The work reported in thirty-six articles on the ignition of wood is surveyed. The information contained in each article is reviewed with attention given to the following areas of interest: the method of analysis and general results of the work, the mathematical model used to correlate results obtained, and the conclusions drawn by each author regarding his findings.

The method used most often to study the ignition of wood is to heat a small (a 4-inch square sample is common) specimen of wood at a known rate while at the same time monitoring its temperature history. Results of such analysis indicate that the ignition process is most influenced by the rate of application and spectral quality of the incident thermal energy, the time of exposure, the surface temperature attained in the specimen, the size and density of the specimen, and the color of the exposed surface.

No common explanation as to the effect each of the above factors has upon the ignition process is found in the literature. It is found, however, that for a given rate of heating, the majority of the authors whose work is considered in this survey agree that a specimen will ignite most readily if its surface is black, if its exposed area is large in comparison to its thickness, if it is heated by a flame source, and if it is of low density and moisture content.

Concluding recommendations are made that point out the need to fill existing gaps in the study of the ignition process.

COMMITTEE APPROVAL: