

EXPERIMENTAL TEMPERATURE HISTORIES AND THERMAL
CONDUCTIVITIES FOR ALPHA-CELLULOSE
AND ALPHA-CELLULOSE CHAR

By

JACK BRADFORD HENDERSON

Bachelor of Science in Mechanical Engineering

University of Tulsa

Tulsa, Oklahoma


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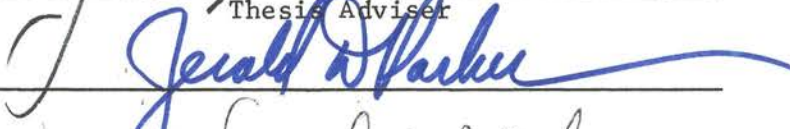
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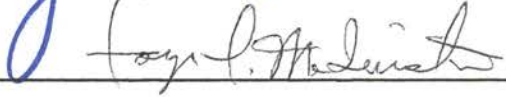
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Thesis Approved:



Thesis Adviser






Dean of the Graduate College

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PREFACE

This work represents an effort by Oklahoma State University to examine the pyrolysis phenomenon in porous materials. This work was supported by the United States Air Force Contract Number F08635-71-C-0199. I am extremely grateful for the support during this work.

I wish to express my gratitude to my thesis adviser, Dr. John Wiebelt, for his guidance and availability throughout this work. Also, I would like to thank Dr. J. D. Parker and Dr. F. C. McQuiston for serving on my graduate committee; Mrs. Barbara Moore for her excellent typing; Mr. Eldon Hardy for his fine work in drawing the figures; and my wife, Linda, for her encouragement throughout this work.

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CHAPTER I

INTRODUCTION

The objectives of this work were to experimentally determine the temperature profiles in a pyrolyzing cellulosic material when exposed to several different constant radiant heat fluxes and to compare the results with those predicted by the analytical work in Appendix A. The measurements of the thermal conductivity as a function of density of virgin alpha-cellulose and alpha-cellulose char were also undertaken in this work.

When a heat flux is applied to the surface of a porous solid such as wood, cellulose or fabric, the temperature rise in that organic solid will be dependent upon the rate of heat conduction into the material and the rate of surface heating. When the temperature of the material becomes high enough, the rate of temperature rise in the solid is governed, in part, by chemical reactions which begin to occur in the material. These chemical reactions, pyrolysis, not only affect the temperature rise in the material, but also distinctly change the thermal properties. These temperature profiles and thermal properties for porous materials become important in the evaluation of flame retardents, fire prevention systems and ignition times for any porous material which is exposed to high temperatures.

Because of the drastic changes occurring in the thermal properties during pyrolysis, the temperature profiles are extremely difficult to

predict. Since no consistent property data could be found in the literature for alpha-cellulose or alpha-cellulose char, it was decided that research should be undertaken to determine these properties, in addition to the temperature profile measurements.

This report is comprised of four major chapters and two appendices. Chapter I, the introduction, states the objectives and outlines the contents of the remaining report.

Chapter II deals with the previous experimental methods used to measure temperature profiles during pyrolysis and reviews the previous work done on thermal conductivity measurements. Also, the theory used in the experimental procedures employed, and an explanation of the thermal conductivity computer program is included.

Chapter III examines the experimental procedures used in both the temperature profile measurements and the thermal conductivity measurements. Chapter III also includes the preparation of the samples, types of equipment used in the experiments, and the results of the work.

The results and interpretations of the experimental data obtained in the temperature profile measurements and the conductivity measurements are contained in Chapter IV. This includes a discussion of error analysis for the conductivity measurements.

Appendix A is a section covering the analytical and computer techniques used to predict the temperature profiles during pyrolysis. Appendix A was written by Professor J. A. Wiebelt of Oklahoma State University, and is included in this report because the analysis was done in conjunction with the experimental work to obtain the temperature profiles.

Appendix B is a listing of the thermal conductivity program used in this work.

CHAPTER II

REVIEW OF PREVIOUS WORK AND THEORY

Review of Experimental Methods for Temperature Profile Measurements¹

Many methods have been devised to experimentally measure the temperature profiles and the heat of pyrolysis in a pyrolyzing material. These different methods are due, in part, to the availability of equipment and to the type of investigation being made. The purpose of this section is to review the specific methods used by researchers in the past.

Alpha-cellulose ($(C_6H_{10}O_5)_n$) and wood (no definite chemical formula has been obtained), are the most common porous materials used in this type of experimental work because of their availability. Also their thermal properties are better known, although much disagreement can be found in the literature.

The two most commonly used geometries are rectangular slabs and cylindrical samples. The heat flux for the cylindrical sample is usually furnished by a resistance wire heater, which is usually platinum or nickel-chromium wire, that runs axially inside the cylinder. This method is particularly attractive because of the well defined boundary conditions associated with it. Brown (1) used the resistance wire

¹The reader is referred to Appendix A for the development of the analytical and computer techniques used to predict the temperature profiles in alpha-cellulose.

heater technique to obtain the thermal conductivity, thermal diffusivity and the temperature profiles in cylindrical samples of white pine and oak wood. Brown performed all experimental work in a nitrogen atmosphere to prevent ignition of the sample. He also was able to accurately predict experimental values obtained by Havens (2) in earlier work (see Figure 1). Brown's mathematical model predicted Haven's temperature profiles to within 15% in the worst case. The following references also report experimental work done with cylindrical geometries: Blackshear and Murty (3) and Akita (4).

Rectangular geometries are also used extensively in experimental work. Several methods have been devised to irradiate the surface of the rectangular samples, the most common of which is a tungsten filament lamp. Martin (5) used sheets of alpha-cellulose, which were bonded together using a methyl-cellulose solution. Martin used a modified Mitchell thermal source, which gave irradiance levels up to 22 $\text{cal/cm}^2 \text{ sec.}$, to obtain the temperature profile, surface temperatures and the rate of production of volatile pyrolysis products. The temperature profiles of one of Martin's tests is shown in Figure 2, which is for a cellulose sheet containing 2.0% carbon black, with an irradiance level of 6.0 $\text{cal/cm}^2 \text{ sec.}$ Martin's method is particularly attractive because of the wide range of irradiances which can be applied to the sample; however, the boundary conditions are not as well defined as with cylindrical samples. The following references also report work done on sheets of paper, alpha-cellulose or cloth: Lincoln (6), Lipska (7), and Schaffer (8).

There has also been work done with geometries and materials other than those previously mentioned. The following papers report work done

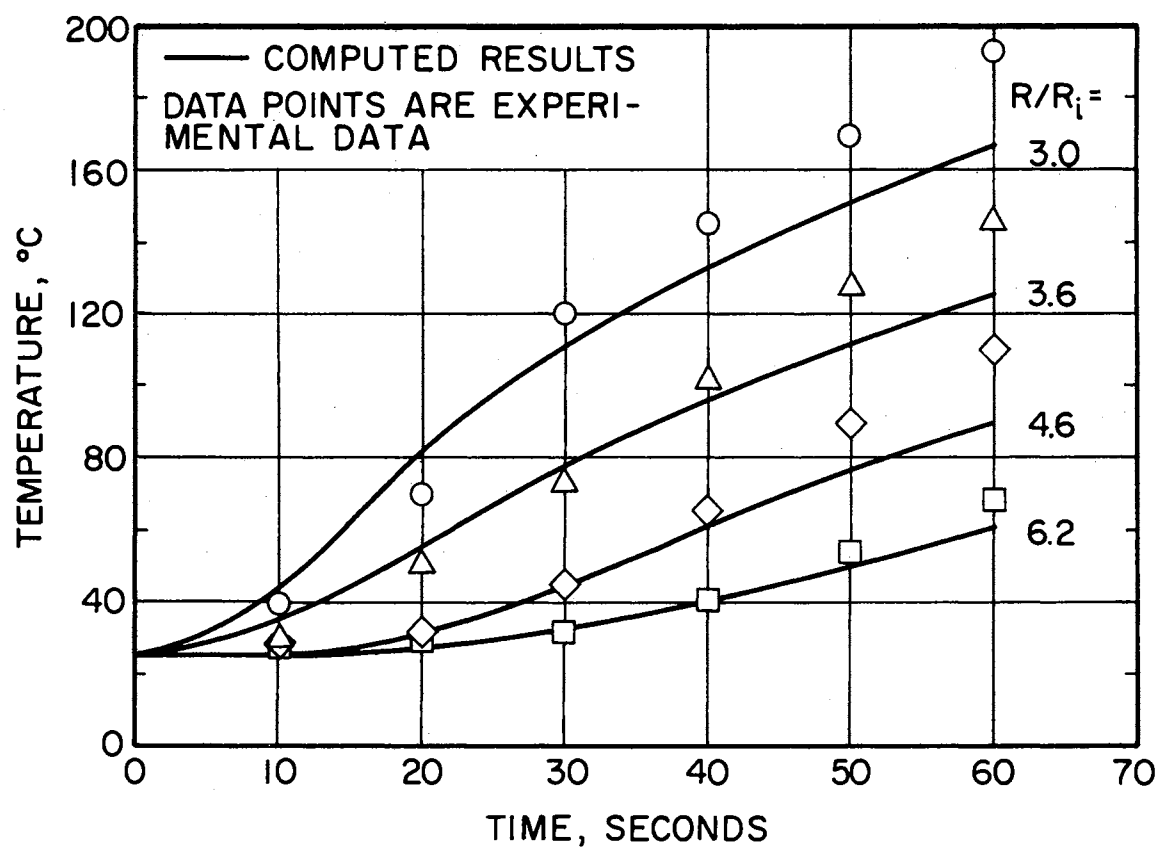


Figure 1. Comparison of Havens Experimental and Browns Computed Temperature Profiles for White Pine Cylinders (1)

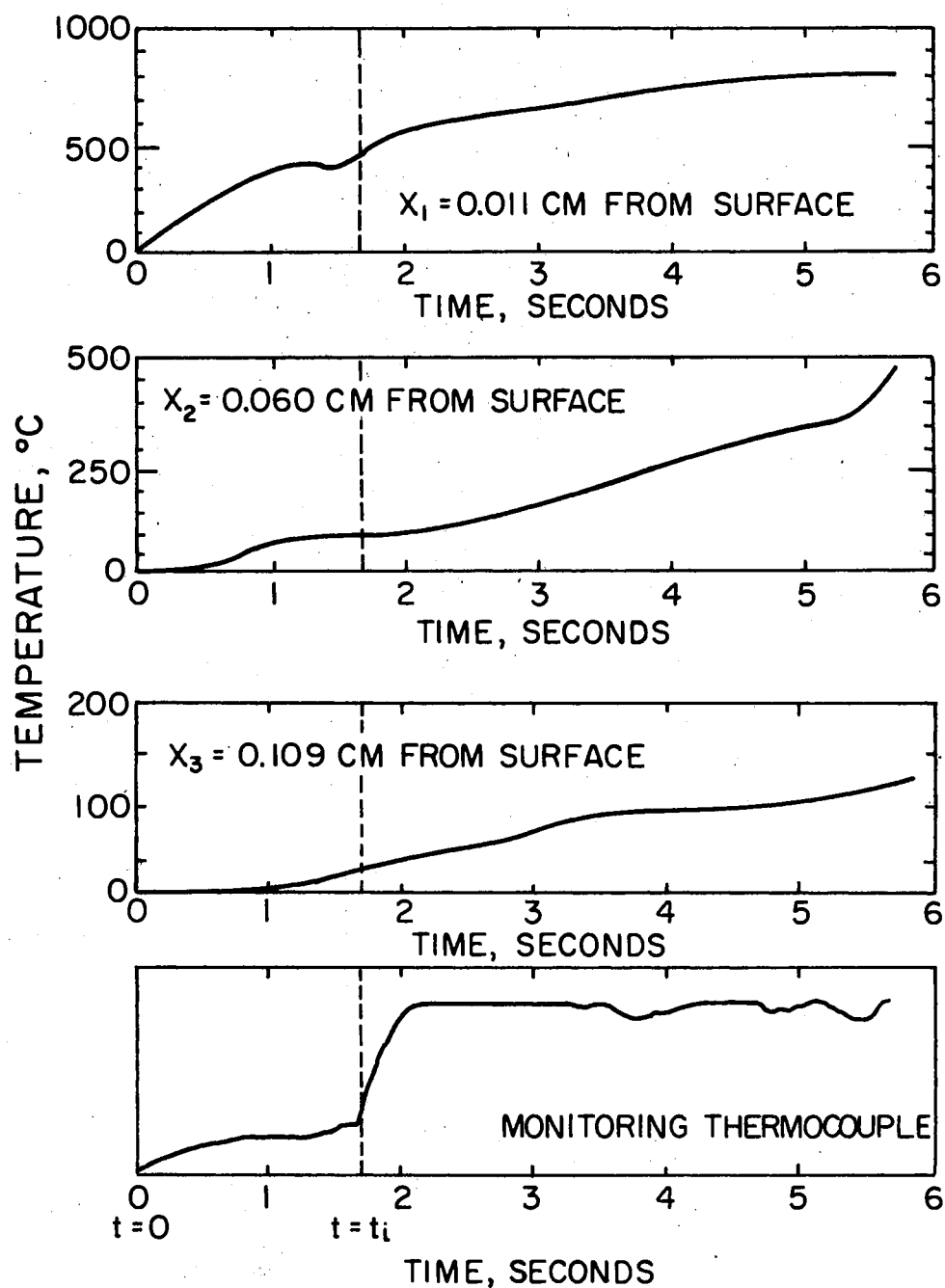


Figure 2. Temperature Profiles at Various Depths From Surface for Alpha-Cellulose Sheets (6)

on wood-sawdust, either in pressed or loose form: Bowes (9), Browne (10).

In addition to the previously mentioned heating sources, there are others worthy of discussion. Ulrich (11) used 144 solar mirrors, 2 inches square, to provide the heat flux to 3.0 inch square white pine samples. Another unique method was reported by Murty (12). Murty's test specimens were cylindrical, and were heated by being inserted into a hollow copper cylinder twice the size of the sample. The copper cylinder was then heated from the underneath side by a flat-flame bunsen burner. By using this method, the sample was heated only by the radiation from the copper cylinder. Perhaps the most unique, for its extremely high heating rate, is a method reported by Lincoln (6). Lincoln used a helical xenon flash tube which yielded, in 30 millisecond pulses, intensities up to $3000 \text{ cal/cm}^2 \text{ sec}$.

Background and Review of Experimental Methods to Measure Thermal Conductivity

One of the greatest problems associated with the prediction of the temperature profiles in any material in which pyrolysis is occurring is the large changes in the thermal properties. Densities can range from 0.67 gm/cm^3 for virgin alpha-cellulose to 0.0938 gm/cm^3 for alpha-cellulose char. The thermal conductivities will vary from $0.000201 \text{ cal/cm-sec-}^\circ\text{C}$ for a density of 0.07 gm/cm^3 to $0.00002814 \text{ cal/cm-sec-}^\circ\text{C}$ for a density of 0.0938 gm/cm^3 . It should be pointed out that these property values were taken from the literature and are, at best, only approximate. The values of thermal conductivity, thermal diffusivity, density and specific heat were found to be inconsistent in the literature. This, coupled with the fact that these properties must be reasonably

accurate in order to predict temperature rises during pyrolysis, indicates the need for additional research to obtain consistent thermal data for alpha-cellulose. The property values listed above and the values listed in Appendix A are for alpha-cellulose. These values were taken from references 4, 5, and 13.

In the past, several methods have been used to measure the thermal conductivity of porous materials such as wood, alpha-cellulose and fibers. A discussion of these methods and results follow.

Maclean (14) studied the effect of density, moisture content, compression, and direction of heat flow on the thermal conductivity of 32 types of wood. Experiments were made using the guarded hot plate method with a mean sample temperature of 30°C with temperature drops for 22° to 28° across the sample. Maclean was able to describe the variation of thermal conductivity as a function of density in moisture-free wood by the linear relationship:

$$k = 0.00478 \times \rho + 0.0000568 \quad (2.1)$$

where

k = thermal conductivity (cal/cm²-sec-°C/cm)

ρ = wood density (gm/cm³)

As shown in Equation (2.1), the thermal conductivity approaches the conductivity of air at zero density. Maclean compared experimental values of conductivity for 18 wood species in 84 tests to those values predicted by Equation (2.1). He found an average absolute deviation of 2.9 percent with a maximum error of only 8.4 percent.

Griffith and Kaye (15) also studied the effect of wood structure, direction of heat flow, and moisture content on the thermal conductivity

of eight different woods by using the guarded hot plate method. In addition, Wangaard (16, 17) used the guarded hot plate method to study the thermal conductivity of 40 types of wood.

The guarded hot plate method for determining thermal conductivities is probably the most accurate and accepted method used. However, it suffers the drawback of taking long periods of time (8 to 24 hours) to complete a test. It is a rather expensive method, and it is difficult to prepare the samples because of the uniformity required.

The thermal conductivity of wood at temperatures up to the threshold of pyrolysis were obtained by Kanury (18), Koohyar (19), and Havens (2). All of these investigators used a transient technique proposed by Chung and Jackson (20) for materials with a low conductivity. This technique assumes that the thermal diffusivity is independent of temperature, even though the thermal conductivity, specific heat and density are strong functions of temperature. This is shown in Equation (2.2):

$$k = \alpha \rho C \quad (2.2)$$

where

α = thermal diffusivity (cm^2/sec)

C = heat capacity ($\text{cal/gm-}^\circ\text{C}$)

Thus by Equation (2.2), if the density and specific heat are known as a function of temperature, the thermal conductivity may be calculated.

Both Koohyar and Havens immersed cylindrical pine samples in hot liquid baths and monitored the temperatures at different internal radial positions. The dependence of thermal conductivity on temperature from the work of Haven's (2) is shown in Table I.

Kanury (18) obtained the thermal conductivity of alpha-cellulose by

inserting cylindrical samples into a heated copper tube, which is shown in Figure 3. Kanury formed cellulose cylinders by pressing wet alpha-cellulose into molds and then drying.

TABLE I
TEMPERATURE DEPENDENCE FOR THE THERMAL
CONDUCTIVITY OF WHITE PINE (2)

| Temperature °C | Thermal Conductivity cal/cm-sec-°C |
|-------------------|---------------------------------------|
| 30 | 0.0023 |
| 40 | 0.000253 |
| 200 | 0.000273 |
| 240* | 0.00032 |

*Data extrapolated to 240°C assuming thermal diffusivity to be independent of temperature.

Although no data are available in the literature for wood char or partially pyrolyzed wood, Havens (2) proposed that the thermal conductivity of wood char can be obtained by modifying Maclean's correlation of wood thermal conductivity, given by Equation (2.1), to account for the density change during pyrolysis. Haven's correlation is given by Equation (2.3).

$$k = 0.00478 \times \rho \times f + 0.0000568 \quad (2.3)$$

where

f = fraction of wood pyrolyzed.

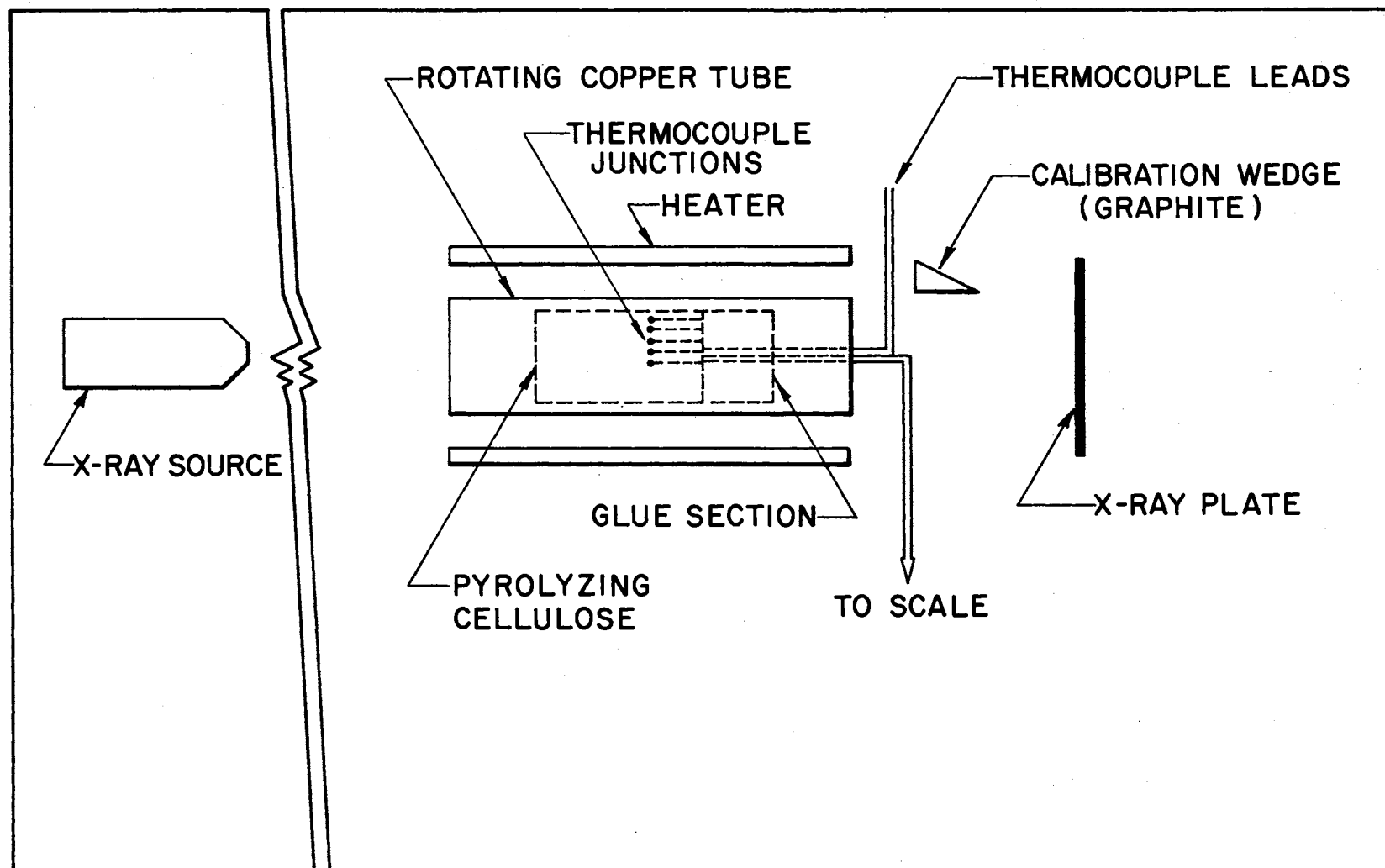


Figure 3. Experimental Apparatus Used by Kanury (18)

A review of the material revealed that for low-density samples, such as wood, fibers, cellulose, and other materials with similar densities, the thermal conductivity does not vary greatly with the type of solid material, but depends more directly on the density. This observation suggests that the change in the composition of wood during its thermal decomposition should not strongly affect its thermal conductivity, except in relation to its density (excluding temperature effects). Thus, Equation (2.3) should be a valid expression for the change in thermal conductivity.

Using the values of f that Havens obtained from experimental work, he was able to graph the thermal conductivity as a function of temperature for wood and wood char. This correlation is shown in Figure 4. Havens assumed that the thermal conductivity was constant as a function of temperature until pyrolysis began to occur. After pyrolysis was completed, the conductivity was again assumed to be constant with temperature. The value of $0.000112 \text{ cal/cm-sec-}^{\circ}\text{C}$ predicted for the char region is in complete agreement with the value of $0.000114 \text{ cal/cm-sec-}^{\circ}\text{C}$ obtained by extrapolation of data taken from the Handbook of Chemistry and Physics (45th edition) as shown in Figure 5.

Nix, Vachon, Lowery and McCurry (21, 22) used the line heat source method to obtain the thermal conductivity of RTV-60 silicone rubber. These results are presented in Table II. The values of the thermal conductivities were compared to the values obtained by the guarded hot plate method with good agreement. The line heat source method used by Nix, Vachon, Lowery and McCurry has the advantage that the thermal conductivity may be obtained with no prior knowledge of the density of the sample and can be extended to obtain the thermal diffusivity.

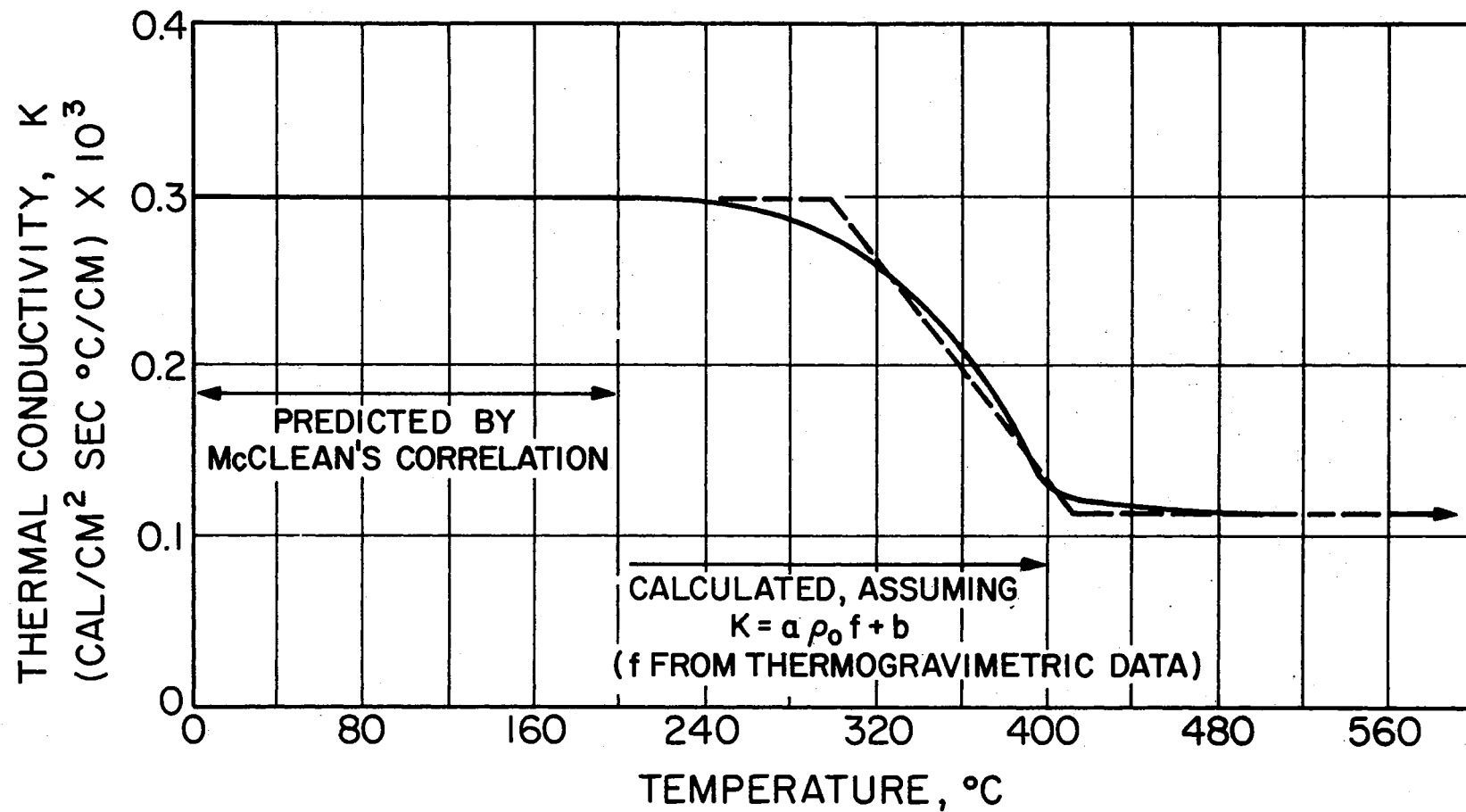


Figure 4. Estimated Thermal Conductivity of Wood as a Function of Temperature and Decomposition History (2)

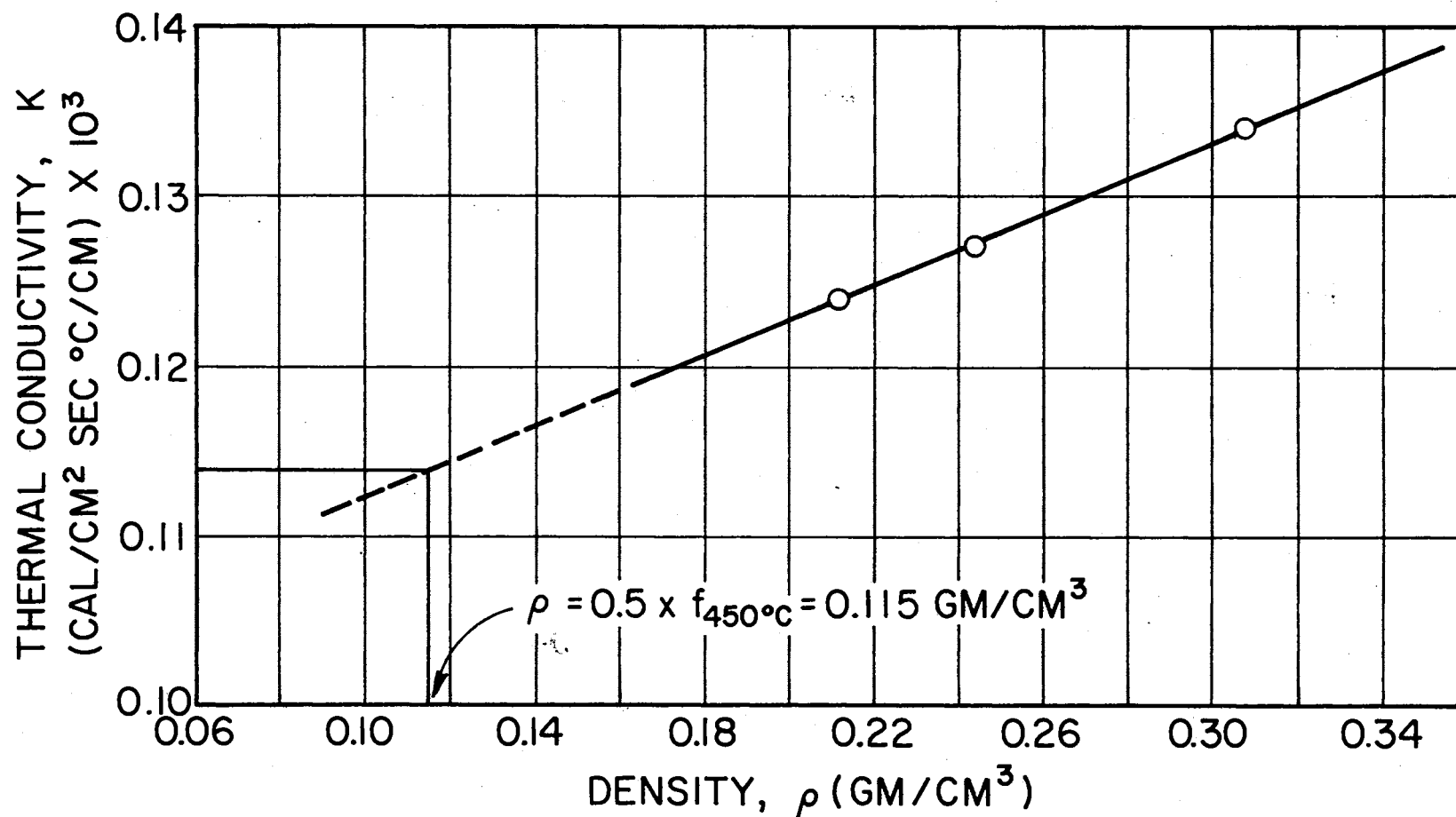


Figure 5. Thermal Conductivity vs Density for Charcoal (From Handbook of Chemistry and Physics, 45th Edition) (2)

TABLE II

SUMMARY OF THERMAL CONDUCTIVITY TESTS FOR SILICONE RUBBER (21)

| Sample Number | Test Number | Density kg/m^3 | Initial Temperature, $^{\circ}\text{K}$ | Temperature Rise, $^{\circ}\text{K}$ | Heat Input W/m | k $\text{J/ms}^{\circ}\text{K}$ | \bar{k} $\text{J/ms}^{\circ}\text{K}$ | Per Cent Diff. From Average |
|---------------|-------------|-------------------------|---|--------------------------------------|-------------------------|-----------------------------------|---|-----------------------------|
| 1 | 1 | 1515.4 | 302.9 | 4.9 | 3.51 | .375 | .375 | 0.00 |
| | 2 | | 304.1 | 0.4 | 1.07 | .371 | | -1.06 |
| | 3 | | 304.5 | 0.4 | 0.69 | .379 | | +1.06 |
| | 4 | | 305.3 | 1.0 | 1.52 | .371 | | -1.06 |
| | 5 | | 308.5 | 1.5 | 2.23 | .381 | | +1.60 |
| 2 | 6 | 1457.8 | 303.1 | 1.9 | 1.50 | .376 | .362 | +3.86 |
| | 7 | | 303.9 | 4.9 | 3.52 | .353 | | -2.48 |
| | 8 | | 305.3 | 1.6 | 1.39 | .356 | | -1.65 |
| | 9 | | 306.7 | 1.6 | 2.10 | .366 | | +1.10 |
| | 10 | | 308.4 | 2.8 | 2.10 | .363 | | +0.27 |
| 3 | 11 | 1485.0 | 300.6 | 2.5 | 2.66 | .351 | .352 | -0.28 |
| | 12 | | 301.6 | 1.4 | 1.65 | .353 | | +0.28 |
| | 13 | | 302.5 | 2.9 | 2.66 | .353 | | +0.28 |
| | 14 | | 302.8 | 3.4 | 3.54 | .342 | | -2.84 |
| | 15 | | 302.9 | 2.3 | 2.66 | .364 | | +3.40 |
| 4 | 16 | 1461.0 | 298.5 | 2.5 | 5.10 | .371 | .360 | +3.05 |
| | 17 | | 299.1 | 1.3 | 2.66 | .373 | | +3.61 |
| | 18 | | 300.4 | 1.3 | 2.66 | .353 | | -1.94 |
| | 19 | | 301.3 | 0.8 | 1.65 | .353 | | -1.94 |
| | 20 | | 301.6 | 1.2 | 2.66 | .354 | | -1.66 |

Underwood and McTaggart (23) also used the line heat source method to measure the conductivity of polystyrene and polyethylene over a wide range of temperatures. Upon completing the experimental work, a test specimen was sent to a commercial testing laboratory where the tests were run using the guarded hot plate method. As in the comparison tests in reference (21, 22), close agreement was obtained between the two methods.

The line source method was chosen for this work because of the advantages over the guarded hot plate method and the constant thermal diffusivity method. The line source technique is attractive because of the simple test apparatus, short testing time, small sample size, and accuracy. Also, the conductivity and diffusivity may be determined simultaneously.

Development of the Line Source Technique

The temperature rise at some point in a solid with a suddenly initiated constant heat rate from a line heat source is a function of time, thermal properties, position, and line heat source strength. Carslaw and Jaeger (24) give the equation for the temperature in an infinite solid for region around a line heat source at some time greater than zero as:

$$V = \frac{q}{4\pi\alpha} \int_0^t \phi(t') e^{-r^2/4\alpha(t-t')} \frac{dt'}{(t-t')} \quad (2.4)$$

where α = thermal diffusivity

$$r^2 = (x-x')^2 + (y-y')^2$$

Now if $\phi(t) = \text{constant} = q$

$$V = \frac{q}{2\pi\alpha} \int_{r^2/4\alpha t}^{\infty} (e^{-u^2}/u) du \quad (2.5)$$

where $u^2 = r^2/4\alpha(t-t')$

Now by integrating Equation (2.5):

$$V = \frac{q}{2\pi\alpha} \text{Log} \left(\frac{4\alpha t}{r^2} \right) - \frac{\gamma q}{4\pi\alpha} + \text{Higher order terms} \quad (2.6)$$

where $\gamma = \text{Euler's constant} = 0.5772$

$$\text{Higher order terms} = C \left(\frac{u^2}{2} - \frac{u^4}{8} + \dots \right); C = \text{constant}$$

If Equation (2.6) is written for some differential temperature and the higher order terms are dropped, Equation (2.7) results. The condition $0 < u < 0.16$ must be satisfied to drop the higher order terms with no significant error.

$$T_2 - T_1 = \frac{q}{2\pi\alpha} \ln(t_2/t_1) \quad (2.7)$$

where $t = \text{time}$
 $T = \text{temperature}$
 $q = q'/\rho c$; $c = \text{specific heat}$

If $q = q'/\rho c$ is substituted into Equation (2.7), Equation (2.8) results.

$$T_2 - T_1 = \frac{q'}{2\pi k} \ln(t_2/t_1) \quad (2.8)$$

where $k = \text{thermal conductivity.}$

Hence, if the rate of heat input, the temperatures at t_1 and t_2 are known, the thermal conductivity can be calculated from Equation (2.8). The only restrictions governing (2.8) are $0 < u < 0.16$ must be satisfied and L/D ratio must be greater than 4 to assure radial heat flow only.

As shown in Equation (2.7), the dependence of r has been eliminated from the equation. This implies that any value of r is valid if the restriction on u is satisfied. However, Equation (2.8) as it stands will yield discrepancies between theory and experiment. Those differences are due to the fact that the hypothetical line heat source is infinitely small which in reality is a wire of finite dimensions in a finite sample. These discrepancies have been compensated for by Underwood and McTaggart (23) by adding a time correction term, (t_o) to Equation (2.8). Underwood and McTaggart demonstrated that the finite diameter of the heater wire, contact resistance and the difference in thermal properties between the source and sample could be considered in causing a constant error in the observation of time. With the time correction term added to (2.8), Equation (2.9) results. With this addition, Equation (2.9) may now be used to calculate the conductivity of a finite sample.

$$T_2 - T_1 = \frac{q'}{2\pi K} \ln \left(\frac{t_2 - t_o}{t_1 - t_o} \right) \quad (2.9)$$

where t_o = time correction factor.

The time correction term can be calculated if the data from the thermocouple close to the line source is plotted versus the natural log of time. If the line described by Equation (2.8) were plotted, it would yield a straight line. However, since the discrepancies arise that were described earlier, the line should be straight with a slight curvature at some small value of time. By using the graph, different values of the time correction term may be tried until the temperature versus the natural log of time is represented by a straight line. The same operation may be carried out on a digital computer.

The line heat source method is particularly attractive because it can

be modified to calculate the thermal diffusivity by placing a second thermocouple at some known distance from the line heat source. This method will be discussed further in Chapter III, and a schematic of the experimental apparatus will be shown.

Computer Program for the Line Source Method

A fortran computer program was written by reference (21, 22) to calculate the thermal conductivity. The method utilized the least squares fit in conjunction with the Newton-Raphson method to choose new values of the time correction term, t_0 .

The method used in the program takes the output data from the monitoring thermocouple (millivolts versus time), and assumes the data can be expressed in terms of an equation of the form of (2.10).

$$y = a + bx + cx^2 \quad (2.10)$$

By the standard least squares method, the summation to be minimized is Equation (2.11).

$$\sum_{i=1}^m (a + bx_i + cx_i^2)^2 \xrightarrow{\text{Minimum}} \quad (2.11)$$

Differentiating partially with respect to a , b , and c , results in three linear simultaneous Equations (2.12), (2.13), (2.14).

$$ma + b\sum x_i + c\sum x_i^2 = \sum y_i \quad (2.12)$$

$$a\sum x_i + b\sum x_i^2 + c\sum x_i^3 = \sum x_i y_i \quad (2.13)$$

$$a\sum x_i^2 + b\sum x_i^3 + c\sum x_i^4 = \sum x_i^2 y_i \quad (2.14)$$

The program utilized Cramer's rule to solve Equations (2.12), (2.13), and (2.14), and seeks to minimize the coefficient c by changing the time correction term after each iteration. By forcing the coefficient c to a minimum, the program forces Equation (2.10) to approach a linear equation.

After each iteration, a new t_o is selected by using the Newton-Raphson method. After a minimum value of c is obtained, the program takes the slope of the line and calculates k from Equation (2.9) which when solved for the thermal conductivity becomes:

$$k = qV/4\pi S \quad (2.15)$$

where

q = heat input

V = thermocouple constant

S = slope

A listing of the computer program is shown in Appendix B.

CHAPTER III

EXPERIMENTAL PROCEDURES AND RESULTS

Temperature Profile Measurements

The experimental work was undertaken in order to verify the temperature profiles predicted by the mathematical models described in Appendix A. Three sets of data were obtained for the temperature profiles, each for a different heat flux.

Preparation of Samples

The samples were prepared from 8.5 inches by 8.5 inches by 0.057 inches sheets of alpha-cellulose obtained from the National Bureau of Standards. The sheets were then cut into 3.0 inches by 3.0 inches squares and the thickness of each individual sheet was measured and then averaged to obtain a mean density of each set of three sheets.

The thermocouple wire used in all samples was 30 gage iron-constantan. The thermocouple wire was stripped of its insulation to allow the samples to be pressed together as closely as possible. The thermocouple junctions were welded with a Dynatech model 116 thermocouple welder.

The thermocouple wire junctions were placed in the center on both sides of one of the 3 inch by 3 inch sheets of alpha-cellulose. The two remaining sheets were then pressed on either side of the middle sheet. The alpha-cellulose sheets were bonded together by using a

methyl-cellulose and water solution for adhesive (5). The sample was then placed in a press for a period of 24 hours. After a short period of time, the water evaporated from the methyl-cellulose solution, leaving a reasonably homogenous sample, with no significant changes in the thermal properties between the alpha-cellulose and the methyl-cellulose. Both faces of the sample were then blackened with Sargent-Welch graphite powder, to allow most of the incident radiation to be absorbed. Figure 6 shows a completed sample, before the graphite powder has been applied.

Heat Flux Apparatus and Equipment

The radiant heat flux apparatus was constructed using two Thermofax, 1000 watt, tungsten filament lamps for the heating source. The tungsten filament lamps were enclosed in 4.0 inch by 5.0 inch, 24 gage, 304 stainless steel hoods. The hoods were mounted on a track, to allow the hoods to be set at a distance from 0.0 inch to 7.0 inches from the surface of the sample. The hoods were constructed to obtain a heat flux of $0.5 \text{ cal/cm}^2\text{-sec.}$, at a distance of 4.0 inches from the surface of the sample, with a variance of 5.0% in the heat flux over the surface of a 3.0 inch by 3.0 inch sample. Depending on the distance the hoods were set from the sample a radiant heat flux of 0.0 to $0.8 \text{ cal/cm}^2\text{-sec}$ could be applied to each face of the sample. The incident radiation was also controlled by a variac. The radiant heat flux apparatus is shown in Figure 7.

The thermocouple outputs were recorded on a Sanborn 320 dual channel D.C. amplifier-recorder and a Clevite Brush Mark 220 dual channel recorder. In all experimental work the thermocouple junctions

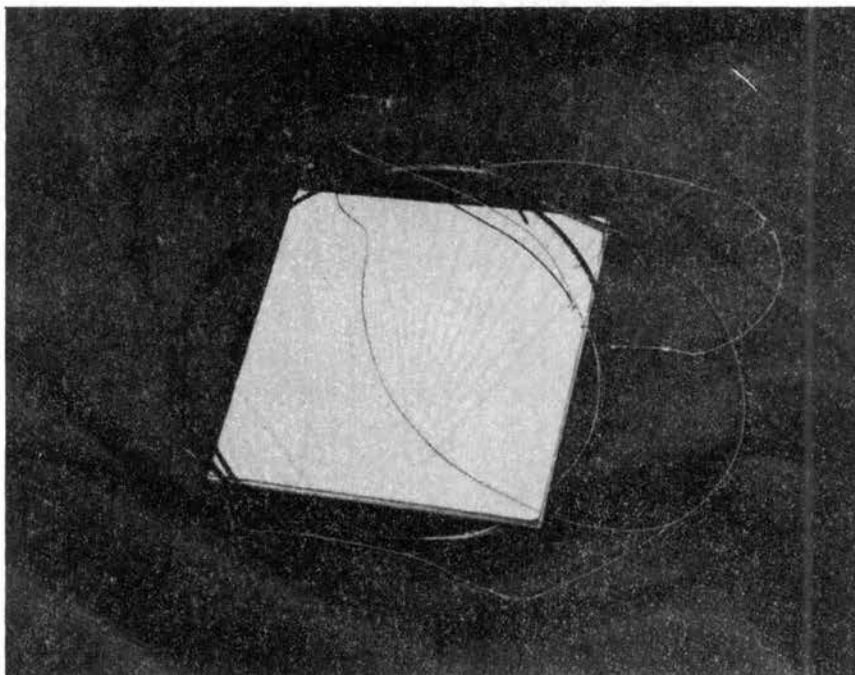


Figure 6. Completed Alpha-Cellulose Sample,
Without Graphite Powder

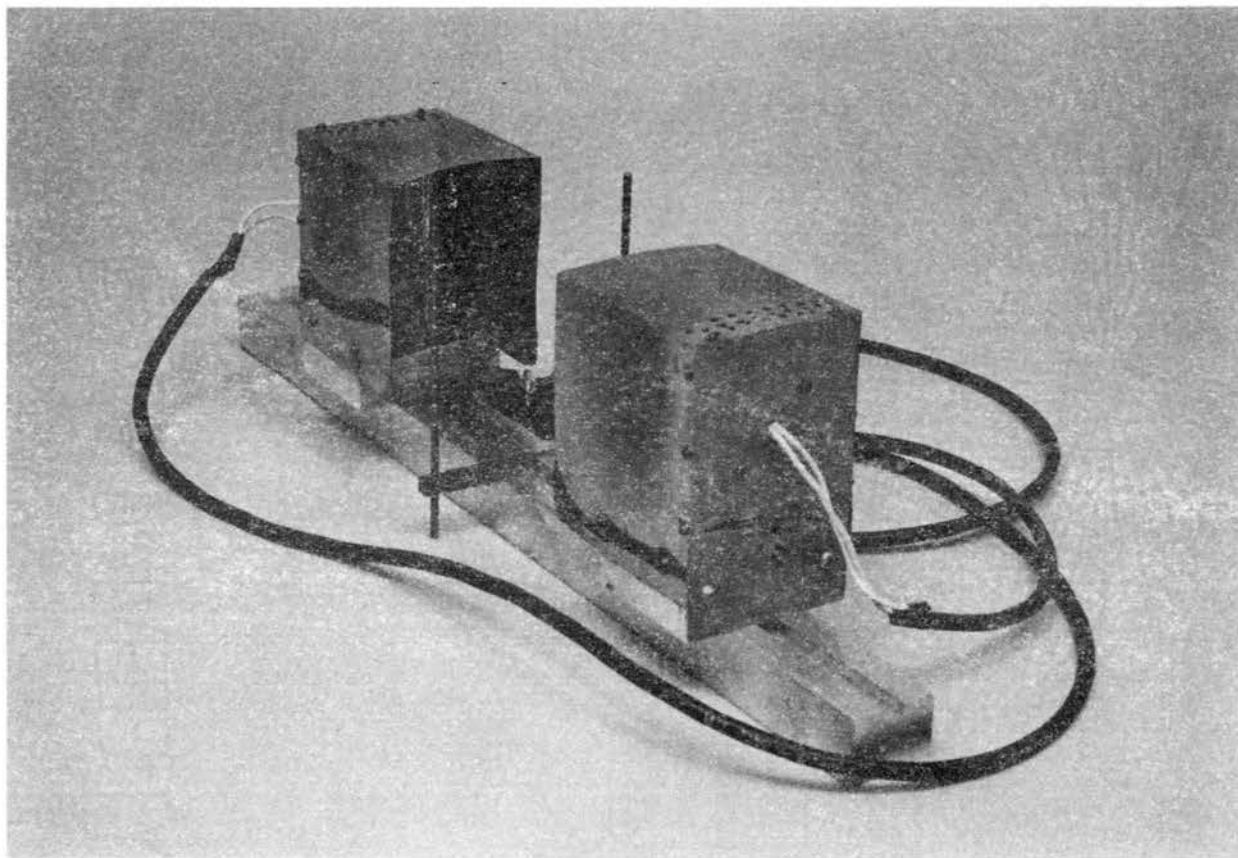


Figure 7. Radiant Heat Flux Apparatus

were referenced to an ice water bath.

The radiant heat flux was measured by a Hy-cal model P-1400-B-10-000-072 pyroheliometer, which is calibrated in solar constants.

$$1.0 \text{ solar constant} = 0.123 \text{ BTU/ft.}^2\text{-sec.}$$

The pyroheliometer calibration curve is shown in Figure 8.

Results

The accuracy of the data obtained is good to about 380°C , at which time separation in the sample begins to occur. The separation was caused by the decomposition of methyl-cellulose at high temperatures. Approximately 40 seconds after separation began to occur, ignition occurred in the sample. Since all experimental work was done in an air atmosphere, ignition occurred in each test. Figure 9 shows a picture of one of the alpha-cellulose samples after pyrolysis has occurred.

Figure 10 shows the temperature, in degrees Centigrade, as a function of time (sec) for 5 test runs, with a heat flux between $0.398 \text{ cal/cm}^2\text{-sec}$ and $0.447 \text{ cal/cm}^2\text{-sec}$. The thermocouple depth in each test was 0.1448 cm from the surface of the sample. Curves for Tests I, II and III were obtained for heat fluxes of about $0.32 \text{ cal/cm}^2\text{-sec}$.

Tests I, II and III were run with the same heat flux in order to establish the validity of the experimental technique. Because each of the first three tests yielded, almost identically, the same curve, it was assumed the experimental procedure used was accurate.

Test IV was conducted with a higher heating rate of $0.41 \text{ cal/cm}^2\text{-sec}$. Test V was run for a heat flux of $0.447 \text{ cal/cm}^2\text{-sec}$.

The experimental values of Tests I, II, III and V are discussed and

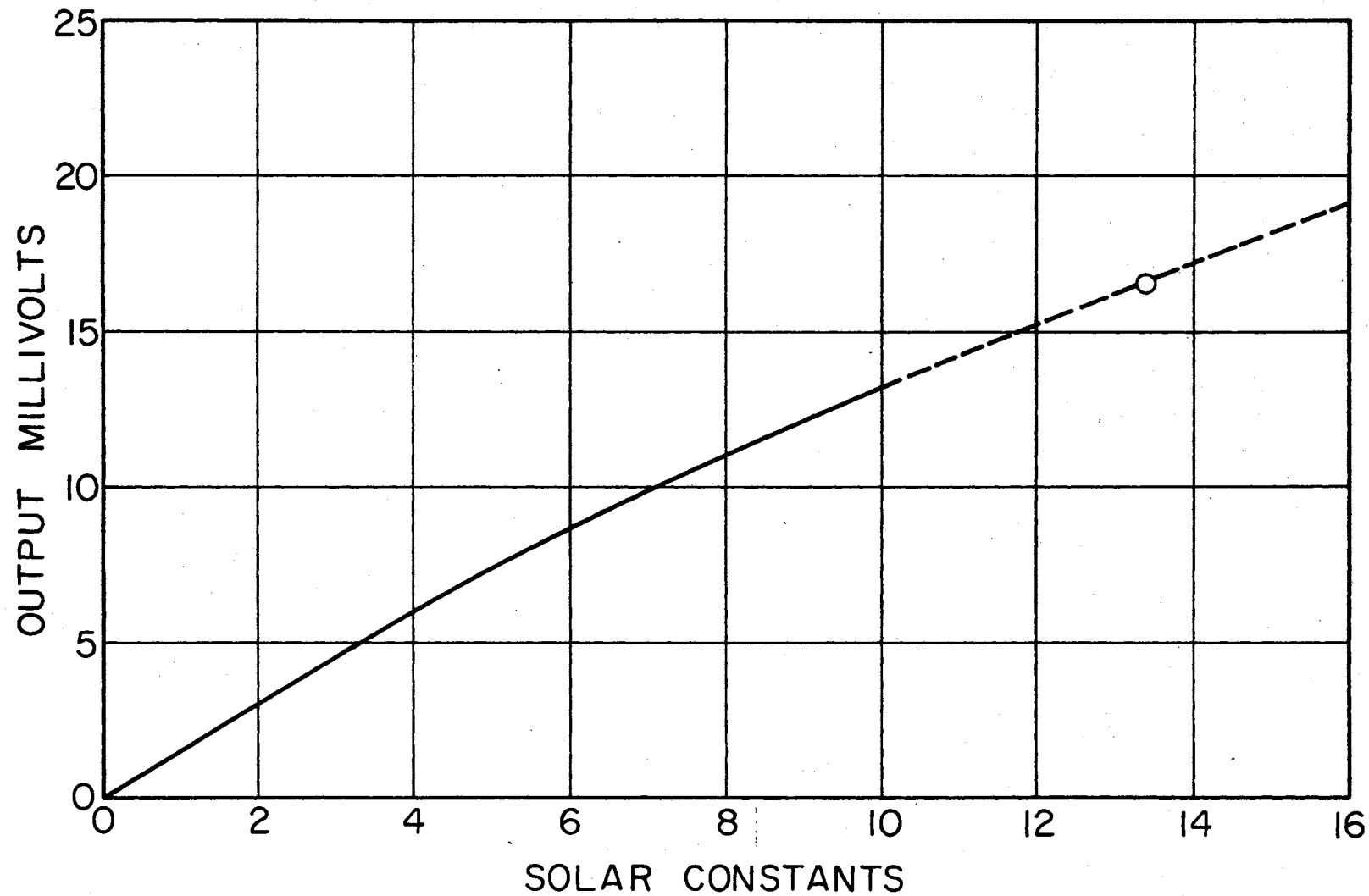


Figure 8. Calibration Curve for Hy-Gal Pyroheliometer

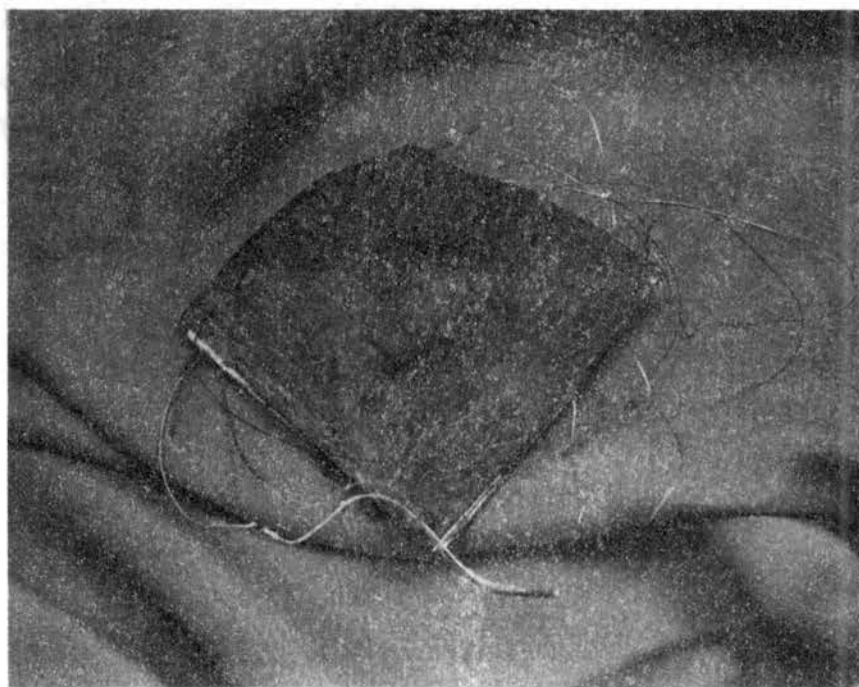


Figure 9. Charred Sample of Alpha-Cellulose
After Pyrolysis

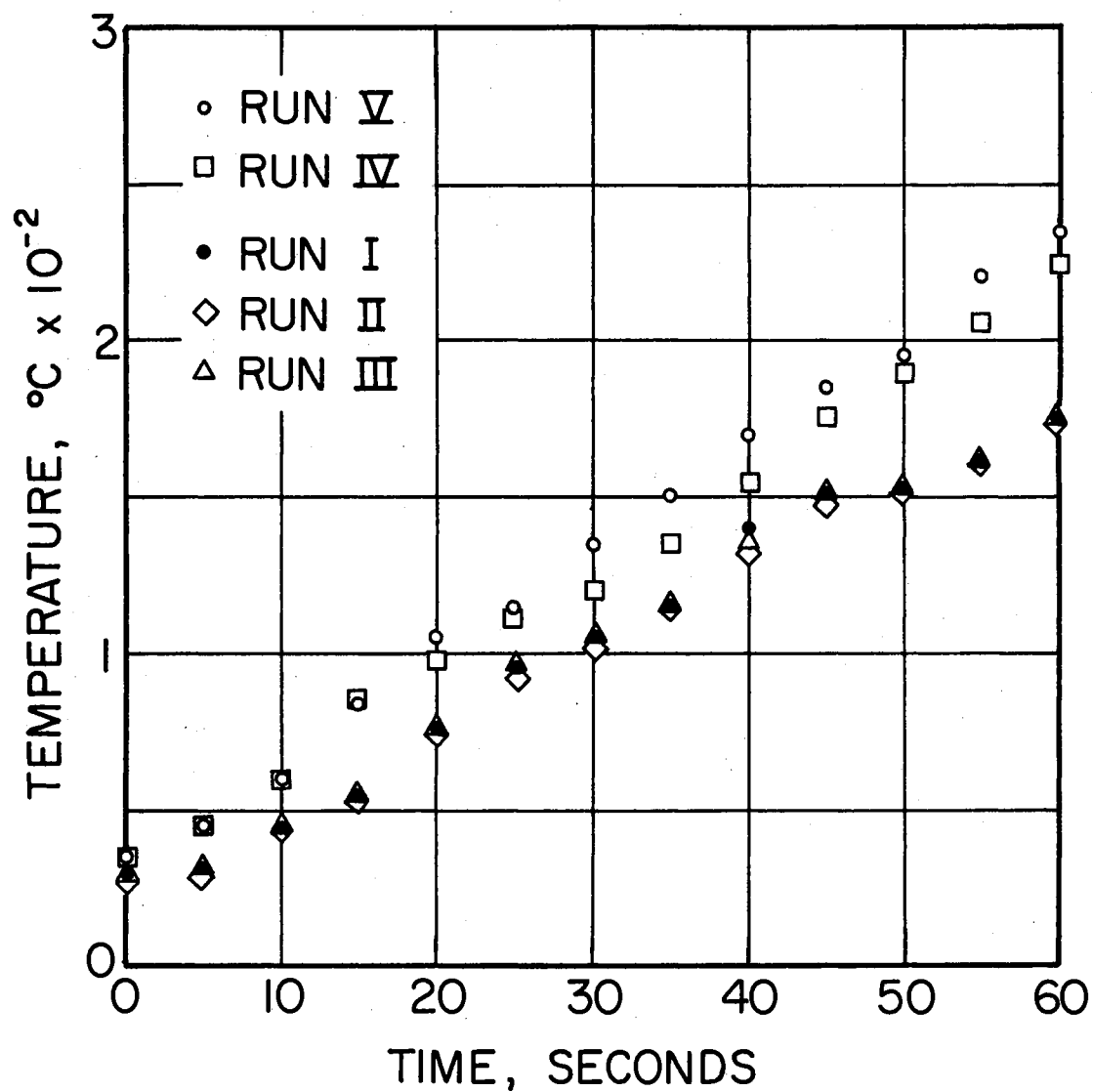


Figure 10. Temperature Profiles in 3.0 Inch by 3.0 Inch Samples of Alpha-Cellulose for Different Heat Fluxes

compared to the predicted values in Appendix A of this report.

Thermal Conductivity Measurements

The experimental work was initiated in order to obtain temperature-time data for input into the thermal conductivity program in Appendix B. Four sets of data was obtained for the virgin alpha-cellulose and three sets of data were obtained for alpha-cellulose char. Each set of data was taken using a different density.

Preparation of Samples

The virgin alpha-cellulose samples were prepared from alpha-cellulose powder obtained from Sigma Chemical Company. A cylindrical aluminum mold 8.66 inches in length and 1.905 inches inside diameter was used to form the cellulose powder.¹ Thirty gage chromel-alumel thermocouple wire was run axially through the mold along with thirty gage constantan heater wire. After the wires were inserted into the mold, the alpha-cellulose powder was packed inside the mold with different densities for each run. A schematic of the resistance wire heater and thermocouple wire in the cellulose cylinder is shown in Figure 11.

Constantan was chosen for the heater wire because the resistance of the wire is a very weak function of temperature within the ranges which the experimental work was carried out (70°F to 120°F). The near constant resistance of the constantan wire allowed a near constant heat flux to be applied to the inside of the sample. The resistance of

¹The dimensions of the mold were not critical so long as the length to diameter ratio was greater than or equal to four.

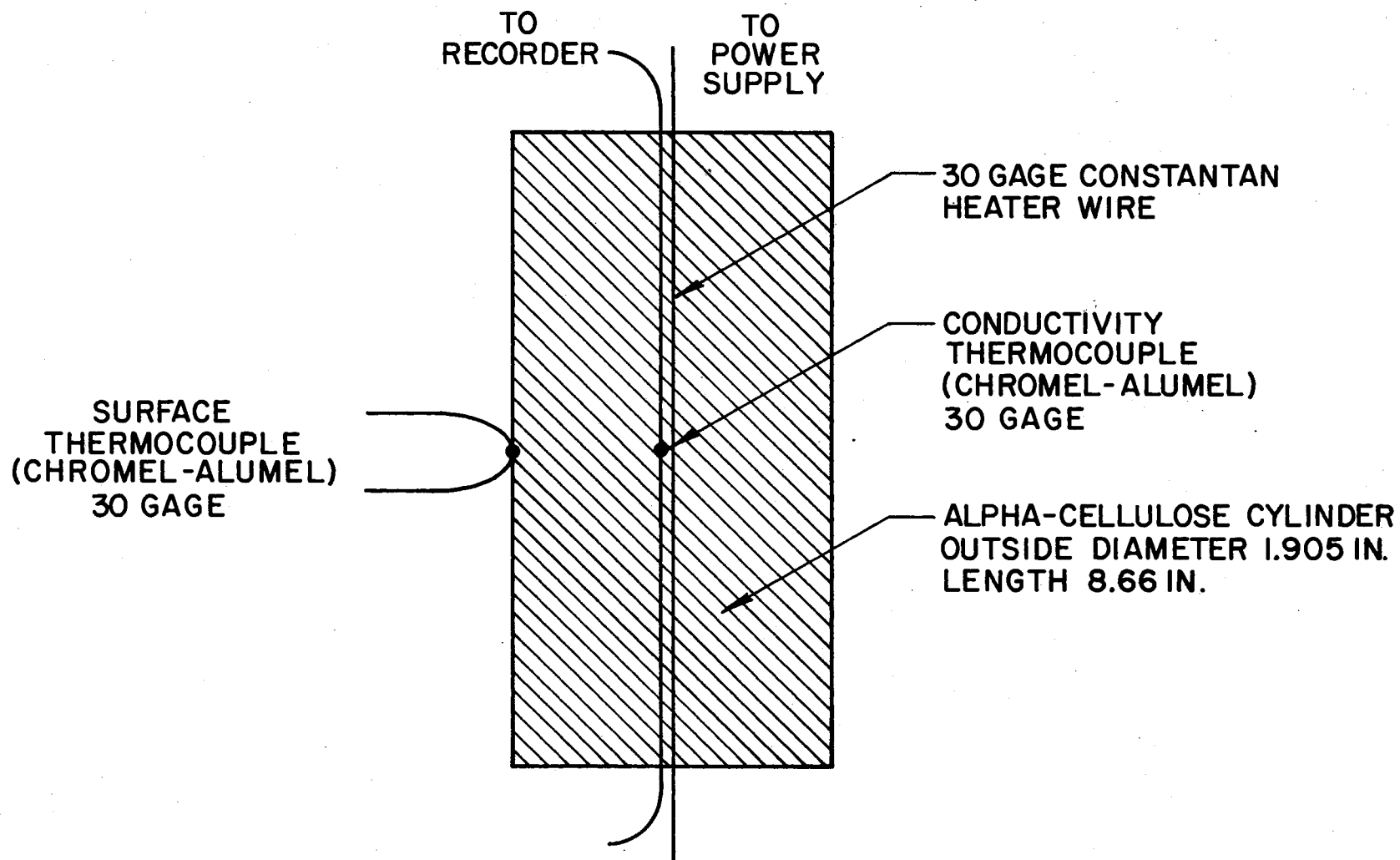


Figure 11. Diagram of Instrumented Alpha-Cellulose Cylinder

constant as a function of temperature is shown in Figure 12.

Samples were checked for moisture content by being weighed and then placed in a vacuum for a period of 24 hours. The samples were then weighed again to determine the moisture content by weight. The virgin alpha-cellulose samples were found to contain 4.95% water. The moisture content of the char was zero.

To obtain the char, samples of virgin alpha-cellulose were placed in a furnace and heated to 800°F, for approximately one-half hour. The samples were burned in a nitrogen atmosphere to prevent ignition. The char was then repacked into the cylinders and instrumented in the same manner as the virgin alpha-cellulose samples. Pictures of the instrumented samples of virgin alpha-cellulose and alpha-cellulose char are shown in Figures 13 and 14 respectively.

Instrumentation

A Kepco model SM160-2 am dc power supply was used for the power input into the samples. Power inputs ranged from 150 milliamps to 500 milliamps. A Digitec model 262 digital ammeter was used to read the current input into the samples. The accuracy of the meter was ± 0.001 amperes.

The internal thermocouple was monitored with a Leeds & Northrup model H strip chart recorder. The surface thermocouple was monitored with a Digitec model 451F digital millivolt meter. The model 451F has an accuracy of ± 0.001 millivolts. The surface thermocouple was installed to monitor the surface temperature of the sample since the

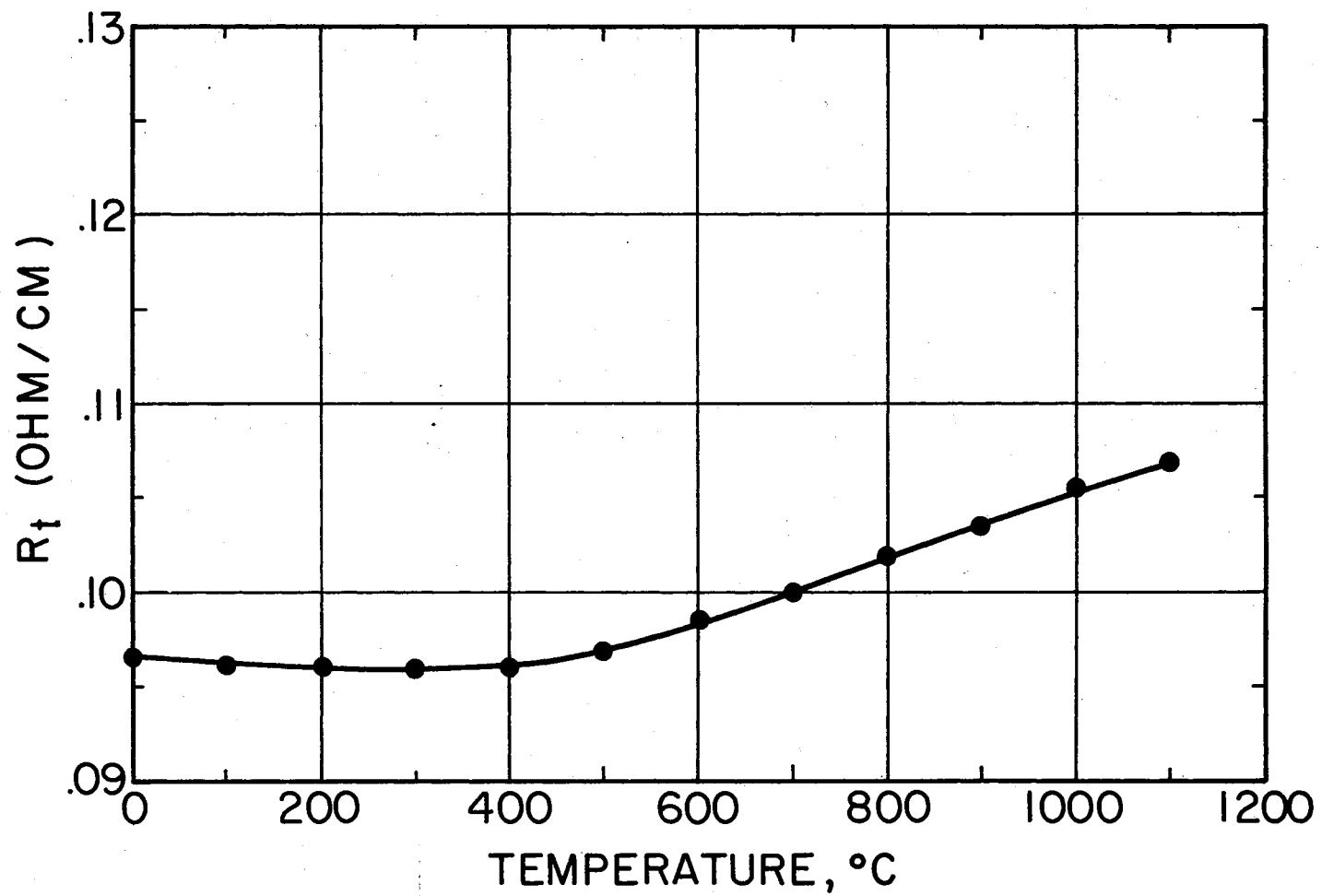


Figure 12. Resistance of 30 Gage Constantan as a Function of Temperature

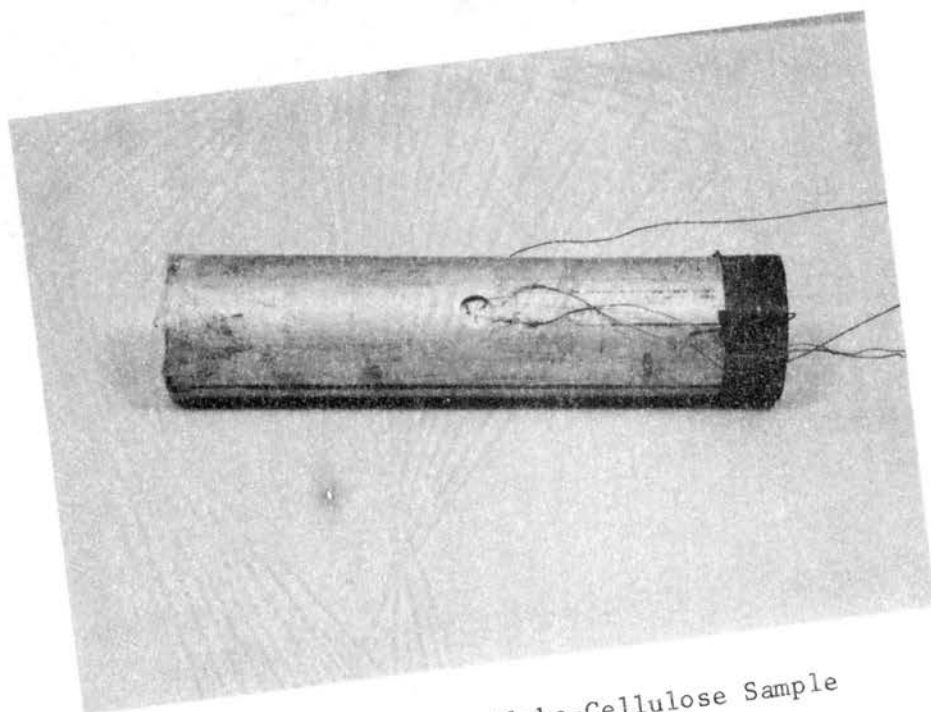


Figure 13. Virgin Alpha-Cellulose Sample
Used in Conductivity
Measurements

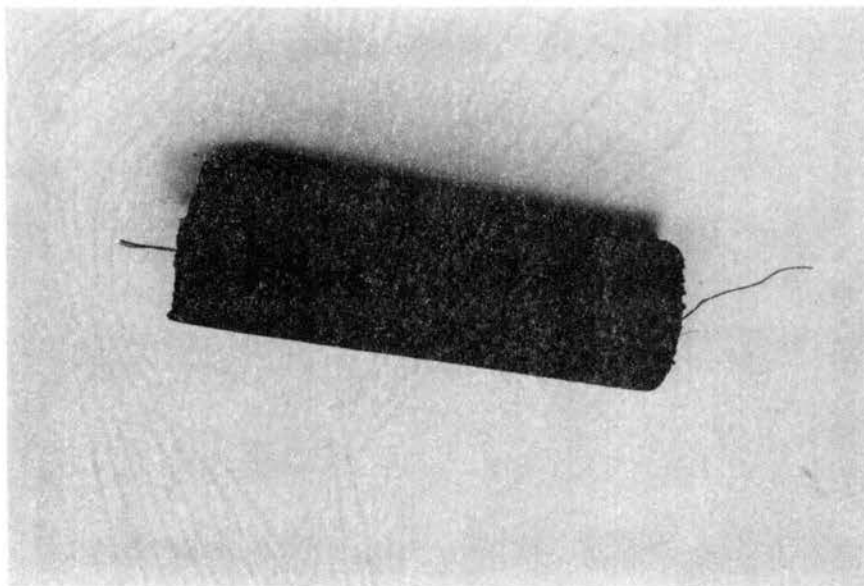


Figure 14. Charred Alpha-Cellulose Sample
Used in Conductivity
Measurements

test was concluded when the surface temperature started to rise.² The thermocouples were referenced to an ice bath at 32°F in all conductivity tests.

Results

Figure 15 shows the thermal conductivity of virgin alpha-cellulose in cal/cm-sec-°C as a function of density in gm/cm³. Figure 15 shows this thermal conductivity as a straight line which approaches the conductivity of air at zero density.

The thermal conductivity for alpha-cellulose char is also shown in Figure 15. Again, the thermal conductivity is a straight line which approaches the thermal conductivity of air.

The thermal conductivities in Figure 15 show the same behavior. The only difference is that the slope of the char conductivity line is less than the slope of the virgin alpha-cellulose conductivity line. From Figure 15, the equations for the thermal conductivity of alpha-cellulose and alpha-cellulose char as a function of density are given by Equations (3.1) and (3.2) respectively.

$$k_a = 5.525 \times 10^{-4} \times \rho + 0.57 \times 10^{-4} \quad (3.1)$$

$$k_c = 1.43 \times 10^{-4} \times \rho + 0.57 \times 10^{-4} \quad (3.2)$$

where k_a = thermal conductivity of the alpha-cellulose and;

k_c = thermal conductivity of the char.

Equation (3.1) was validated by experimental data in the density

²This point will be discussed further in Chapter IV.

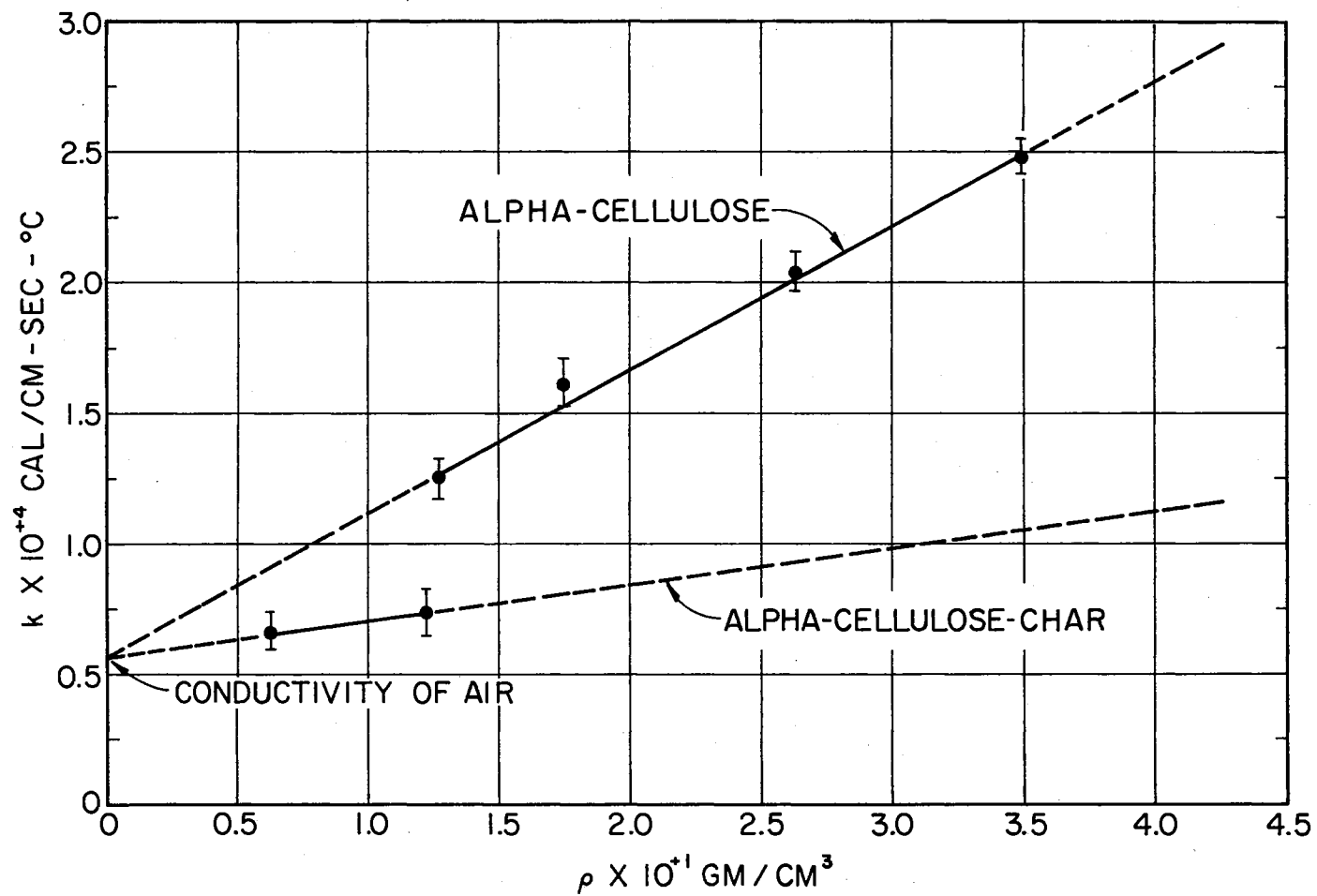


Figure 15. Thermal Conductivity as a Function of Density for Virgin Alpha-Cellulose and Alpha-Cellulose Char

range of 0.126 gm/cm^3 to 0.346 gm/cm^3 . For values less than 0.126 , the data was extrapolated to the conductivity of air at zero density. At density values greater than 0.346 , the data was extrapolated to a density of 0.425 gm/cm^3 . The same extrapolation method applied to Equation (3.2) outside the densities of 0.069 gm/cm^3 to 0.123 gm/cm^3 . The dashed lines in Figure 15 represent the extrapolated values of conductivity. The vertical line drawn at each data point in Figure 15 represents the range of uncertainty obtained by performing an error analysis on the data.

CHAPTER IV

SUMMARY

Interpretation of Experimental Data for Temperature Profile Measurements

The experimental procedure used to obtain the temperature profiles was satisfactory; however, the method used to prepare the sample should be improved for any future research. Separation of the sample occurred at about 380°C. The separation occurred just after the pyrolysis interface had passed the location where the sample was bonded with the methyl-cellulose solution. Because of the difficulties encountered with the sample, the experimental check of the mathematical model in Appendix A was undertaken only up to 380°C. This separation was unfortunate since the temperature profiles should be predicted after pyrolysis has occurred.

Thus, the experimental technique was satisfactory, but the samples were not. The separation of layers must be avoided in order to obtain a complete set of data.

Interpretation of Experimental Data for Thermal Conductivity Measurements

As discussed in Chapter I, the conductivity measurements were carried out because of the poor property data found in the literature. Thus, the greatest problem associated with predicting the temperature profiles during pyrolysis was not the preparation of samples, but the

inconsistent published data. The experimental data obtained for the virgin alpha-cellulose is about 50% greater than the values found in the literature. However, the data obtained for the alpha-cellulose and cellulose char were consistent and the error analysis revealed a fairly low range of uncertainty (see Figure 15). Therefore, the data obtained by the line source method is probably more accurate than the data found in the literature. There was no published data for alpha-cellulose char.

The line heat source method is accurate and reliable if certain sources of error are handled properly. A discussion of these errors, other than instrumentation, follows.

A certain amount of error can be introduced by dropping the higher order terms in Equation (2.6). However, for conductivity measurements, this error is negligible when $0 < u < 0.16$.

There are also errors introduced by the finite length of the sample. This can be minimized by keeping the length to diameter ratio greater than or equal to four.

As discussed briefly in Chapter II, a time correction term must be used in Equation (2.8). This time correction term accounts for the error introduced by the presence of a finite diameter wire in the sample. The presence of this finite wire is the equivalent of causing heat production before the start of measured time.

In addition, an error can be introduced due to the finite size of the sample. This error can be avoided by inserting a thermocouple to monitor the surface temperature and concluding the test when the temperature increases.

Finally, an error can be introduced due to constant resistance between the heater wire and test material, but this error is small if

the power input is small.

In this work, these sources of error were handled properly. In addition, the error for each data point in Figure 15 is small. This indicates that reasonable results were obtained for the thermal conductivities.

The new values of the thermal conductivity were used in the computer program in Appendix A, with no improvement in the results. This seems to imply that other input values into the program were not correct. Possible sources of error other than the conductivity are the specific heat, activation energy, and the heat of pyrolysis.

Error Analysis for the Thermal Conductivity Data

The error analysis was carried out for the data in Figure 15 by varying the five input parameters in the conductivity program. Each parameter was varied with a maximum positive and negative error while the other parameters were held constant. The errors were then added for the positive and negative values to obtain the maximum possible error for each data point. These errors appear as a vertical line in each data point in Figure 15.

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APPENDIX A

ANALYTICAL AND COMPUTER TECHNIQUES TO PREDICT TEMPERATURE PROFILES IN PYROLYZING ALPHA-CELLULOSE

Introduction

This research effort is the conclusion of the efforts undertaken and reported upon by Dr. R. L. Panton, W. M. Brooks, J. G. Rittman, and Mr. L. B. Samartin (25, 26). The basic problem in their research efforts was to develop analytical models which would adequately represent the complex energy transfer problem when a cellulosic material such as wood is heated. Initial efforts by Drs. Panton and Rittman examined the complex chemical kinetic problem associated with the pyrolysis of cellulosic materials. Their effort was directed toward development of analytical techniques which could be used when the pyrolysis was assumed to consist of three simultaneous reactions. This effort was reported in Reference 25. After the Panton, Rittman work was complete, Panton, Brooks and Samartin continued. This effort, reported in Reference 26, expanded the effort of Panton and Rittman to include the effects of moisture present in the cellulosic material.

As a result of their initial efforts, this research activity was initiated in an attempt to experimentally verify the analytical work of the previous investigators.

Background

The problem of the burning or pyrolyzing of wood or cellulosic materials has been of interest for many years. A literature survey by Browne (10) covers the extensive literature up through 1963. During the initial research activity the main interest was the characterization

of the chemical kinetics involved in the physical process. Since the effort dealt with a highly variable biological material, many variations were reported. After initial efforts to predict the pyrolysis as a single first order reaction, suggestions were made that several competing simultaneous reactions were occurring. These results were at least partially confirmed by further work at the Forest Products Laboratory at Madison, Wisconsin (27, 28). As a result of these reports, the initial effort by Panton and Rittman was directed toward the application of this phenomenon to a mathematical model of the pyrolysis. Use of three simultaneous competing reactions during pyrolysis was incorporated into the model. This model was very complex and required solution by integral techniques. Although the established model was analytically tractable, the values of kinetic parameters for the model were not readily available. Thus, solutions obtained were limited to alpha-cellulose which had been more extensively investigated than wood. In the work of Panton-Rittman the differential equation for the one dimensional case used is presented in Equation (A-1).

$$\frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial t} \right) = c \rho \frac{\partial T}{\partial t} + Q \left(\frac{\partial \omega}{\partial t} \right) \quad (A.1)$$

in which

T is the local temperature

x is the spatial variable

t is time

ω is the density of the pyrolyzable material

c is the specific heat

ρ is the density (char and pyrolyzable material)

Q is the heat of pyrolysis

k is the thermal conductivity.

In the work of Panton and Rittman (25), the term $Q \frac{\partial \omega}{\partial t}$ was considered to be represented by three simultaneous and competing reactions. They also assumed that the thermal conductivity k was variable. In their work k was assumed to vary with the density such that $k = k_0 (\rho/\rho_0)$ where k_0 was the thermal conductivity of the original material, ρ was the instantaneous density and ρ_0 was the original density.

In the subsequent work by Panton, Brooks, and Samartin (26) the model for the energy transfer was basically Equation (A-1) with the addition of a term which considered vapor mass flow from water present. In this analysis it was necessary to make several simplifying assumptions in order to solve the system of integral equations which resulted.

Several reports of work primarily directed toward the determination of ignition characteristics are given References 5 and 29. Martin (5) reported the results of intense radiant energy input to alpha-cellulose. As a result of these experiments a semi-empirical method of predicting temperature levels in the heated sample was presented. This correlation requires the time to ignition which must be determined experimentally. Weatherford and Sheppard (29) studied the ignition characteristics of cellulosic materials when exposed to convective heating.

The results of an extensive study of ignition and energy transfer characteristics of cellulosic materials are presented in References 1 and 2. L. E. Brown (1) in a rather extensive study observed that the predictions of energy transfer were very sensitive to the thermal conductivity used in the evaluation of the model (Equation A-1). For this reason, measurement of the thermal conductivity in wood was undertaken.

Their measurements indicated a surprising increase in the thermal conductivity after the pyrolysis. This indication of the thermal conductivity of the char being larger than the thermal conductivity of the original material is rather unique.

As reported in Reference 1, very few serious attempts have been made to predict the temperature as a function of time in the pyrolysis problem with subsequent verification by experiment. One of these is reported in Reference 1 with results which are reported as satisfactory with discrepancy in prediction and experiment at a point near the surface being attributed to boundary condition difficulties.

Analytical Method

The model proposed for the energy transfer in the pyrolysis of cellulosic materials in the initial research of this project was Equation (A-1) with the addition of a term to consider moisture present in the material. This expanded model is presented as Equation (A-2).

$$\frac{k_o}{\rho_o c} \frac{\partial^2 T}{\partial x^2} + \frac{1}{\rho_c} \left[\frac{k_o}{\rho_o} \frac{\partial \omega}{\partial x} + \dot{m} c_v \right] \frac{\partial T}{\partial x} + \frac{Q}{\rho_c} \frac{\partial \omega}{\partial t} = \frac{\partial T}{\partial t} \quad (A.2)$$

in which all terms are the same as defined for Equation (A.1) with additional terms defined as

\dot{m} = mass flow rate of the vapor

c_v = specific heat of the vapor.

In Equation (A.2) the variation of the thermal conductivity is taken as $k = k_o (\rho/\rho_o)$ as previously indicated. In order to obtain this form $\omega = \rho - \rho_c$, where ρ_c is the density of the char remaining, was used.

The term $\partial \omega / \partial t$ is the term which represents the energy absorbed

or liberated by the pyrolysis of the active portion of the cellulosic material. This term was considered to consist of three separate reactions in the work of Rittman and Panton(25). In this work the term was considered to be represented by a single first order reaction, thus $\partial\omega/\partial t$ was represented by the rate expression $A \exp \left[-\frac{E}{RT} \right]$ in which A is the frequency function, E is the activation energy, and R is the gas constant. With this assumption the model for the energy transfer was as presented in Equation (A.3).

$$\frac{k_o}{\rho_o c} \frac{\partial^2 T}{\partial x^2} + \frac{1}{\rho_o c} \left[\frac{k_o}{\rho_o} \frac{\partial \omega}{\partial x} + \dot{m} c_v \right] \frac{\partial T}{\partial x} + \frac{Q}{\rho_o c} A \exp \left(-\frac{E}{RT} \right) = \frac{\partial T}{\partial t} \quad (A.3)$$

The experimental system which was modeled consisted of a slab with radiant input to one face with the other face insulated. These boundary conditions are:

$$T = T_o, \text{ at } t = 0 \quad 0 < x < L \quad (A.4)$$

$$q = 0 \quad t < 0 \quad x = L \quad (A.5)$$

$$q_o - \epsilon T^4 = -k \frac{\partial T}{\partial x} \quad t > 0 \quad x = L \quad (A.6)$$

Boundary condition (A.4) is the initial condition which was assumed to be a constant uniform temperature throughout the slab. The boundary at $x = L$ was assumed to be insulated for all time. At the front face, radiant input of q_o with subsequent radiant loss ϵT^4 was assumed for boundary conditions (A.5). Since this model was non-linear with non-linear boundary conditions, the method of solution chosen was a numerical technique.

The integral methods applied in References 25 and 26 were examined

and determined to be intractable for this problem. Other methods were examined and following the suggestion of Gontkovskaya (30), a straightforward implicit numerical technique was used.

Numerical Technique

The numerical technique will be described using the notation T_j^i where T is the temperature, i is the time interval, j is the spatial node where equal spaced nodes were used. Similar notation will be used for the density variable ρ .

With this notation the variables were represented as follows:

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{x^2} \left[T_{j+1}^{i+1} - 2T_j^{i+1} + T_{j-1}^{i+1} \right] \quad (A.8)$$

$$\frac{\partial T}{\partial x} = \frac{1}{2x} \left[T_{j+1}^{i+1} - T_{j-1}^{i+1} \right] \quad (A.9)$$

$$\frac{\partial T}{\partial t} = \frac{1}{t} \left[T_j^{i+1} - T_j^i \right] \quad (A.10)$$

$$\exp \left(- \frac{E}{RT} \right) = \exp \left(- \frac{E}{RT_j^i} \right)$$

$$\frac{\partial \omega}{\partial x} = \frac{1}{2\Delta x} \left[\omega_{j+1}^{i+1} - \omega_{j-1}^{i+1} \right] \quad (A.11)$$

In order to solve the resulting set of algebraic equations when these substitutions were made, it was necessary to determine the density of the pyrolyzing material at the end of the time interval. This was done by solving the following equation system.

$$\omega_j^{i+1} - \omega_j^i = - A \Delta t \omega_j^i \exp \left(- \frac{E}{RT_j^i} \right) \quad (A.12)$$

It was also necessary to determine the rate of propagation of the vaporization front through the wet cellulosic material before pyrolysis occurs. This was accomplished by dividing the region $0 < x < L$ into two regions:

$0 < x < \ell$ in which the vapor front at $x = \ell$ had passed and for which Equation (A.3) was applied.

$\ell < x < L$ in which the vapor front had not passed and for which the equation $\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t}$ was applied.

These two regions were divided by the vaporization interface for which the following energy balance was used.

$$-k \frac{\partial T}{\partial x_-} + \dot{m} h_\ell = -k \frac{\partial T}{\partial x_+} + \dot{m} h_v \quad (\text{A.12})$$

in which

$k \frac{\partial T}{\partial x_-}$ was the energy conducted into the interface on the dry side.

$k \frac{\partial T}{\partial x_+}$ was the energy conducted into the interface on the wet side.

$\dot{m} h_\ell$ was the energy convected into the interface from the wet region.

$\dot{m} h_v$ was the energy convected away from the interface into the dry region.

Since the interface moves through the region $0 < x < L$, it has a velocity of propagation V . A mass balance across the moving interface results in Equation (A.13).

$$\dot{m} = V \rho_\ell \quad (\text{A.13})$$

| | |
|--|--------------------------|
| Heat capacity original material | 0.3 cal/gm-°C |
| Heat capacity water vapor | 0.49 cal/gm-°C |
| Heat of pyrolysis - endothermic | 88 cal/gm |
| Frequency factor | 2.63×10^9 1/sec |
| Activation energy | 33.1 Kcal/mole |
| Thermal conductivity original material | 0.001 cal/cm-sec-°C |
| Thermal conductivity dry material | 0.000201 cal/cm-sec-°C |

These property values were obtained from References 4, 5, and 13 for alpha-cellulose. In the examination of the properties, it was determined that the thermal diffusivity, density, specific heat and thermal conductivity values were not consistent. For this reason, the values of thermal conductivity were suspected and several different values were used to determine the effect of the uncertainty in these values.

Using these properties, a system with thickness 0.22098 cm (initial experimental thickness), radiant heat flux of $0.323 \text{ cal/cm}^2\text{-sec}$, the results shown in Figure 16 were obtained. These indicate the difference between the temperature history at the heated surface and at a depth of two thirds of the thickness when a non-reactive system is compared to a reactive system.

Since the value of thermal conductivity and, therefore, the diffusivity were uncertain, cases with ± 10 percent variation in thermal conductivity and thermal diffusivity were run. The results for the 2/3 depth were run and the results are shown in Figure 17. The properties used for the evaluations are shown in Figure 17.

Measurement of the density of the alpha-cellulose material used in the experiments indicated the material had a density closer to 0.5208 gm/cm^3 than to the literature value of 0.67 gm/cm^3 . For this reason,

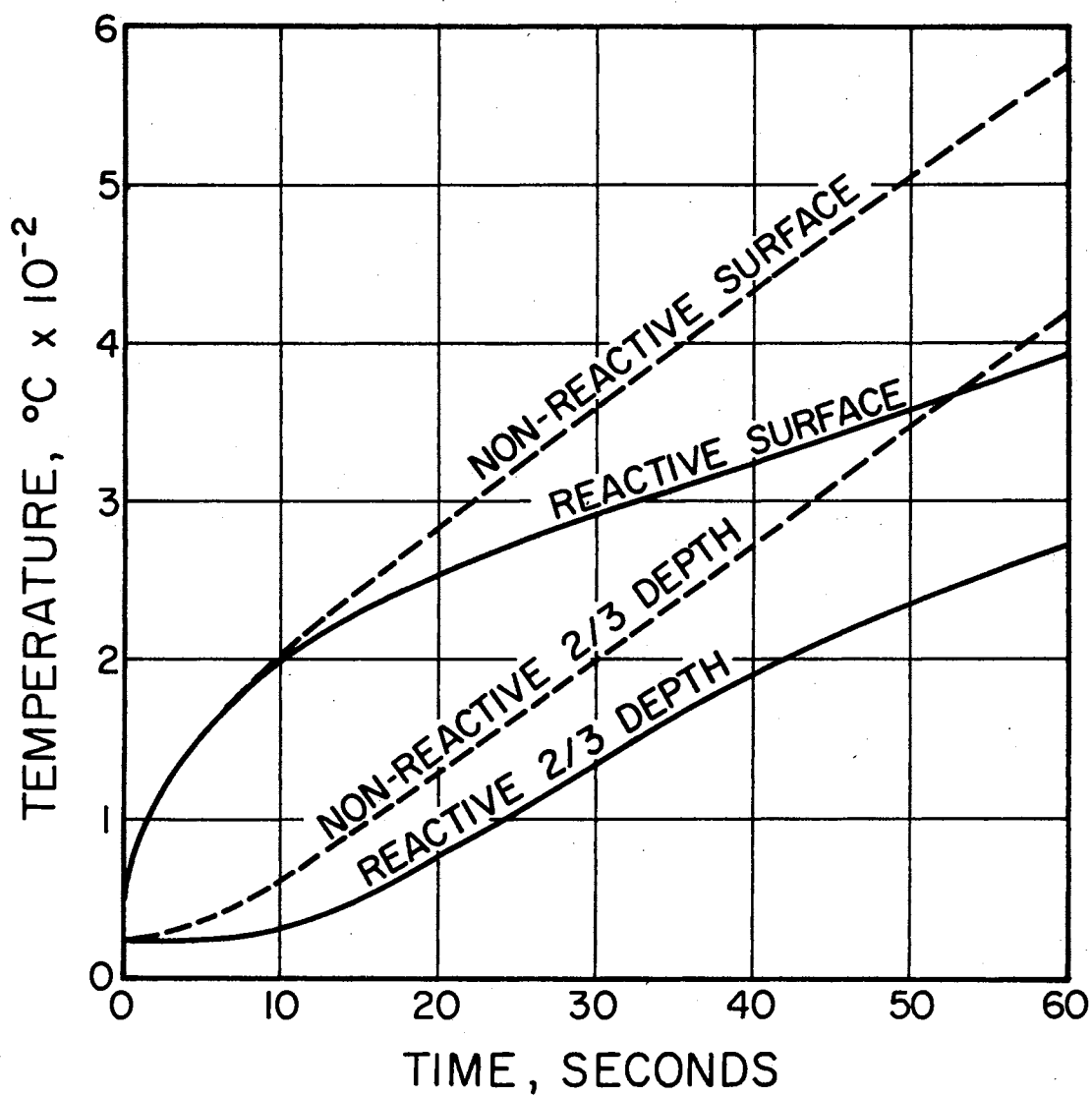


Figure 16. Comparison of Reactive and Non-Reactive Temperature Histories

in which V is the velocity of propagation and ρ_l is the density of the liquid in the material. (Note ρ_l equals the mass of liquid per unit volume in the cellulosic material not the intrinsic density of water.)

Numerical solutions of the simultaneous algebraic equations resulting when the approximations of Equations (A.8), (A.9), (A.10) and (A.11) were substituted into the differential equations were obtained using a digital computer.

The equations were implicit in the temperature variable and explicit in the density variable. For this reason, stability of the solutions was improved over the totally explicit technique but was not completely assured for all solutions. The non-linear boundary condition (A.6) also was not completely stable and required care in the selection of the time interval Δt .

Results - Analytic

After several abortive attempts to apply simplified mathematical models, the model described by Equations (A.3), (A.4), (A.5), and (A.6) was used to obtain the results described hereafter. In the application of this model several physical properties were required. It was determined that several of the properties required were ambiguous in the literature so best estimate values were used.

Using the property values:

| | |
|---------------------------------------|---------------------------------|
| Thermal diffusivity original material | $0.001 \text{ cm}^2/\text{sec}$ |
| Thermal diffusivity char | $0.001 \text{ cm}^2/\text{sec}$ |
| Density original material wet | 0.67 gm/cm^3 |
| Density original material dry | 0.5686 gm/cm^3 |
| Density char | 0.0938 gm/cm^3 |

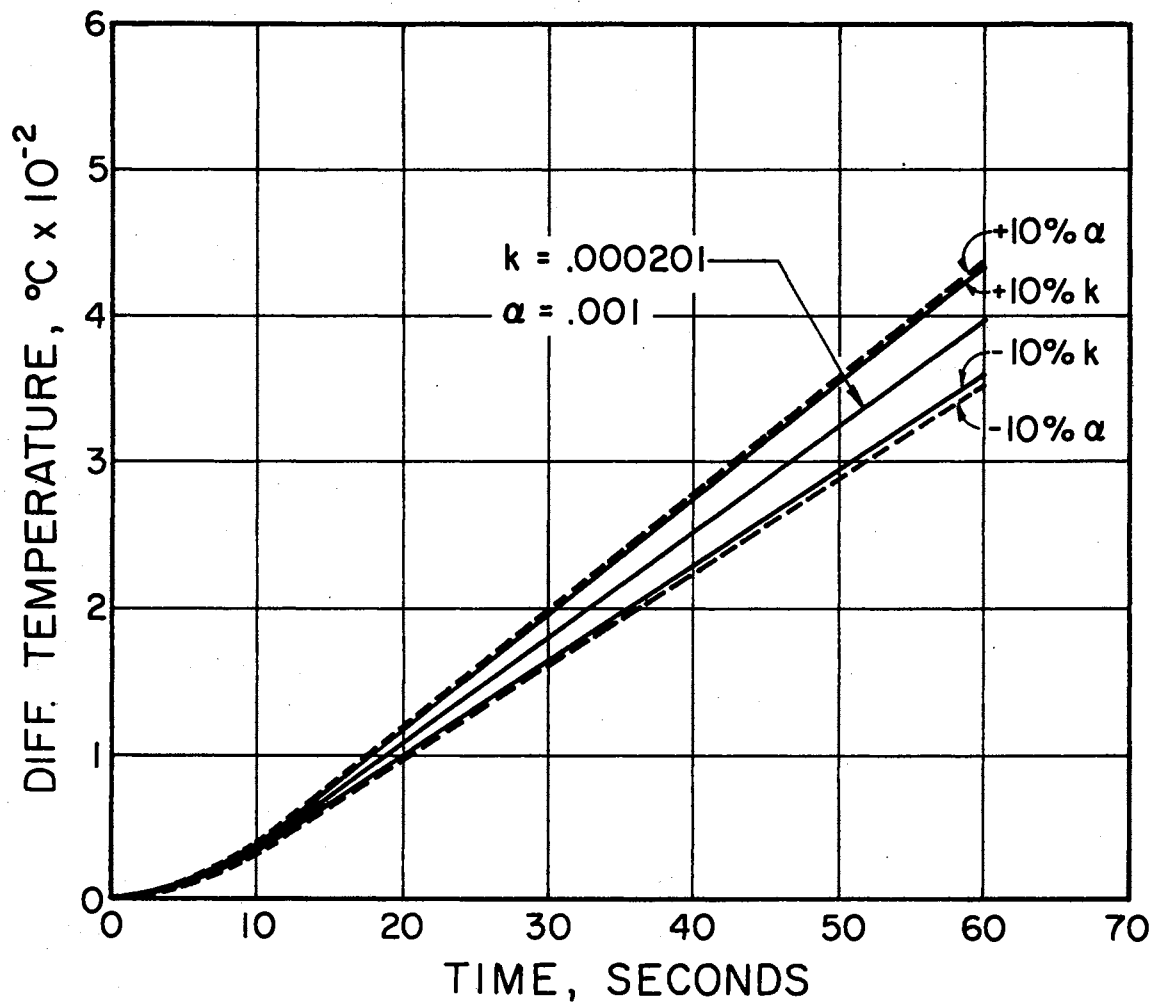


Figure 17. Variation of Temperature of $2/3L$ Depth From Thermal Conductivity and Diffusivity Variation

the results of Figure 18 were obtained. These results were obtained using all properties as indicated before except the density of the material was used as 0.5208 gm/cm^3 .

Further measurements of the density of the alpha-cellulose used indicated the wet material density of 0.5322 gm/cm^3 and the dry material density of 0.5208 gm/cm^3 . Using these property values, the results indicated in Figure 19 were obtained. The depth of 0.1326 cm indicated was the best approximation of the depth of the thermocouple in the experiments.

L. E. Brown (1) indicated that the thermal conductivity of the wood used in experiments varied as shown in Figure 20. Experiments by Havens, et. al., (2) for a hollow cylinder were presented in both References 1 and 2. Since these experimental results were available, the mathematical model presented here was modified to cylindrical coordinates and thermal conductivity variations as indicated by Figure 20. Temperature histories obtained from this modification with experimental values from Reference 1 are presented in Figure 21. The following property values used in obtaining these results were obtained from the literature.

| | |
|---------------------------------------|--------------------------------------|
| Thermal diffusivity original material | $0.002 \text{ cm}^2/\text{sec}$ |
| Thermal diffusivity char | $0.002 \text{ cm}^2/\text{sec}$ |
| Density | 0.500 gm/cm^3 |
| Density of char | 0.100 gm/cm^3 |
| Heat capacity | $0.30 \text{ cal/gm-}^\circ\text{C}$ |
| Heat of Pyrolysis-Endothermic | 43.2 cal/gm |
| Frequency factor | $6.52 \times 10^{16} \text{ 1/sec}$ |
| Activation energy | 54 Kcal/mole |

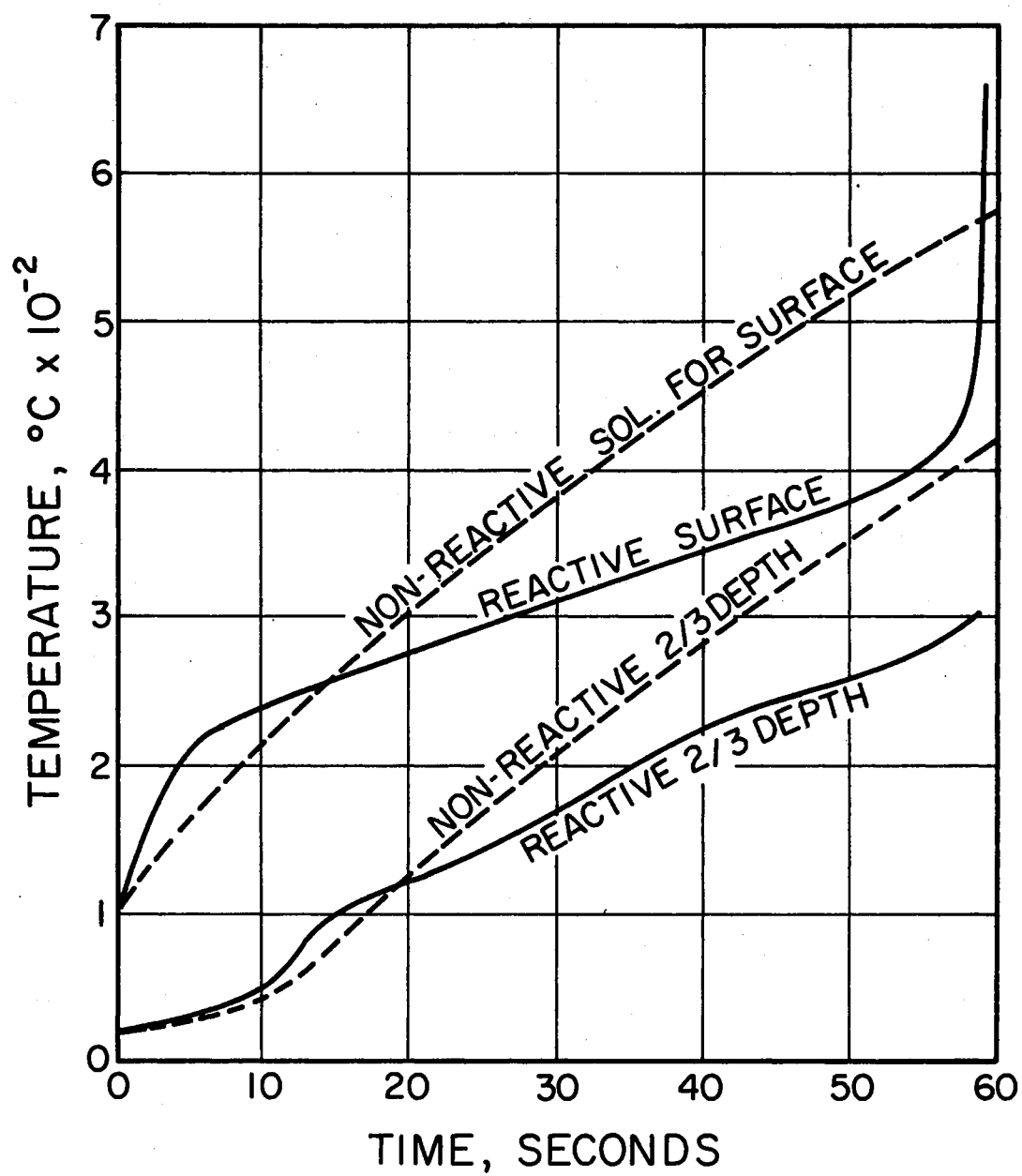


Figure 18. Temperature Histories With Experimental Density

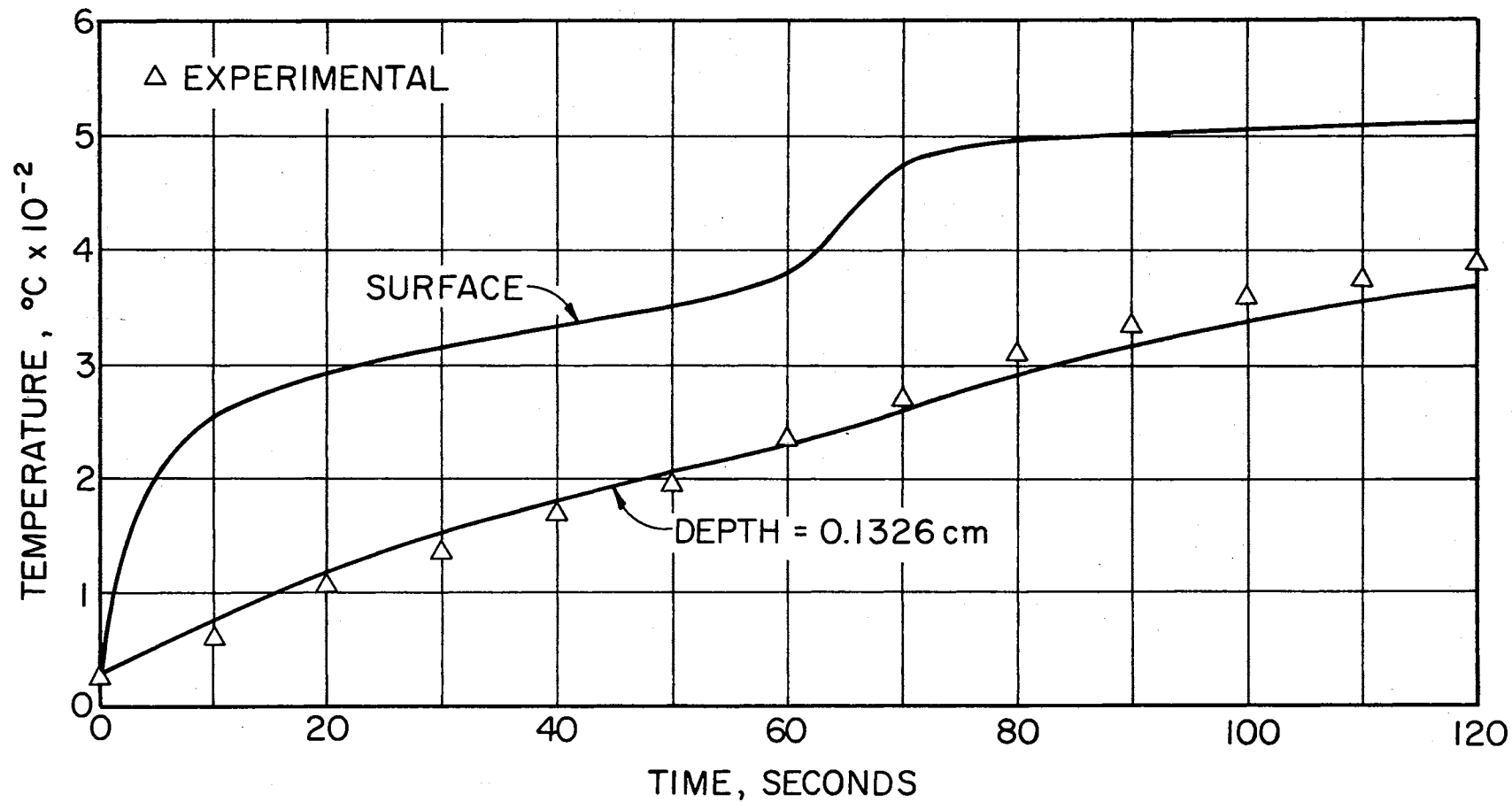


Figure 19. Temperature Histories Using Wet Material Density

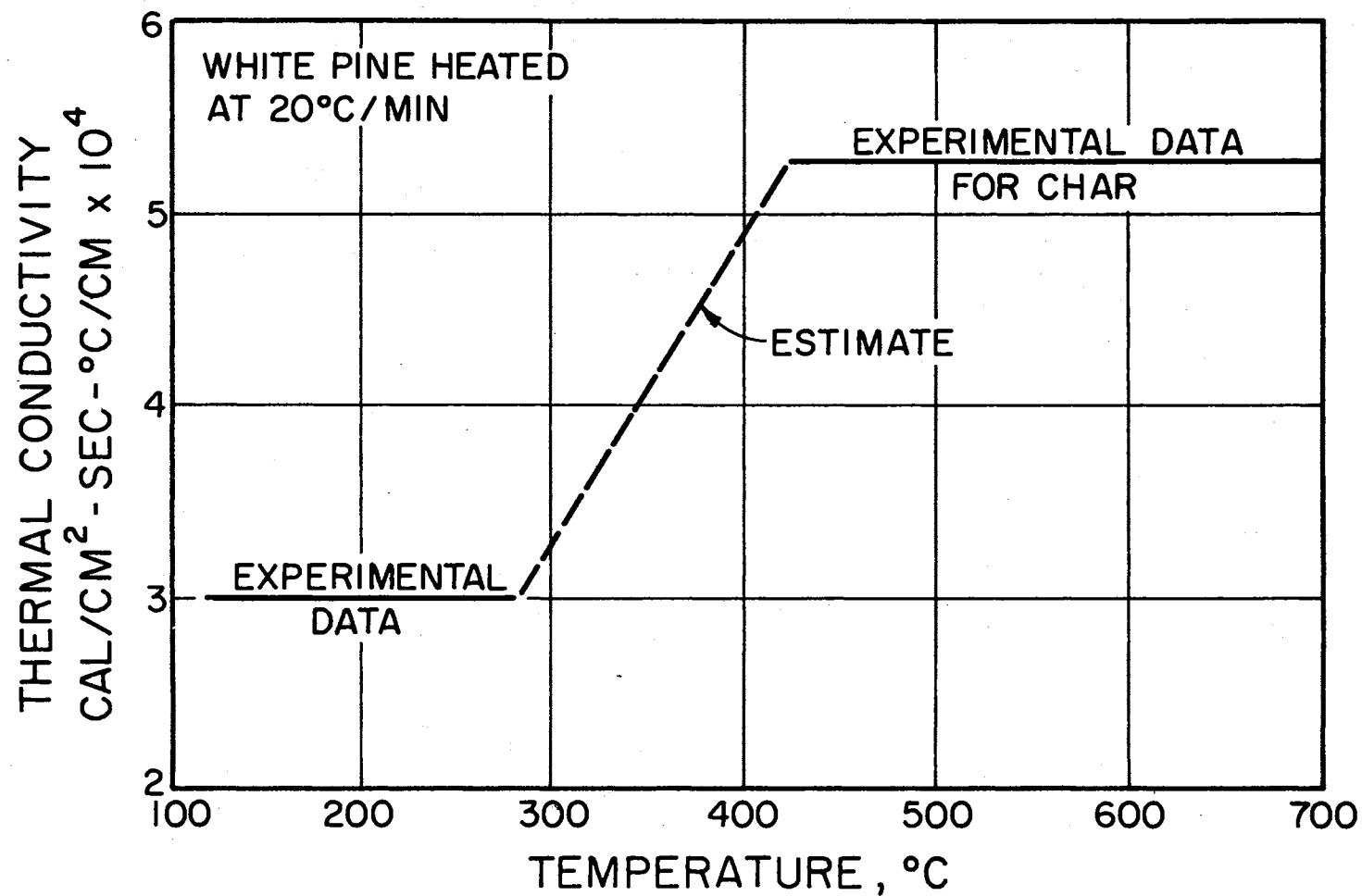


Figure 20. Thermal Conductivity by L. E. Brown (1)

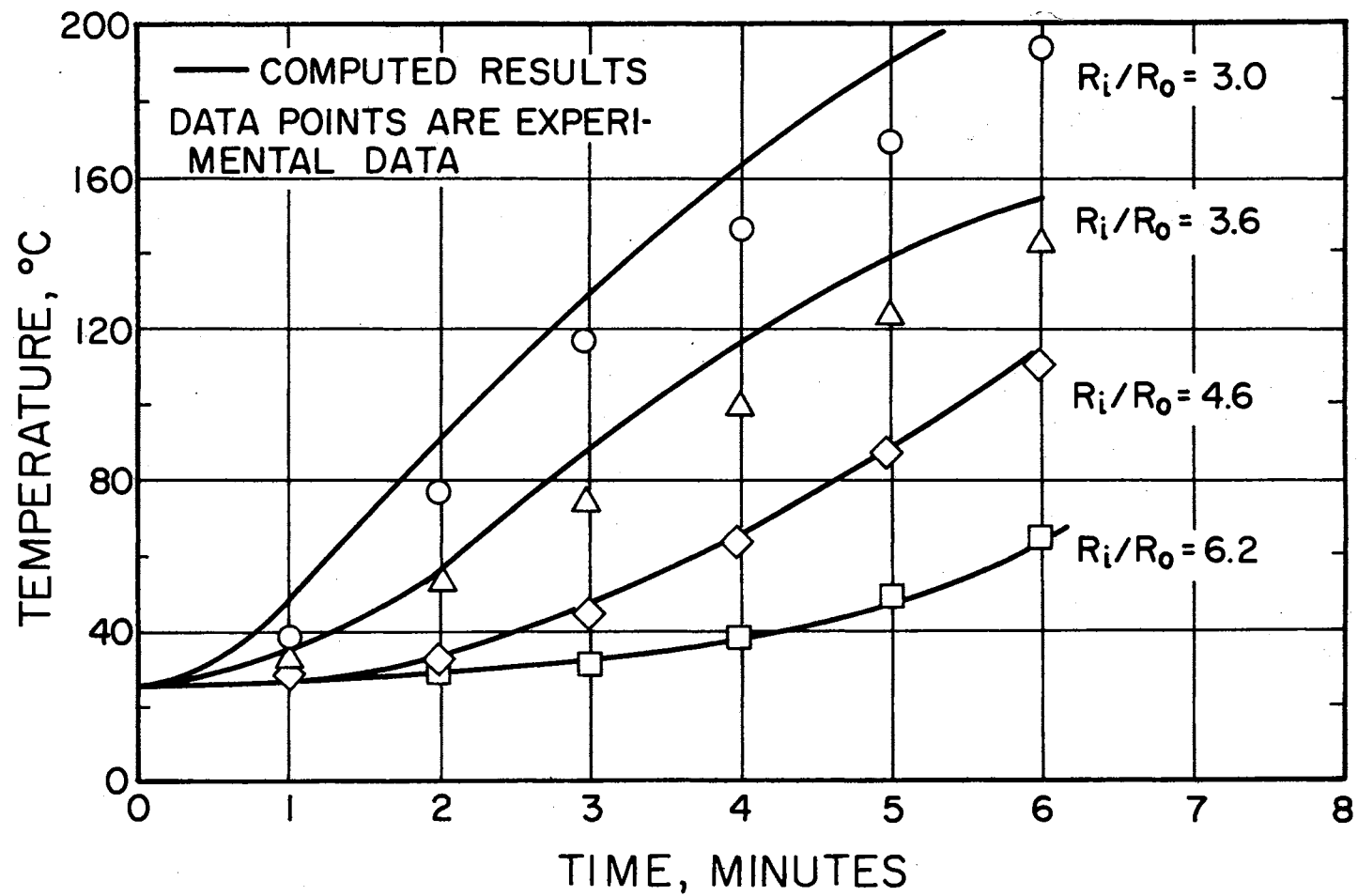


Figure 21. Temperature Histories for Cylindrical Coordinates Compared to Experimental Values From Reference (1)

APPENDIX B

COMPUTER PRINTOUT

80/80 LIST

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CARD

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1 C AUTOMATIC COMPUTATION OF THERMAL CONDUCTIVITY FROM LINE-SOURCE DATA
2 C NSAMP=SAMPLE NUMBER
3 C NRUN=RUN NUMBER
4 C TINIT=INITIAL TEMPERATURE (DEG F)
5 C TOL=TOLEPRANC
6 C NP=NUMBER OF SETS OF DATA POINTS
7 C EMINIT=INITIAL TEMPERATURE 7MILLIVOLTS)
8 C EM=ACTUAL MILLIVOLTS (NOT CHANGE IN MILLIVOLTS)
9 C TIME=TIME (SEC)
10 C C=CURRENT, AMPS
11 C V=THERMOCOUPLE CONSTANT (MILLIVOLTS/DEG F)
12 C R=RESISTANCE OF HEATER WIRE (OHMS/FT)
13 C K=THERMAL CONDUCTIVITY (BTU/HR FT DEG F)
14 DIMENSION EM(100), TIME(100)
15 REAL K
16 1 READ(5,2) NSAMP,NRUN,TINIT,TOL,NP
17 2 FORMAT(2I3,F10.6,E15.8,I3)
18 3 READ(5,4)EMINIT
19 4 FORMAT(F10.5)
20 5 READ(5,6) (EM(I),TIME(I), I=1,NP)
21 6 FORMAT(2F10.5)
22 7 READ(5,8) C,V,R
23 8 FORMAT(3F10.4)
24 9 DO 11 I=1,NP
25 10 EM(I)=EM(I)-EMINIT
26 11 CONTINUE
27 12 SUM=0.0
28 13 SUM1=0.0
29 14 SUM2=0.0
30 15 G=0.0
31 16 G1=0.0
32 17 G2=0.0
33 18 M=0
34 19 M=M+1
35 20 GO TO (21,23,30,40),M
36 21 G=0.0
37 22 GO TO 50
38 23 SUM1=SUM
39 24 G1=0.0
40 25 IF(SUM)26,28,28
41 26 G=4.0
42 27 GO TO 50
43 28 G=-4.0
44 29 GO TO 50
45 30 ZR1=SUM1*SUM
46 31 IF(ZR1) 46,32,32
47 32 M=M-1
48 33 SUM1=SUM
49 34 G1=G
50 35 IF(SUM) 36,38,38
51 36 G=G+2.0
52 37 GO TO 50
53 38 G=G-2.0
54 39 GO TO 50

```

80/80 LIST

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CARD
55      40 M=M-1
56      41 ZR2=SUM1*SUM
57      42 IF(ZR2) 46,46,43
58      43 SUM1=SUM
59      44 G1=G
60      45 GO TO 48
61      46 SUM2=SUM
62      47 G2=G
63      48 G=G-SUM*(G1-G2)/(SUM1-SUM2)
64      49 GG TO 50
65      50 J=0
66      51 SUMX=0.0
67      52 SUMX2=0.0
68      53 SUMX3=0.0
69      54 SUMX4=0.0
70      55 SUMY=0.0
71      56 SUMXY=0.0
72      57 SMX2Y=0.0
73      58 DO 71 I=1,NP
74      59 Z=TIME(I)-G
75      60 IF(Z) 71,71,61
76      61 X=ALOG(Z)
77      62 Y=EM(I)
78      63 SUMX=SUMX+X
79      64 SUMX2=SUMX2+X**2
80      65 SUMX3=SUMX3+X**3
81      66 SUMX4=SUMX4+X**4
82      67 SUMY=SUMY+Y
83      68 SUMXY=SUMXY+X*Y
84      69 SMX2Y=SMX2Y+X*Y*X
85      70 J=J+1
86      71 CONTINUE
87      72 A11=J
88      73 A21=SUMX
89      74 A31=SUMX2
90      75 A12=SUMX
91      76 A22=SUMX2
92      77 A32=SUMX3
93      78 A13=SUMX2
94      79 A23=SUMX3
95      80 A33=SUMX4
96      81 L=1
97      82 EP=A11*A22*A33+A12*A23*A31+A13*A21*A32
98      83 EQ=A31*A22*A13+A21*A12*A33+A11*A32*A23
99      84 E=EP-EQ
100     85 GO TO (86,92,105),L
101     86 D=E
102     87 A13=SUMY
103     88 A23=SUMXY
104     89 A33=SMX2Y
105     90 L=2
106     91 GO TO 82
107     92 CN=E
108     93 SUM=2.0*(CN/D)

```

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1234567890123456789012345678901234567890123456789012345678901234567890

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CARD
109      54 XXX=ABS(SUM)
110      95 YYY=XXX-TOL
111      96 IF(YYY) 97,97,19
112      97 A12=SUMY
113      98 A22=SUMXY
114      99 A32=SMX2Y
115     100 A13=SUMX2
116     101 A23=SUMX3
117     102 A33=SUMX4
118     103 L=3
119     104 GC TO 82
120     105 BN=E
121     106 SLOPE=BN/D
122     107 K=(3.413*C*C*V*R)/(SLOPE*4.0*3.141592654)
123     108 WRITE(6,109) NSAMP,NRUN,TINIT,TOL,NP
124     109 FORMAT(1H1,9X,11HSAMPLE NO =,I3,5X,8HNRUN NO =,I3,5X,11HT INITIAL =
125           1, F10.4,/,/,16X,5HTOL =,E15.8,10X,16HNO DATA POINTS =,I3,/)
126     110 WRITE(6,111) (EM(I),TIME(I), I=1,NP)
127     111 FORMAT(/,10X,12H MILLIVOLTS =,E15.8,10X,11HTIME(SEC) =,F10.4)
128     112 WRITE(6,113) C,V,R
129     113 FORMAT(/,10X,15HCURRENT(AMPS) =,F10.3,10X,16HV (MV/TEMP(F)) =,
130           1F10.4,/,/,10X,37HRESISTANCE OF HEATER WIRE (OHMS/FT) =,F10.4)
131     114 WRITE(6,115) K,G,SLOPE
132     115 FORMAT(/,10X,22HTHERMAL CONDUCTIVITY =,E15.8,/,/,9X,
133           1234TIME CORRECTION (SEC) =,E15.8,/,/,10X,7HSLOPE =,E15.8)
134     116 GO TO 1
135     END

```

VITA [✓]

Jack Bradford Henderson

Candidate for the Degree of

Master of Science

Thesis: EXPERIMENTAL TEMPERATURE HISTORIES AND THERMAL CONDUCTIVITIES
FOR ALPHA-CELLULOSE AND ALPHA-CELLULOSE CHAR

Major Field: Mechanical Engineering

Biographical:

Personal Data: Born in Caney, Kansas, July 29, 1943, the son of
Mr. and Mrs. H. J. Henderson.

Education: Graduated from Copan High School, Copan, Oklahoma, in
May, 1961; received Bachelor of Science degree in Mechanical
Engineering from the University of Tulsa in 1972; completed
requirements for the Master of Science degree at Oklahoma
State University, Stillwater, Oklahoma, in December, 1973.

Professional Experience: Junior Engineer, Butler-Culvern and
Associates from June, 1972, to September, 1972; graduate
research assistant, School of Mechanical Engineering,
Oklahoma State University, September, 1972, to December, 1973.