

AN ABSTRACT OF THE THESIS OF

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Title: Kinetics of Cellulose Pyrolysis Under High Heating Rates

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Pyrolysis of cellulose was studied by electrically heating in helium, at atmospheric pressure, 20-25 mg of powdered cellulose sample supported inside a folded-wire screen heating element. The screen was mounted and heated within a sealed vessel. The samples were heated to peak temperatures between 300-1100°C using different heating rates. The heating rates studied were 100, 500 and 1000°C/s. The holding time at peak temperature varied between 0-20 seconds. The final products--char, tar and gases--were quantitated for experiments carried out at 1000°C/s and zero holding time. The gaseous products formed were analyzed to determine the amounts of CO, CO₂, CH₄, C₂H₄ and C₂H₆ formed. At heating rates of 100 and 500°C/s (zero and non-zero holding times) and 1000°C/s (non-zero holding times), only the amounts of char (and hence total volatiles) formed were determined.

The non-isothermal temperature-time history, to which the sample

was subjected, was recorded by a chromel-alumel thermocouple on a fast response strip chart recorder. This temperature-time history, along with the final yields of total volatiles, was used to obtain the kinetic parameters described by a single reaction, first-order decomposition model. The kinetic parameters obtained for overall devolatilization varied widely for the different heating rates studied suggesting a difference in reaction mechanism. The values obtained for activation energy and pre-exponential factor for the different heating rates were: 15.60 kcal/mole and $0.413 \times 10^5 \text{ sec}^{-1}$ for 100°C/s; 22.27 kcal/mole and $64.01 \times 10^5 \text{ sec}^{-1}$ for 500°C/s; 23.26 kcal/mole and $46.5 \times 10^5 \text{ sec}^{-1}$ for 1000°C/s.

Use of a multiple reaction model based on a set of independent parallel first-order reactions represented by Gaussian distribution of activation energy was also investigated. The values obtained for 1000°C/s, zero holding time, were: pre-exponential factor of $45.08 \times 10^5 \text{ sec}^{-1}$, activation energy of 23.61 kcal/mole and a standard deviation of 0.034 kcal/mole. Comparison of these values, to those shown above for 1000°C/s, along with the low value of standard deviation, indicates that the single reaction first-order decomposition model suffices to correlate the data.

The main conclusions reached from this study were that both temperature and solids residence times play an important role in the rate of formation, yield and composition of the product gases,

char and tar. The reaction mechanism appears to be significantly different at the various heating rates studied. And finally, secondary cracking of tar at high temperatures results in the formation of CO, CH₄, C₂H₄ and C₂H₆.

Kinetics of Cellulose Pyrolysis
Under High Heating Rates

by

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KINETICS OF CELLULOSE PYROLYSIS UNDER HIGH HEATING RATES

I

INTRODUCTION

Substantial increases in the price of crude oil in the last few years, as well as concern over the ultimate availability of fossil fuels, has prompted a growing interest in using biomass as a renewable resource for chemical feedstocks. Wood and other cellulose materials form a large portion of urban wastes. Pyrolysis of these solid wastes offers a promise for commercially producing fuel gases and liquids suitable for replacing petroleum-based products.

Pyrolysis of wood, cellulose and other forms of renewable materials is a complex process not yet fully understood. It produces a host of chemical species and is influenced by a variety of factors such as the chemical and physical characteristics of the cellulosic material, heating rate, temperature, pressure, and the residence times of both the solids and vapor products. Fairly minor changes in any of these factors may affect not only the yield and rate of production of pyrolysis gases, liquids and char, but also the actual course of the reaction mechanism. The design of optimum incineration or pyrolysis process therefore requires an improved fundamental understanding of the mechanism of cellulose degradation under severe thermal treatment. Furthermore, pyrolytic decomposition supplies the volatiles to sustain flaming combustion of most polymeric materials and is thus of interest in the areas of fire

research, fabric flammability and explosion phenomena. Cellulosic materials are of special interest because of their widespread utilization in fibers, textiles and construction materials and in the fabrication of temperature-resistant materials.

The objective of the present study was to focus on the effects of temperature, heating rate and solids residence time, on yield, composition and rates of formation of products from the rapid pyrolysis of cellulose at atmospheric pressure. A descriptive model of the process was determined from the results. To obtain a clear picture of only the kinetics of the process, the effects of heat transfer, mass transfer and secondary chemical reactions were eliminated or minimized.

The cellulose studied was powdered, purified wood cellulose. An electric grid apparatus was used to subject small amounts (20-25 mg) of captive cellulose sample to different heating rates, peak temperatures and solids residence times. The temperature-time history to which the sample was subjected, was recorded. Peak temperatures in the range 300-1100°C were achieved using heating rates of approximately 100, 500 and 1000°C/s. The holding times at these peak temperatures varied from 0-20 seconds. For heating rate of 1000°C/s and zero holding time, the end products of pyrolysis, namely char, tar and gases were quantitated. The gases were subjected to further analysis by gas chromatography to determine their

composition and yields of each species formed. For other heating rates, and holding times, only the char formed (and hence the total volatiles) was measured. The kinetic parameters, obtained by fitting data to single step first-order reaction model, showed significant differences in values for the different heating rates, indicating difference in reaction mechanism.

II

LITERATURE REVIEW

Techniques Used in Studying Pyrolysis

The literature on the thermal degradation of cellulosic materials is extensive and several reviews have appeared in the past few years (1,2,3). Pyrolysis mechanism is extremely complicated, and in order to simplify the analysis and evaluation of pyrolysis it has been a common practice to make either of the two following assumptions:

- 1) Reaction is controlled by chemical kinetics and the physics of heat transfer is unimportant and may be accounted for by lumping these considerations into an apparent activation energy and frequency factor.
- 2) Reaction is controlled by heat transfer considerations and the chemical kinetics are of less importance and may be accounted for by lumping the chemical kinetics into an effective thermal conductivity.

Based on the broad assumptions made above, several investigators have utilized different experimental techniques to study the pyrolysis of pure cellulose (6,7,8), cottons (5,9), cellulosic derivatives (10), and wood (4,11,12,13), in atmospheres ranging from vacuum and inert gases to air. A lot of these studies were

related to the phenomena of fire and combustion. In more recent times, investigators have studied cellulose pyrolysis as an alternative source of fuel gases and chemical feedstock.

Shafizadeh (3) proposed a general reaction scheme for pyrolysis and combustion of cellulose; heating at lower temperatures favors dehydration and charring reactions. Formation of levoglucosan takes place at temperatures above 250°C and leads to further decomposition reactions. Heating at higher temperatures favors the generation of combustible volatiles. Figure 1 proposed by Maa (4) describes the physical and chemical processes interacting in pyrolysis and combustion.

One of the most commonly used techniques to study cellulose pyrolysis has been the thermogravimetric analysis or TGA. The TGA technique can be utilized to study reaction kinetics by isothermal and non-isothermal methods. The isothermal (static) method involves determination of the sample weight as a function of time at constant temperature. The disadvantages of this method are: (a) it cannot be used to study the effect of heating rate; (b) it requires many experimental runs in order to complete a data set; and (c) there is a time lapse before sample attains required temperature, during which the reaction has already proceeded to a certain extent. The non-isothermal (dynamic) TGA method requires determination of weight change as a function of time, while temperature

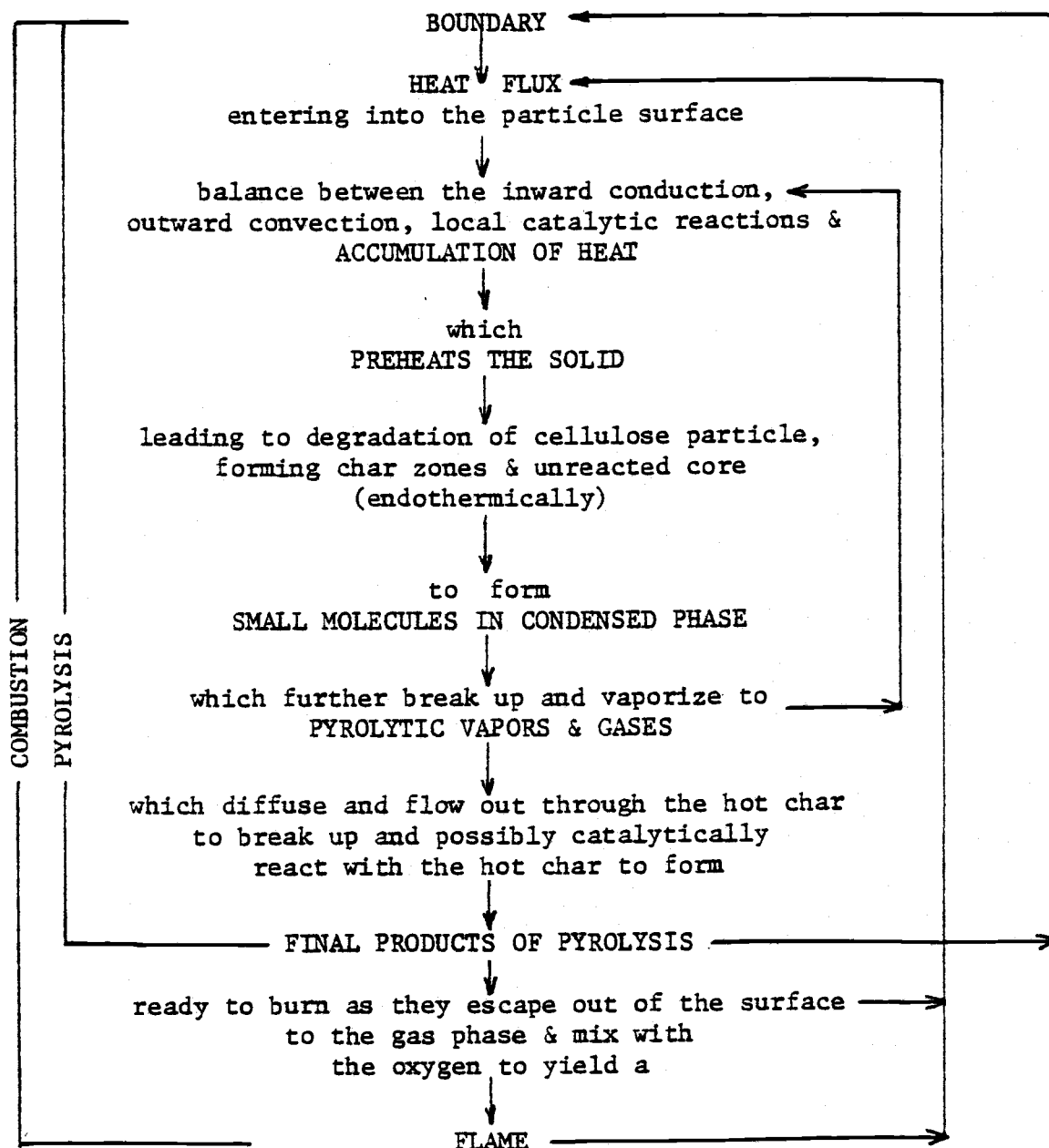
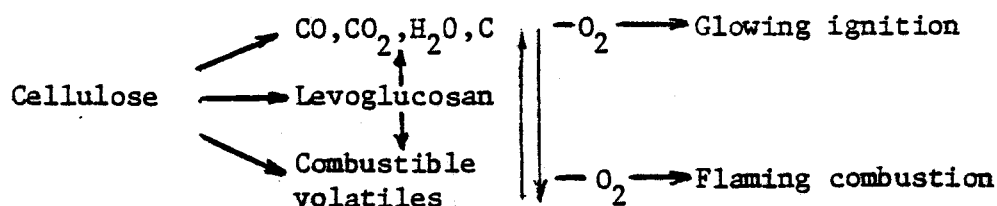


Figure 1. Physical and Chemical Processes Interacting in Pyrolysis and Combustion.

increases linearly; the disadvantages being that the reaction mechanism cannot be studied.

Another experimental technique used is the differential thermal analysis or DTA. This method measures the change in enthalpy as a function of temperature involving measuring the temperature difference between that of the sample under study and a chosen standard. This method is not widely used because the results depend on the kinetics as well as the energetics of the reaction and are, therefore, more difficult to interpret. Also, there are too many parameters which could affect the DTA curve, such as sample size, characteristics of the sample, composition of the atmosphere used and nature of the reaction being studied. The results from these studies vary widely. Studies by Tang and Neill (14) showed an endothermic heat of reaction (-90 cal/gm) for cellulose pyrolysis. However, studies conducted by Roberts and Clough (15) on large samples of wood in an inert atmosphere yielded a value of 420 cal/gm (exothermic).

Flow techniques using fluidized bed (12) has also been employed to study pyrolysis. Maa and Bailie (16) utilized fluidized bed along with TGA to conduct pyrolysis of wood samples in the temperature range $400-1200^{\circ}\text{C}$. A mathematical model based on the shrinking core model was used to correlate data, and the parameters derived from TGA experiments were used in the model to predict the experimental results in the fluidized bed.

Calvin et al. (17) utilized a CO_2 - laser radiation source to study wood pyrolysis at fire level surface heat flux. Investigations through the measurement of decomposition rates, solid temperatures and thermal properties, pyrolysis gas composition and crack formation, showed that wood pyrolysis process is dependent upon the external heating rate, the total time of heating, and the anisotropic properties of wood and char relative to the internal flow of heat and gas.

Studies conducted by Kanury (8) involved simultaneous measurement of density, by x-rays, and temperature profiles, by thermocouples imbedded in the pyrolyzing solid which, when combined, yielded the kinetics. The findings concluded that a first-order Arrhenius-type rate equation satisfactorily described the pyrolysis of α -cellulose. A recent study by Thurner and Uzimann (13) of wood pyrolysis in the temperature range 300-400°C at atmospheric pressure, using TGA, interpreted their data by three competitive parallel first-order reactions, as suggested by Shafizadeh and Chin (18).

Most of the above studies were characterized by long heat-up times, with periods at final temperatures extending to several hours (6) or days (19). In some work, volatile products were separated and then subjected to further chemical characterization (20). Rapid heating of cellulosic materials has been employed in a few studies. Radiative heating of thin samples was used to obtain

heating rates estimated to approach 60°C/s with cellulose in air (21) and $300\text{--}1500^{\circ}\text{C/s}$ for treated and untreated cottons in helium (22). One investigation achieved very rapid rates estimated to exceed 20000°C/s by flash heating optically black material embedded in a matrix of untreated cellulose (23). The resulting degradation, however, probably reflects predominantly heterogeneous decomposition at the absorbing sites rather than the true pyrolysis of the cellulose.

An electrically heated grid system developed to study rapid pyrolysis of coal (24) was recently used to study cellulose pyrolysis by Lewellen et al. (25) and Peters et al. (20). The use of this method allows great flexibility in varying heating rate, temperature and solids residence time of the sample subjected to pyrolysis. The captive products formed--namely, gas char and tar--can be subjected to detail analysis relative to composition and yield. The non-linear temperature-time history to which the sample is subjected is recorded, and along with the product yield can be used to obtain not only the kinetics of the reaction, but offers an insight into its mechanism. This technique has been used in the present study.

Kinetic data on the pyrolysis of cellulosic materials has been obtained, usually as Arrhenius constants for an assumed single-step first-order decomposition. The values of the kinetic parameters

obtained have been found to vary over a wide range, with variations of several factors of 10 in the rate constant over the temperature range 200-1100°C, while activation energies range widely from 4.0 kcal/mole to more than 70.0 kcal/mole. These large discrepancies can probably be attributed to the differences in sample sizes, as well as their physical and chemical characteristics. Also, pyrolysis samples generally have low thermal conductivity. Since the tests were carried out under transient conditions, significant temperature non-uniformity might have existed within the samples, the extent of non-uniformity depending on sample size and heating rate.

Tables 1 and 2 list the feedstock and experimental techniques used by various workers and the kinetic parameters obtained from their studies.

Chemistry of Pyrolysis

Cellulose $(C_6H_{10}O_5)_n$ is a high molecular weight (between 250,000 and 1,000,000) polysaccharide. It consists of at least 1500 units of $C_6H_{10}O_5$. The structure of each unit is as shown below:

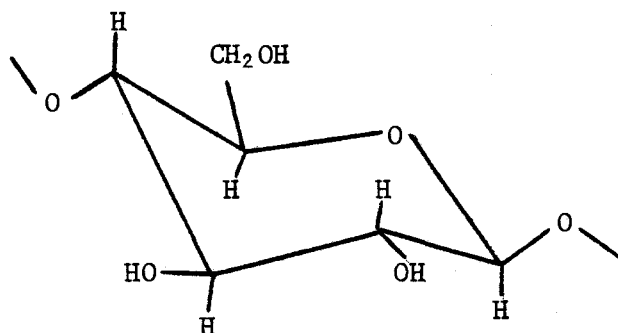


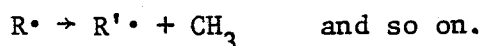
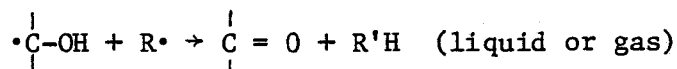
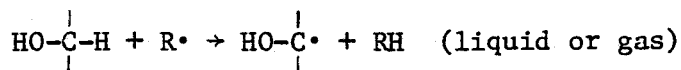
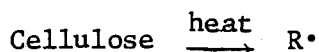
TABLE 1. FEEDSTOCK AND EXPERIMENTAL CONDITIONS OF PYROLYSIS

Author	Technique Used	Atmosphere	Temperature Range °C	Material	Sample: Size or Weight
Browne & Tang (1962)	Static TGA	Nitrogen & vacuum	130-400	Wood: Ponderosa Pine	250-500 mg.
Chatterjee (1966)	Isothermal TGA	Helium	270-300	Ball-milled Cellulose	100 mg.
Chatterjee (1966)	Isothermal TGA	Helium	270-310	Cotton	100 mg.
Lipska & Parke (1966)	Fluidized bath	Nitrogen	250-300	α -Cellulose	173-191 mg.
Mark & Donaldson (1967)	DSC	Nitrogen	300-450	Cotton	13-17 mg.
Akita & Kase (1967)	Dynamic TGA	Air and nitrogen	Room temp. -500	α -Cellulose Modified cellulose	100-260 mg.
Kanury (1972)	Radiography	Nitrogen	300-400	α -Cellulose	Cylinder: 1.75 cm. rad.
Barooah & Long (1976)	Fluidized bed	Nitrogen	150-400	Wood	40 mg.
Min (1977)	Vapor phase therm. analy.	Nitrogen	300-450	Filter paper	6 cm x 6 cm
Lewellen et al. (1977)	Electric grid	Helium	250-1000	Filter paper	.75 cm x 2.5 cm; .01 cm thickness
Maa (1978)	TGA	N ₂ , air & CO ₂	400-1200	Birch wood	Cylinder: 3.8 cm x 0.5 cm dia.
Peters et al. (1980)	Electric grid	Helium	300-1100	Filter paper	2 cm x 6 cm; 0.01 cm thickness
Thurner et al. (1981)	Dynamic TGA	Nitrogen	300-400	Wood	Mean size: 1 mm.

TABLE 2. KINETIC PARAMETERS OBTAINED BY VARIOUS WORKERS

Author	Material	Reaction Order	Activation Energy, kcal/mol.	Pre-exponential Factor, s ⁻¹
Brown & Tang (1962)	Wood: Ponderosa Pine	pseudo 1	35.8	
Chatterjee (1966)	Ball-milled Cellulose	before 40%: 0	75.0	
		after 40%: 1	37.1	
Chatterjee (1966)	Cotton	before 40%: 0	54.3	
		after 40%: 1	33.0	
Lipska & Parke (1966)	α-Cellulose	3 stages: Ini. Per., 0 & then 1	42.0	
Mark & Donaldson (1967)	Cotton	1	41.2	
Akita & Kase (1967)	α-Cellulose	1	53.5	1.05 x 10 ¹⁷
	Modified Cellulose		32.0	1.67 x 10 ¹⁰
Kanury (1972)	α-Cellulose	1	19.0	1.70 x 10 ⁴
Barooah & Long (1976)	Wood	Pri. decomp. 1	4.3 (<330°C)	0.05
		Sec. decomp. 2	20.1 (>330°C)	2.30 x 10 ⁴
Min (1977)	Filter paper	1	54.3	3.00 x 10 ¹⁶
Lewellen et al. (1977)	Filter paper	1	33.4	6.79 x 10 ⁹
Maa (1978)	Birch wood	Shrinking core model	7.5	0.10 cm/sec
	Douglas fir		3.5	0.028 cm/sec
Peters et al. (1980)	Filter paper	1	31.79	2.00 x 10 ⁸
Thurner et al. (1981)	Wood	3 parallel first-order reactions	21.1	14.35 x 10 ³
			26.9	41.20 x 10 ⁵
			25.4	7.40 x 10 ⁵

The thermal decomposition behavior of such a structurally complex compound might well be expected to defy simple description. A mechanism suggested by Martin (27) describes that when cellulose is heated, the weaker oxygen-carbon bonds may break to form fragments $R^\bullet$, the fragments can be stabilized by attracting hydrogen in other molecules or fragments to form either gas or liquid depending on the size of $R^\bullet$. The fragments can be broken down further to smaller molecules and free radicals such as $CH_3^\bullet$, $C_2H^\bullet$, $C_2H_3^\bullet$, $CHO^\bullet$, $C_2H_5^\bullet$, etc., these small free radicals being very reactive, can react with hydrogen to form gases. The size of $R^\bullet$ is dependent on the rate of heating. The amount of further degradation is dependent on the vapor phase residence time. High temperature promotes rapid heating and favors the formation of small molecules or carbonaceous gas and less char, whereas low temperature promotes slower heating and favors the formation of larger volatile molecules and more char. The above description, in terms of the reactions taking place, is summarized below:



A more adequate and likely pathway contributing to weight loss, and consistent with much of the pertinent literature, has been suggested by Lewellen et al. (25) as shown in Figure 2. Cellulose could decompose rapidly to an intermediate identified as levoglucosan. The levoglucosan may then (1) be transferred from the cellulose matrix to give a product tar; (2) repolymerize, crack or be cross-linked to yield char; (3) be pyrolyzed to lighter volatile products including CO, CO₂, fixed gases, organic acids, ketones, esters, aldehydes and free radicals, some of which could (4) inhibit char formation or (5) autocatalyze step 3. Lighter stable products could also (6) escape the matrix to yield volatiles.

This mechanism would explain the increased tar yields under vacuum as opposed to atmospheric pressure (10), because of reduced time available for primary volatile products to undergo secondary reactions such as cracking and repolymerization. It would also explain the differences in yields and compositions observed when heating rate, temperature, sample size and residence are varied. For thin or small-sized samples subjected to high heating rates and high temperatures, step 3 would be dominant along with 1, 4, and 6, resulting in less char and tar. For similar samples, low temperatures and heating rates, step 1 would be dominant, resulting in greater tar formation. For larger samples subjected to low heating rates and temperatures, the primary products

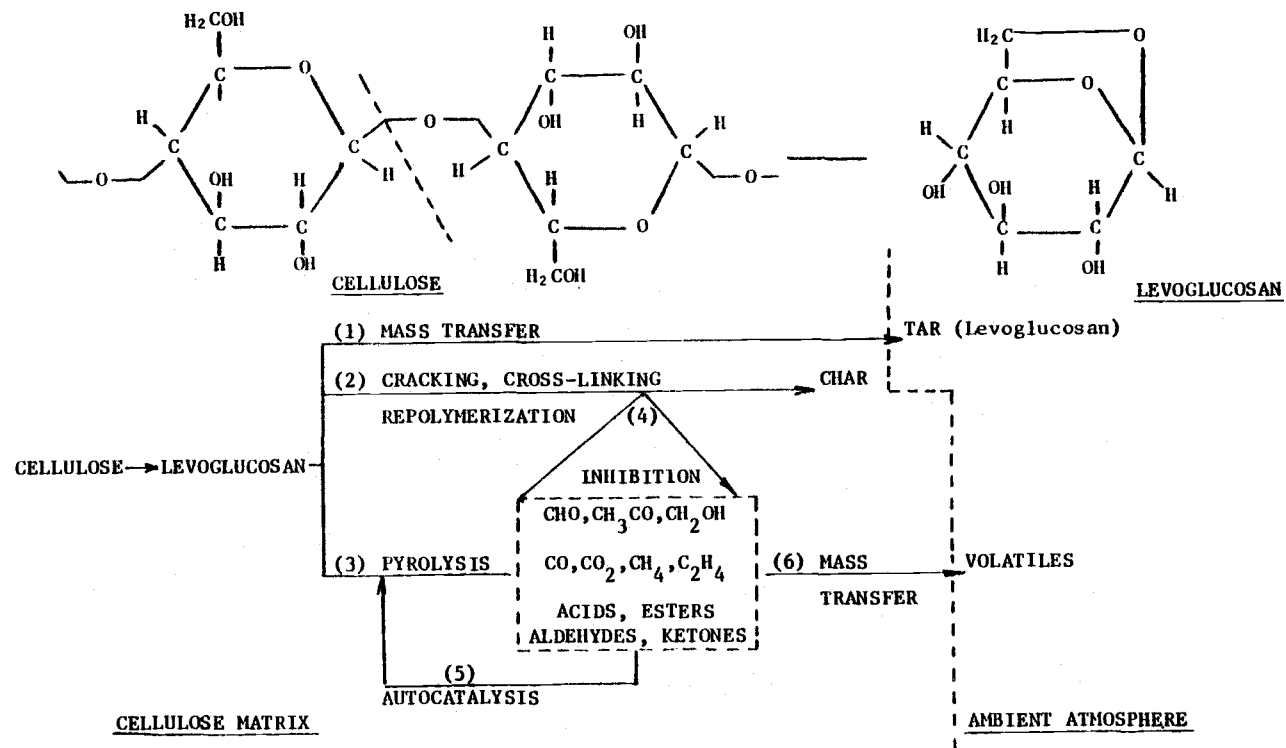


Figure 2. Possible Reaction Pathways for Thermal Degradation of Cellulose Under Rapid Heating Conditions.

formed would have a longer residence time within the pyrolyzing matrix and step 2 would dominate resulting in large char yields (6,19).

III

APPARATUS AND PROCEDURE

Selection of Apparatus

The techniques used by previous investigators and the drawbacks of these methods have been discussed in the previous chapter. A thermogravimetric analysis system, with an ability to heat and track weight losses at heating rates up to 5000°C/s , and up to 1100°C , does not exist. Also, to understand the reaction mechanism, it is necessary to know the yield and composition of the gases evolved at different temperatures. The time lag in gas analysis, using TGA, would make this analysis difficult.

The apparatus selected for the present work is a modified version of the electric grid system used by Suuberg (24) to study rapid coal pyrolysis and by Lewellen et al. (25) and Peters et al. (20) to study rapid pyrolysis of cellulose. The advantages of this system are:

- a) independent control of heating rate, peak temperature and holding times,
- b) good heat transfer characteristics,
- c) ability to measure the temperature-time history accurately,
- d) near-zero residence time of volatiles in the region of the heated cellulose sample.

This method, unlike TGA which yields differential data, yields

integral data.

Apparatus Description

A schematic of the experimental apparatus used is shown in Figure 3. It consists of three components: the reactor which was designed to contain a cellulose sample in a gaseous environment of known pressure and composition; the electric grid system, which controls the temperature-time history to which the sample was subjected; and the temperature recording system. The product gases were analyzed by gas chromatography.

The reactor consists of a pyrex glass dome, 25.4 cm internal diameter and 1.27 cm wall thickness, which was blind flanged by a 1.27 cm thick stainless steel plate having gas inlet and outlet ports and the electrical feed-throughs. The cellulose sample was held and heated by a folded strip of stainless steel screen stretched between massive brass electrodes, as shown in Figure 4. All tubing was standard wall 0.32 cm stainless steel, with compression type fittings.

The screen used to hold the sample was 325 mesh, type 316 stainless steel cut to 14 cm x 4 cm. It was folded over onto itself to form a "sandwich" 14 cm x 2 cm. Of this, only 6 cm x 2 cm of the screen held the cellulose sample to be heated. The small size of the screen was dictated by the desire to obtain uniform temperature

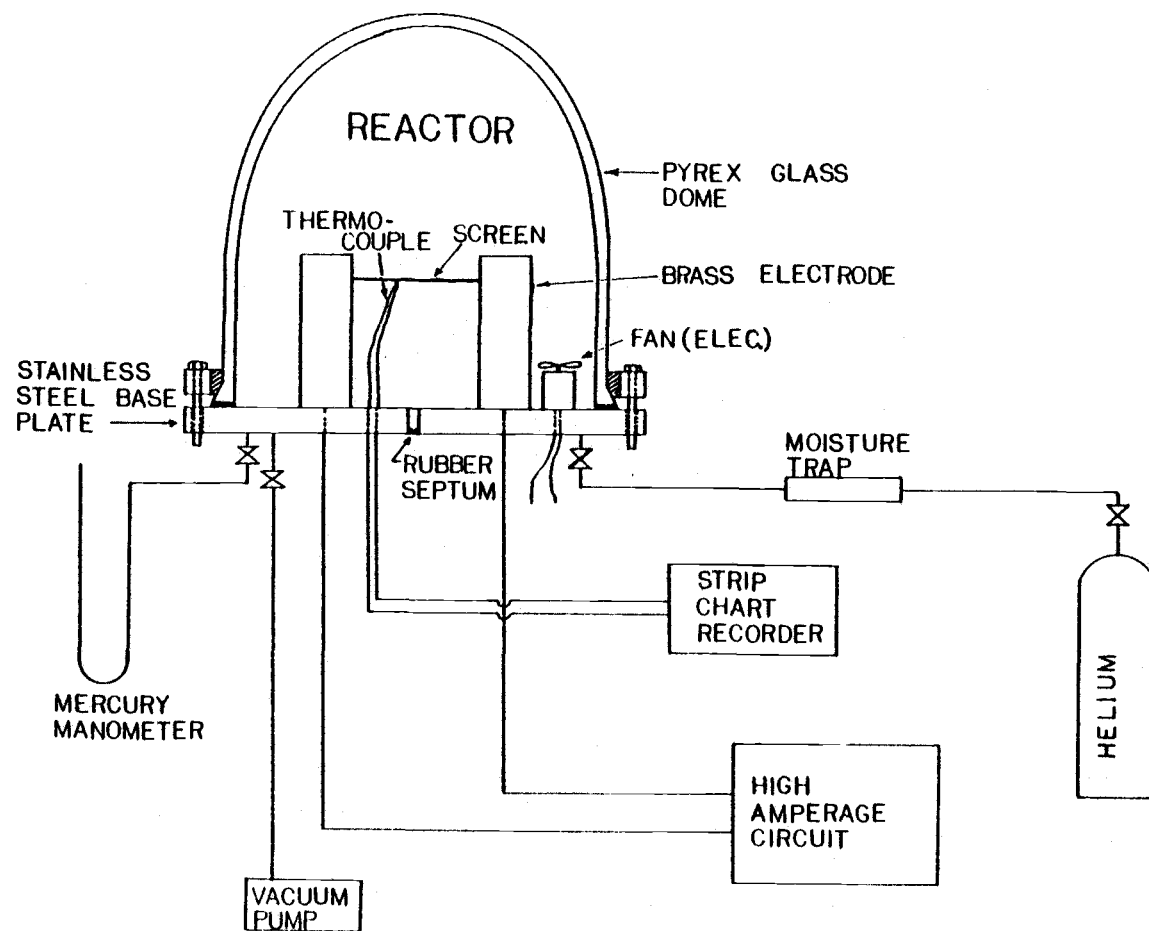


Figure 3. Schematic of Apparatus

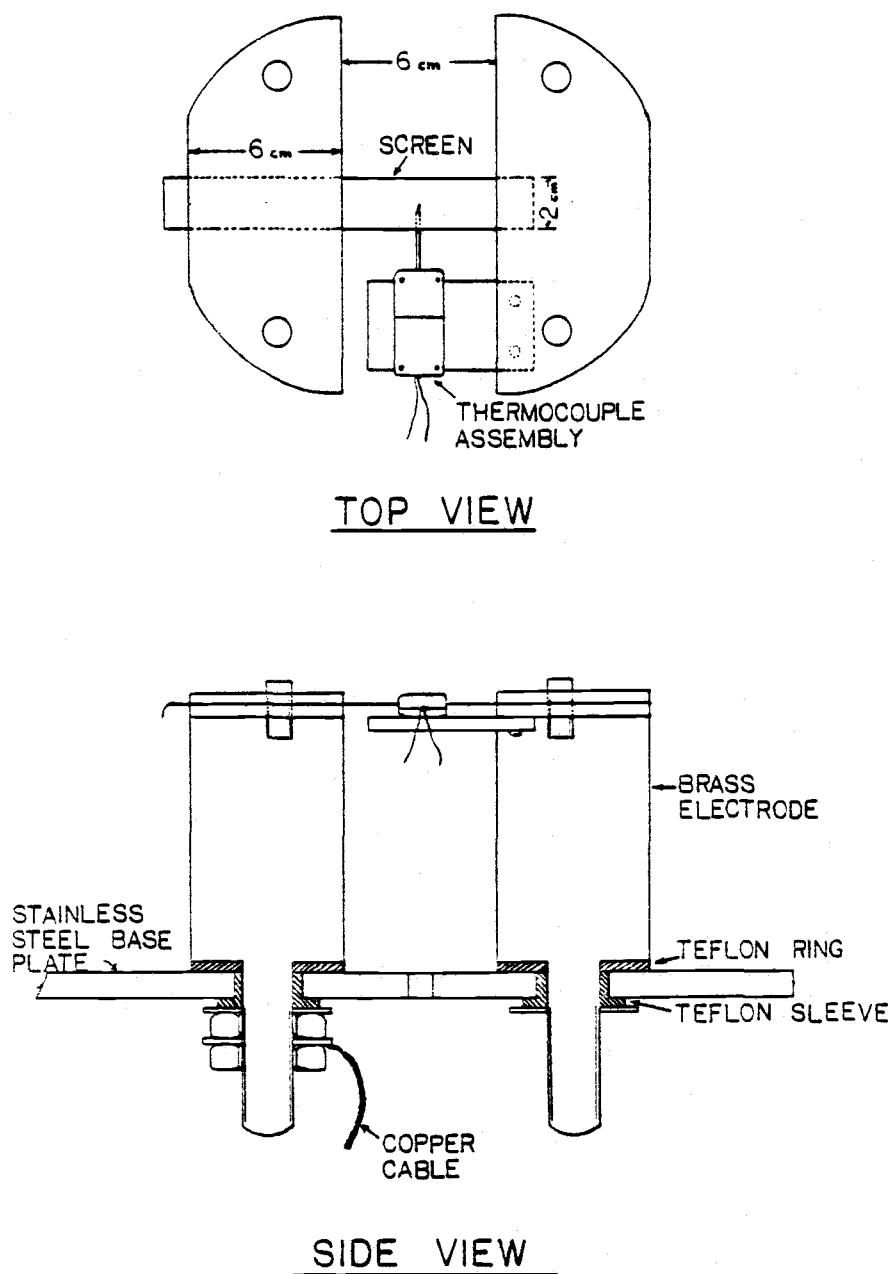


Figure 4. Details of Apparatus Internals

across its surface. Attempts with larger screen sizes showed significant differences in temperature along the length of the screen. Each run was carried out with a new screen. Before loading with the sample, the screen was pre-heated to a high temperature to ensure cleanliness and stable screen weight during and after the run.

A small motor and fan (operated by a 3.0V battery) arrangement within the reactor was used to mix the product gases after completion of each run and before withdrawing a known volume of these gases for analysis.

The electrical system consists of two 12-volt automobile storage batteries connected in series to the brass electrodes, through variable resistors and timer-operated relay switches, to achieve desired heating of the screen and sample. This electrical system, shown in Figure 5, permits heating rates between 100-5000°C/s, final temperatures between 100-1100°C and holding times of up to 30 seconds. Because of the high current being drawn to heat the screen, three variable resistors (each 3.0 ohms) in parallel were used to vary the resistance in the primary heating stage circuit. Heavy duty, 50 amp. relay switches (two in parallel) were used to handle the large currents being drawn.

The temperature-time history of the sample being heated was recorded by a chromel-alumel thermocouple, 0.025 mm wire diameter and approximately 75 μ m bead diameter, placed between the screen

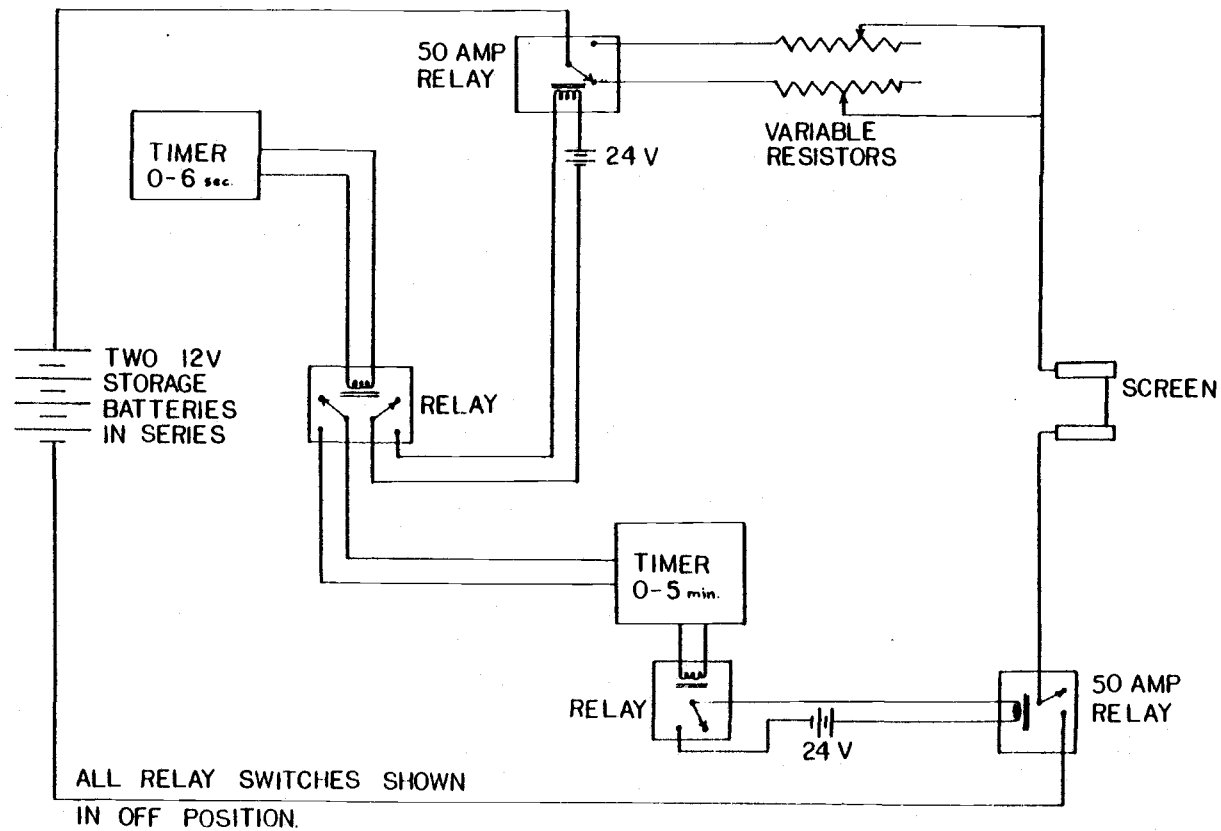
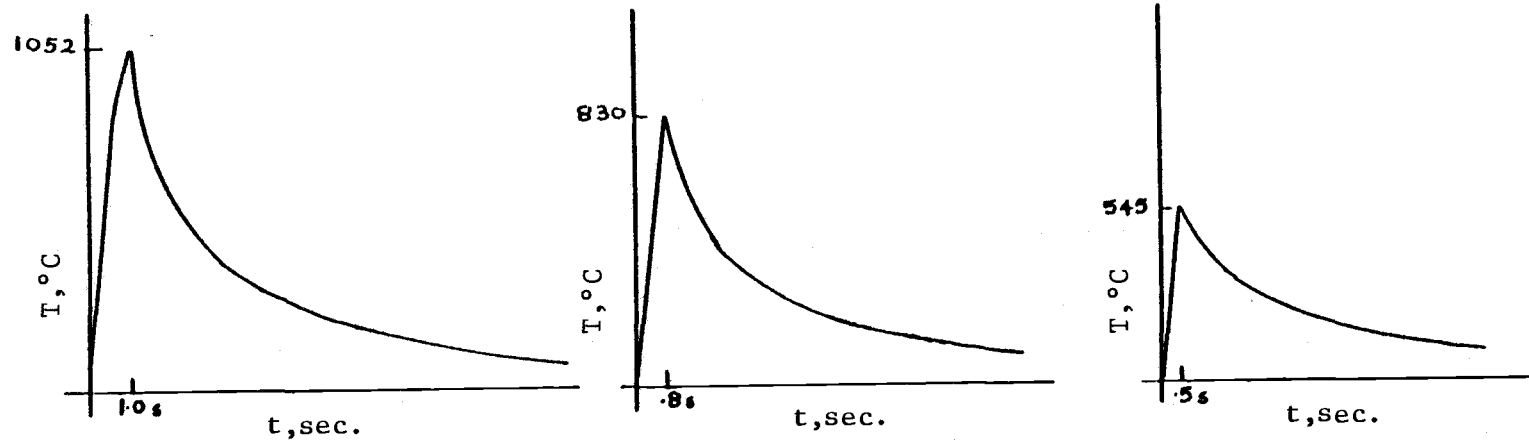


Figure 5. Circuit used for the Control of Time-Temperature Histories

and connected to a fast response strip chart recorder. The fine wires of the thermocouple were protected by passing them through a 0.8 mm O.D., double-bored alumina sleeve, which in turn was fixed to a thermocouple connector. The connector rests on a brass plate, level with the screen and extending from one of the clamps on the electrode. The details are shown in Figure 4. The thermocouple bead extends about 0.3 mm beyond the free end of the alumina sleeve.

Tests conducted, with and without the thermocouple bead touching the hot screen surface, showed a difference of nearly 100°C in the temperature recorded at the same point on the screen. At the heating rates of interest in this study, this would result in an inaccurate recording of the temperature-time history of the sample. Hence, care was taken to ensure that the thermocouple bead touched the screen surface during each run. Some typical temperature-time profiles recorded are shown in Figure 6. The quenching of the sample, after power cut-off, occurs by natural cooling: radiation, convection and conduction. The cooling part of the temperature-time profile varies from run to run, depending on the peak temperature achieved.

The volatiles formed were contained within the reactor. After completion of the run the gases were mixed by operating the fan. A known volume of the gas mixture was then withdrawn through the



Approximate heating rate = 1000°C/s

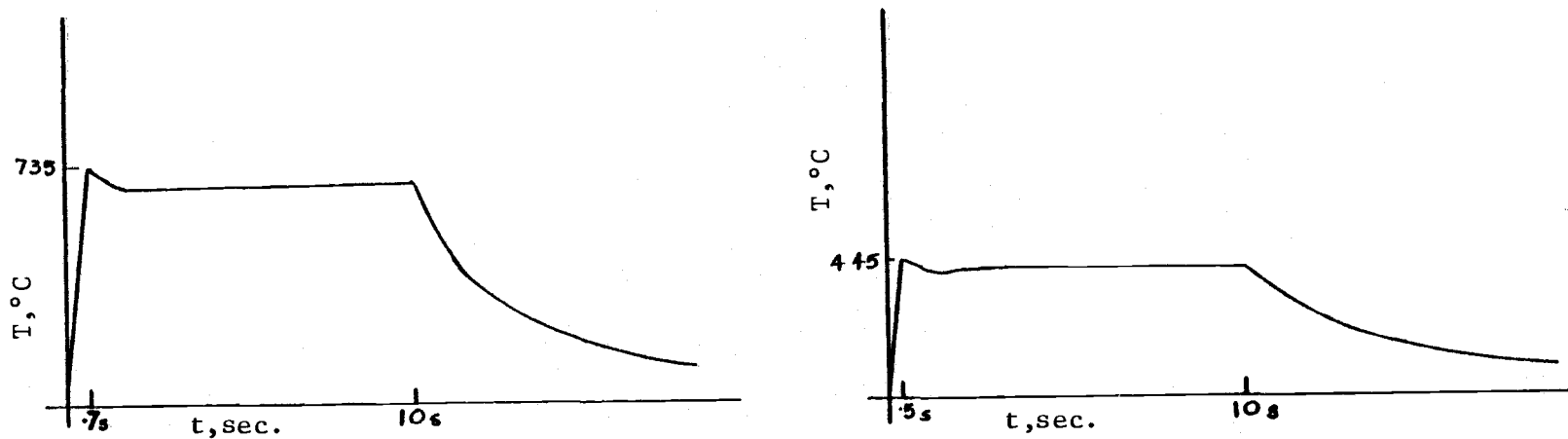


Figure 6. Typical Time-Temperature Histories

rubber septum by means of an air-tight gas sampling syringe. The pyrolysis gas sample was then analyzed by gas chromatography. The tar, present as a mist in the reactor, was prevented from entering the gas syringe by surrounding the tip of the syringe needle with glass wool. Within the reactor, char was completely retained on the screen. Tar was collected on filter paper held firmly at the outlet port. Tar that deposits on the surfaces within the reactor was collected by a solvent (CH_2Cl_2 , reagent grade) wash.

The pyrolysis gases were analyzed on a Hewlett-Packard, Model 5840A, gas chromatograph with dual thermal conductivity detectors. The column used for analysis was 2 m length by 0.32 mm O.D., stainless steel, packed with 80/100 mesh Spherocarb. The chromatograph was temperature programmed from 35°C to 350°C at a rate of 16°C/min. with an initial isothermal holding time of 5 minutes at 35°C. To make up a calibration gas mixture the following procedure was used; the reactor was cleaned, vacuumed and flushed several times with helium. After setting it at atmospheric pressure, known volumes of pure gases were injected into the reactor and mixed thoroughly. The reactor volume was measured to be $4690 \text{ cm}^3 \pm 20 \text{ cm}^3$.

Run Procedure

Approximately 20-25 mg. of powdered cellulose sample was spread in a layer one or two particles deep on a preweighed screen which

was reweighed and stretched taut between the brass electrodes after inserting the thermocouple junction between the folds of the screen. Care was taken to ensure that the thermocouple bead touched the screen surface. The reactor was vacuumed several times and then flushed continuously with helium for 6-7 mins., after which it was set at atmospheric pressure. The sample temperature was then raised to a desired peak temperature at a desired heating rate. The peak temperature was then maintained for a particular time interval or the circuit was immediately broken. Sample cooling then occurred but was not rapid enough to prevent significant weight loss during this period.

After completion of the run, the pyrolysis gases were mixed by operating the fan for 20-30 sec. A known volume of this gas mixture was withdrawn and analyzed by gas chromatography. A slow vacuum was then applied to the reactor and tar was trapped on the filter paper at the outlet port. Tar that condensed on the surfaces within the reactor was collected by wiping with methylene chloride-soaked filter paper. The tar from both these collections was determined gravimetrically by dissolving it in methylene chloride and then evaporating the solvent over a water bath. The char remaining on the screen was also determined gravimetrically. The analysis of the gases produced during pyrolysis permitted components up to 0.1 percent of the cellulose sample weight to be quantitated.

The cellulose used in this study was purified wood cellulose, brand named SOLKA-FLOC, obtained from Brown Co., Berlin, New Hampshire. The general characteristics and analysis of this sample are shown in Table 3. SOLKA-FLOC grade BNB-20 was used.

Experimental Error Analysis

The weight of screen and cellulose was determined to within ± 0.01 mg and hence the uncertainty of the total weight loss measurement was about 0.1 percent by weight of cellulose. Calibration uncertainties, errors in the volume of gas withdrawn for analysis and other factors would introduce uncertainties of up to 5 percent of the species quantitated chromatographically. Water measurements were troublesome because of changes in moisture content of cellulose during or before an experiment. In order to overcome this problem, the cellulose sample was dried in a desiccator for a week and then exposed to atmosphere. The absorbed moisture content was determined gravimetrically to be between 5-7 percent which is in agreement with the analysis of the sample, as shown in Table 3. Chromatographic analysis of water in the product gases also presented problems because of excessive tailing of the water peak and moisture present in the carrier gas helium. Water and other unidentifiable organics in this study were therefore lumped together and determined by difference; char, tar and other gases formed being known. The uncertainty of the thermocouple measurements was $\pm 10^{\circ}\text{C}$ over the present temperature range.

TABLE 3. GENERAL CHARACTERISTICS AND ANALYSIS OF CELLULOSE SAMPLE

Grand name: SOLKA-FLOC, Brown Co., Berlin, N.H.

Grade: BNB-20

Approximate Screen Analysis:

% on 40 mesh	20
% through 100 mesh	48
% through 200 mesh	33

Proximate Analysis:

Ash %	1.7
Volatile %	83.0
Charcoal %	15.3

Ultimate Analysis

Carbon %	45.8
Hydrogen %	6.2
Nitrogen %	0.07
Oxygen %	42.8

Approximate Moisture %	5-7
------------------------	-----

Iron %	0.05
--------	------

Sulphur %	0.0
-----------	-----

Chloride %	0.0
------------	-----

Lignin %	8.0
----------	-----

IV

PYROLYSIS MODELS

Due to the fact that it is impossible to identify all the elementary reactions which occur when cellulosic materials are thermally decomposed, most reported kinetics are based on either the weight of the feedstock or the decomposable weight. Stamm (28) proposed single first-order reaction with respect to the fraction of weight loss, WL:

$$\frac{dWL}{dt} = k(1-WL)$$

This equation implies an equilibrium state of complete weight loss, therefore it is not likely to be valid at high values of conversion. Maa (16) used the unreacted shrinking core model with the assumption of first order kinetics:

$$\frac{dr_c}{dt} = k_{p_0} \exp(-E/RT)$$

where $\frac{dr_c}{dt}$ is the shrinking core rate, cm/s.

k_{p_0} is the apparent frequency factor, cm/s.

E is the apparent activation energy, cal/mole.

Tran (29) assumed the apparent activation energy of pyrolysis to be a linear function of conversion:

$$E = E_0 + ax \quad ; \quad x = \frac{W_0 - W}{W_0}$$

where, W_0 is the initial weight of feedstock, W is the weight of residue at time t and E_0 is the apparent activation energy at zero conversion. An n^{th} order kinetic equation was used to describe the rate of weight loss as:

$$-\frac{1}{W_0} \frac{dW}{dt} = k_0 \exp(-E/RT) f(W)^n$$

where, $f(W)$ is assumed to be $\left(\frac{W}{W_0}\right)$. The logarithmic expression of the above equation at any specific heating rate gives:

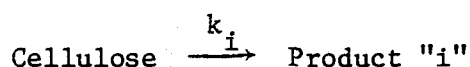
$$\ln \left[-\frac{1}{W_0} \frac{dW}{dt} \right] = - \left[\frac{E_0 + ax}{RT} \right] + \ln k_0 + n \ln \left[\frac{W}{W_0} \right]$$

Some investigators divided the pyrolysis process into two stages (5,12) or three parallel competitive first-order reactions (13). The values for kinetic parameters obtained by various workers are shown in Table 2. The activation energies range from 4.3 kcal/mole to over 70.0 kcal/mole and the pre-exponential factor varies between 0.05 s^{-1} to $1.05 \times 10^{17} \text{ s}^{-1}$. There is, however, a general

consensus amongst the various studies that the pyrolysis step follows a first-order or pseudo first-order kinetics with respect to the weight of the residue.

Single-Step First-Order Reaction Model

A simplified modelling approach that has proved useful in the past for correlating similar data on the rapid pyrolysis of coal (24) and cellulose (20,25) has been used in this study. As a first test of this approach, the appearance of product "i" is modelled as a reaction first order in the amount of "i" yet to be produced. Thus for the reaction,



the assumed first-order reaction rate equation written in the Arrhenius formalism is given by,

$$\frac{dV_i}{dt} = k_{oi} (V_i^* - V_i) e^{-E_i/RT} \quad (1)$$

where, k_{oi} is the pre-exponential factor, E_i is the activation energy for reaction "i", V_i is the amount of product "i" produced up to time t , V_i^* is the amount of product "i" which could potentially be produced (i.e., at $t = \infty$), T is the absolute temperature

and R the universal gas constant. The analytical treatment of Equation (1) for pyrolysis of cellulose conducted under a non-linear temperature-time history has been dealt with by Kayihan (30). The approximate analytical solution is as follows:

Integration of Equation (1) at any time t is given by,

$$V_i = V_i^* \left[1 - \exp(-k_{oi} \int_0^t e^{-E_i/RT} dt) \right] \quad (2)$$

Since temperature, T , is a non-linear function of time, t , for experiments conducted in this study, it becomes necessary to consider time increments of $\Delta t_1, \Delta t_2, \dots, \Delta t_n$, and discrete points in time: $t_0 = 0, t_1 = \Delta t_1, t_2 = \Delta t_1 + \Delta t_2, \dots, t_n = \sum_{j=1}^n \Delta t_j$. Then the integral in Equation (2) can be written as the summation of integrals between two successive times t_{j-1} and t_j .

$$V_i = V_i^* \left[1 - \exp(-k_{oi} \sum_{j=1}^n \int_{t_{j-1}}^{t_j} e^{-E_i/RT} dt) \right] \quad (3)$$

For convenience, define at time t_j ,

$$\phi_i(t_j) = \int_{t_{j-1}}^{t_j} e^{-E_i/RT} dt \quad (4)$$

If $T(t_j) = T(t_{j-1})$, then Equation (4) becomes,

$$\phi_i(t_j) = \Delta t_j e^{-E_i/RT(t_j)} \quad (5)$$

For non-isothermal conditions, assuming Δt_j is small enough to approximate straight temperature profile, the following approximate relation for ϕ_i can be obtained:

$$\begin{aligned} \phi_i(t_j) \approx & \frac{R}{E_i S(t_j)} \left[T^2(t_j) \left[1 - \frac{2RT(t_j)}{E_i} \right] e^{-E_i/RT(t_j)} \right. \\ & \left. - T^2(t_{j-1}) \left[1 - \frac{2RT(t_{j-1})}{E_i} \right] e^{-E_i/RT(t_{j-1})} \right] \end{aligned} \quad (6)$$

where, $S(t_j) = \frac{T(t_j) - T(t_{j-1})}{\Delta t_j}$ and $T(t_j) \neq T(t_{j-1})$

Equation (3) becomes,

$$V_i(t_n) = V_i^* \left[1 - \exp(-k_{oi} \sum_{j=1}^n \phi_i(t_j)) \right] \quad (7)$$

where $\phi_i(t_j)$ is given by Equation (5) and/or Equation (6).

Multiple Reaction Model

The multiple reaction model, to study coal pyrolysis (24) and cellulose pyrolysis (25) was used to further test the validity of the single reaction model. This model is based on the concept that thermal decomposition of a complex compound or compounds consists of a large number of independent parallel first-order decompositions. The rate equation of each may be represented by the

usual Arrhenius Equation 1, having the integrated form shown above in Equation (2). These reactions are further assumed to have identical pre-exponential factors, k_0 , and a continuous distribution of activation energies represented by the Gaussian distribution function,

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp \left[- (E-E_0)^2 / 2\sigma^2 \right] \quad (8)$$

where, E_0 is the mean activation energy (cal/mole) and σ is the standard deviation (cal/mole), with

$$\int_0^{\infty} f(E) dE = 1 \quad (9)$$

$f(E)dE$ represents the fraction of reactions having activation energies between E and $E+dE$. Then V_i^* becomes a differential part of the total volatiles and may be written as,

$$dV^* = V^* f(E) dE \quad (10)$$

The total amount of volatiles yet unreleased is obtained by summing the contribution from each reaction or by integrating Equation (3) over all the values of E using Equation (10). Thus the fractional unaccomplished devolatilization is given by,

$$\frac{V^* - V}{V^*} = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp \left[-k_o \int_0^t \exp\left(\frac{-E}{RT}\right) dt - (E - E_o)^2 / 2\sigma^2 \right] dE \quad (11)$$

recognizing the negligible effect of altering the lower limit of the integral, on the left side, from 0 to $-\infty$. For mathematical tractability, the limits on this integral were set from $E_o - 2\sigma$ to $E_o + 2\sigma$ which includes 95.5 percent of the reaction set.

The experimental data for yields of specific products and total volatiles were fitted to the above models with a finite difference, Levenberg-Marquardt algorithm for solving this non-linear least squares problem. Listings of the computer programs used are included in the Appendix.

V

RESULTS AND DISCUSSION

Effect of Temperature

The commonly used method to represent data obtained by using the electric grid apparatus has been to plot volatile yields as a function of temperature, irrespective of the heating rate, thus not accounting nor representing the differences along the time axis. Secondly, at lower peak temperatures and for the rapid heating rates studied, over 50 percent of the volatilization taking place, occurs in the initial 1-2 seconds of the cooling curve and not during heat-up. Thus a plot of volatiles versus temperature would be misleading and incorrect. In the present study, data have been presented in the form of Tables 4 and 5, indicating the experimental conditions; namely, temperature, heating rate, holding time and yields of individual species or total volatiles obtained at the "so-called" peak temperatures. All yields are expressed as weight percent of the initial cellulose sample.

Keeping the above points in mind, it is seen from Table 4, for conditions mentioned therein, that appreciable decomposition of cellulose begins between 350-400°C. The extent of decomposition increases with temperature until approximately 88 percent of the cellulose is converted to volatiles between 750-800°C. Most of the weight loss appears to take place between 500°C and 650°C. At temperatures above 650°C an asymptotic value, between 87-89 percent,

TABLE 4. ACCEPTED PYROLYSIS RUNS FOR CELLULOSE

Approximate Heating Rate = 1000°C/sec.

Holding Time = 0 sec.

All yields expressed as weight % of initial cellulose sample.

Run #	Peak Temp. °C	Total Volatiles	Char	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	TAR	H ₂ O + HC* (by diff)
1	1052	91.77	8.23	14.33	7.26	1.12	0.58	0.09	22.31	46.08
2	1039	89.28	10.72	15.07	7.96	1.09	0.62	0.15	23.26	41.13
3	992	88.89	11.11	-	-	-	-	-	-	-
4	986	87.65	12.35	13.03	7.62	1.00	0.42	0.16	23.00	42.42
5	985	89.10	10.90	13.81	7.94	1.11	0.50	0.13	23.50	42.21
6	956	88.73	11.27	12.94	8.09	0.95	0.56	0.10	23.50	42.51
7	943	88.07	11.93	-	-	-	-	-	-	-
8	914	88.35	11.65	13.92	7.74	1.16	0.59	0.16	23.40	41.38
9	899	88.00	12.00	-	-	-	-	-	-	-
10	886	87.20	12.80	11.67	8.10	0.97	0.44	0.16	21.31	44.55
11	844	88.50	11.50	12.31	7.20	0.95	0.61	0.10	24.00	43.33
12	830	87.31	12.69	8.98	7.39	0.69	0.30	0.09	22.50	47.36
13	796	88.47	11.53	10.76	8.32	0.81	0.38	0.10	24.91	43.19
14	756	86.48	13.52	9.00	7.34	0.60	0.24	0.12	22.20	46.98
15	752	87.98	12.02	-	-	-	-	-	-	-
16	667	86.12	13.88	5.83	7.10	0.32	0.14	0.00	21.00	51.73
17	652	84.48	15.52	-	-	-	-	-	-	-
18	619	81.22	18.78	3.42	6.12	0.00	0.00	0.00	18.00	53.68
19	618	84.60	15.40	-	-	-	-	-	-	-
20	617	84.95	15.05	4.56	6.80	0.00	0.00	0.00	21.09	52.50
21	606	78.44	21.56	-	-	-	-	-	-	-
22	590	78.19	21.81	-	-	-	-	-	-	-
23	590	73.11	26.89	2.84	6.10	0.00	0.00	0.00	17.00	47.17
24	546	45.35	54.65	0.50	3.33	0.00	0.00	0.00	13.85	27.67
25	522	47.40	52.60	-	-	-	-	-	-	-

TABLE 4, Continued

Run #	Peak Temp. °C	Total Volatiles	Char	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	TAR	H ₂ O + HC * (by diff)
26	519	32.63	67.37	-	-	-	-	-	-	-
27	516	41.40	58.60	-	-	-	-	-	-	-
28	449	8.88	91.12	0.00	0.59	0.00	0.00	0.00	10.25	0.00
29	440	9.67	90.38	-	-	-	-	-	-	-
30	432	9.48	90.52	-	-	-	-	-	-	-
31	426	8.26	91.74	-	-	-	-	-	-	-
32	406	7.87	92.13	-	-	-	-	-	-	-
33	384	8.11	91.89	-	-	-	-	-	-	-
34	345	3.56	96.44	-	-	-	-	-	-	-
35	292	3.50	96.50	-	-	-	-	-	-	-

* HC: Hydrocarbons.

TABLE 5. ACCEPTED PYROLYSIS RUNS

Approximate Heating Rate = 1000°C/s			
Holding time = 10 sec.		Holding time = 20 sec.	
Approx. Peak Temperature °C	Total Volatiles wt %	Approx. Peak Temperature °C	Total Volatiles wt %
862	90.72	951	92.00
782	89.51	900	90.42
702	87.93	816	88.95
602	85.70	697	87.66
522	83.34	603	86.49
420	71.82	491	81.90
317	8.87	408	66.35
		298	8.32

Approximate Heating Rate = 500°C/s			
Holding time = 0 sec.		Holding time = 15 sec.	
Peak Tempera- ture °C	Total Volatiles wt %	Approx. Peak Temperature °C	Total Volatiles wt %
1017	90.08	998	92.01
880	88.54	856	91.43
820	88.13	795	89.44
700	86.40	715	88.00
595	84.30	587	86.33
446	46.39	500	83.30
390	13.15	425	72.11

Approximate Heating Rate = 100°C/s			
Holding time = 0 sec.		Holding time = 20 sec.	
Peak Tempera- ture °C	Total Volatiles wt %	Approx. Peak Temperature °C	Total Volatiles wt %
974	90.92	680	86.65
890	92.21	594	85.62
821	87.71	573	85.27
699	86.15	504	81.30
607	85.11	494	84.01
515	82.78	387	73.43
388	31.29		

is reached for the total volatiles produced. At temperatures above 990°C, zero holding time, there appears to be a slight increase in total volatiles produced. This increase is due to very fine (soot-like) carbon particles being carried away from the hot screen by the evolved gases. This carbon was deposited on the roof of the reactor dome. This is purely a physical transportation process rather than any further chemical change in the pyrolysis mechanism at these elevated temperatures.

At temperatures above 600°C, both CO and CO₂ formed show an increasing trend, the difference being, CO₂ reaches an asymptotic value of approximately 7.7 percent around 750°C, while CO keeps increasing to approximately 14.5 percent at 1050°C and does not show any trend towards achieving an asymptotic value.

Methane and ethylene start forming above 650°C, while ethane forms at 750°C and above. The quantities of these gases formed is small, being ≤ 1 percent for CH₄, ≤ 0.6 percent for C₂H₄ and ≤ 0.15 percent for C₂H₆. Methane formed increases with temperature and reaches an asymptotic value of approximately 1.0 percent at about 850°C. Ethylene shows a more gradual increase with temperature, reaching an asymptotic value of approximately 0.6 percent around 900°C. Because of minute quantities formed, the scatter in values of C₂H₆ formed is more pronounced, arising probably from errors in gas chromatograph analysis.

The method and difficulty in collecting tar and determining it gravimetrically makes its measurements subject to greater errors. At temperatures as low as 450°C, tar formation dominates over all the other products formed, being approximately 10 percent, and then increases to a value of approximately 22 percent at 750°C. Beyond 750°C, tar yields reach an asymptotic value of 23 percent. This pattern observed in tar formation may be explained on the basis that at low temperatures tar formation is favored, but not its cracking to lighter gases and other hydrocarbons. Because of the high heating rate, tar formed does not have a chance to escape from the hot cellulose matrix where it is formed, and at high temperatures undergoes secondary cracking. This is verified by the fact that CH_4 , C_2H_4 , and C_2H_6 start forming at 650°C and above.

Water and other unidentifiable products formed are lumped together and determined solely by difference. These products start forming around 400°C, go through a maximum at approximately 600°C and then decrease to an asymptotic value of approximately 43 percent with any further increase in temperature. The temperature at which the maximum occurs, coincides with the temperature at which tar formed, reaches an asymptotic value of 23 percent. It also coincides with increases in CO and CO_2 formation. All this appears to indicate that at temperatures below 600°C, tar formation (along with possibly liquid products) is favored. Another fact that has not

been looked into nor discussed is the possibility, at high heating rates, of absorbed moisture interreacting with organic compounds formed within the hot cellulose matrix to yield hydrolyzed products.

Thus, for heating rates of approximately 1000°C/s and zero holding time, most of the decomposition is achieved at or above 750°C during the heat-up period itself. Tar which was formed and could not escape from the hot cellulose matrix undergoes secondary cracking resulting in the formation of CH_4 , C_2H_4 , and C_2H_6 and a marked increase in CO and CO_2 formation. This seems to suggest that a dominant portion of the gases formed comes from secondary cracking of tar rather than from the primary decomposition of cellulose.

The kinetic parameters obtained for individual products CO , CO_2 , CH_4 , C_2H_4 , C_2H_6 and tar, by fitting the data to a first-order reaction model, are listed in Table 6. This reaction model, which lays stress on V_i^* (yield of product "i" at $t = \infty$) could not be applied to the data obtained for water plus other organic compounds since these products go through a maxima before reaching an asymptotic value at higher temperatures.

The values obtained for activation energy and pre-exponential factors, for the above products, are much lower than the values for typical organic decomposition reactions (24). The probable reason is that when a single first-order reaction is used to model

TABLE 6. SUMMARY OF BEST-FIT KINETIC PARAMETERS FOR SINGLE-ORDER REACTION MODEL OF CELLULOSE RAPID PYROLYSIS

Heating Rate = 1000°C/s
Holding Time = 0 sec.

Product	E_1 , kcal/mole	k_{o1} , s ⁻¹	V^* , wt %
Carbon Monoxide	16.46	7.3×10^3	14.06
Carbon Dioxide	20.97	7.02×10^5	7.70
Methane	28.80	3.71×10^6	1.06
Ethylene	32.90	2.58×10^7	0.54
Ethane	31.77	1.8×10^7	0.13
Tar	9.58	0.55×10^3	23.29

Product: Total Volatiles

Heating Rate °C/s	Holding Time sec.	E , kcal/mole	k_o , sec ⁻¹	V^* , wt %
1000	0	23.47	44.51×10^5	88.39
1000	0,10,20	23.26	46.5×10^5	87.87
500	0	22.25	62.51×10^5	87.54
500	0,15	22.27	64.01×10^5	86.91
100	0	15.53	0.41×10^5	87.87
100	0.20	15.60	0.43×10^5	86.68
100,500,1000	0	14.96	0.21×10^5	88.80
100,500,1000	0,10,15,20	20.25	6.97×10^5	87.71
500,1000	0,10,15,20	21.12	11.90×10^5	87.80

KINETIC PARAMETERS OBTAINED FOR MULTIPLE REACTION MODEL USING GAUSSIAN DISTRIBUTION OF ACTIVATION ENERGY:

Heating Rate = 1000°C/s
Holding Time = 0 sec.

$$k_o = 45.08 \times 10^5 \text{ sec}^{-1}$$

$$E_o = 23.61 \text{ kcal/mole (mean activation energy)}$$

$$\sigma = 0.034 \text{ kcal/mole (standard deviation)}$$

cellulose pyrolysis, the activation energy and pre-exponential factor are forced to be very low in order to fit the overall temperature dependence that actually results from the occurrence of different reactions in different temperature intervals. It is also important to emphasize that these kinetic parameters serve only as a useful means of correlating the experimental data and in no way do they reflect the detail chemistry of the complex decomposition process of cellulose.

Figures 7 through 12 show the comparison of calculated and experimental fractional weights of products formed at a heating rate of 1000°C/s, zero holding time, and over the temperature range 300-1100°C; best fit being the 45° line. The first-order reaction model, though not a true representation, shows good fits for CO, CO₂, CH₄, and tar. The large scatter observed for C₂H₄, and C₂H₆, as mentioned earlier, is probably due to errors introduced during analysis.

Comparison of the kinetic parameters for overall volatilization at 1000°C/s, obtained using the single reaction model and multiple reaction mode, shows nearly identical values for activation energy, 23.47 kcal/mole and 23.61 kcal/mole, identical values for pre-exponential factor $4.47 \times 10^6 \text{ sec}^{-1}$, and a very low value of 0.034 kcal/mole for σ (standard deviation for the distribution function). These values indicate that the single reaction is

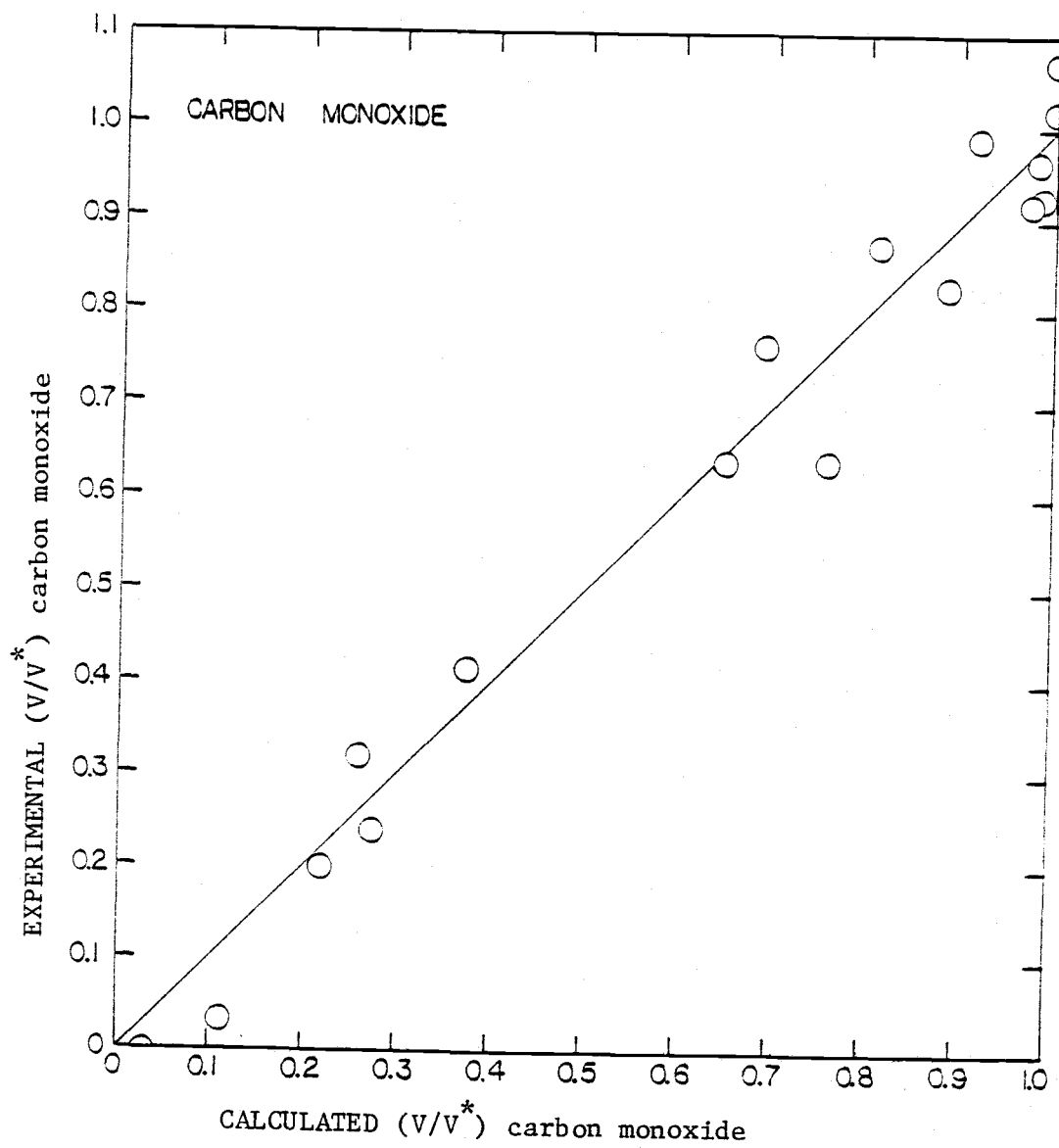


Figure 7

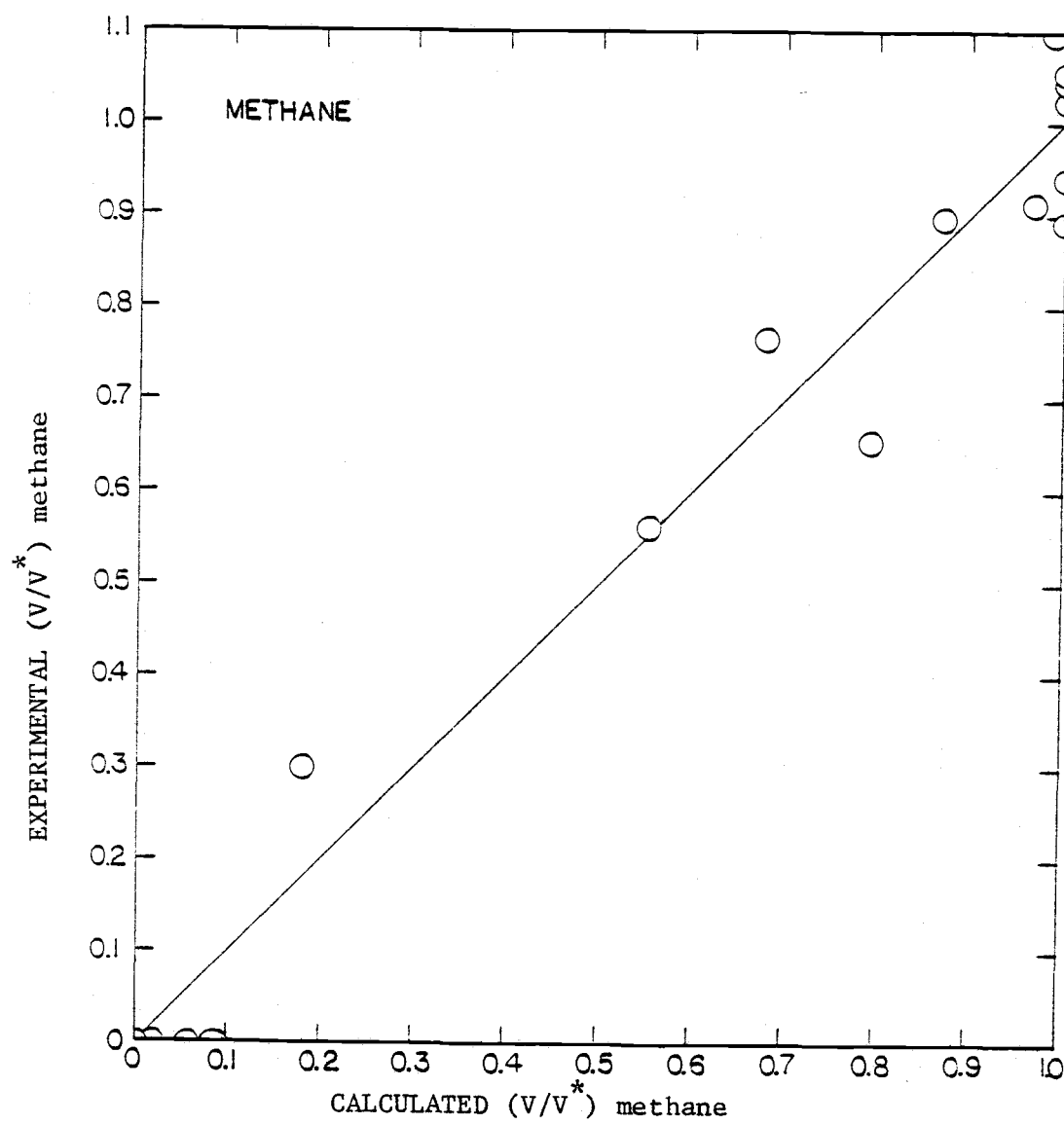


Figure 9

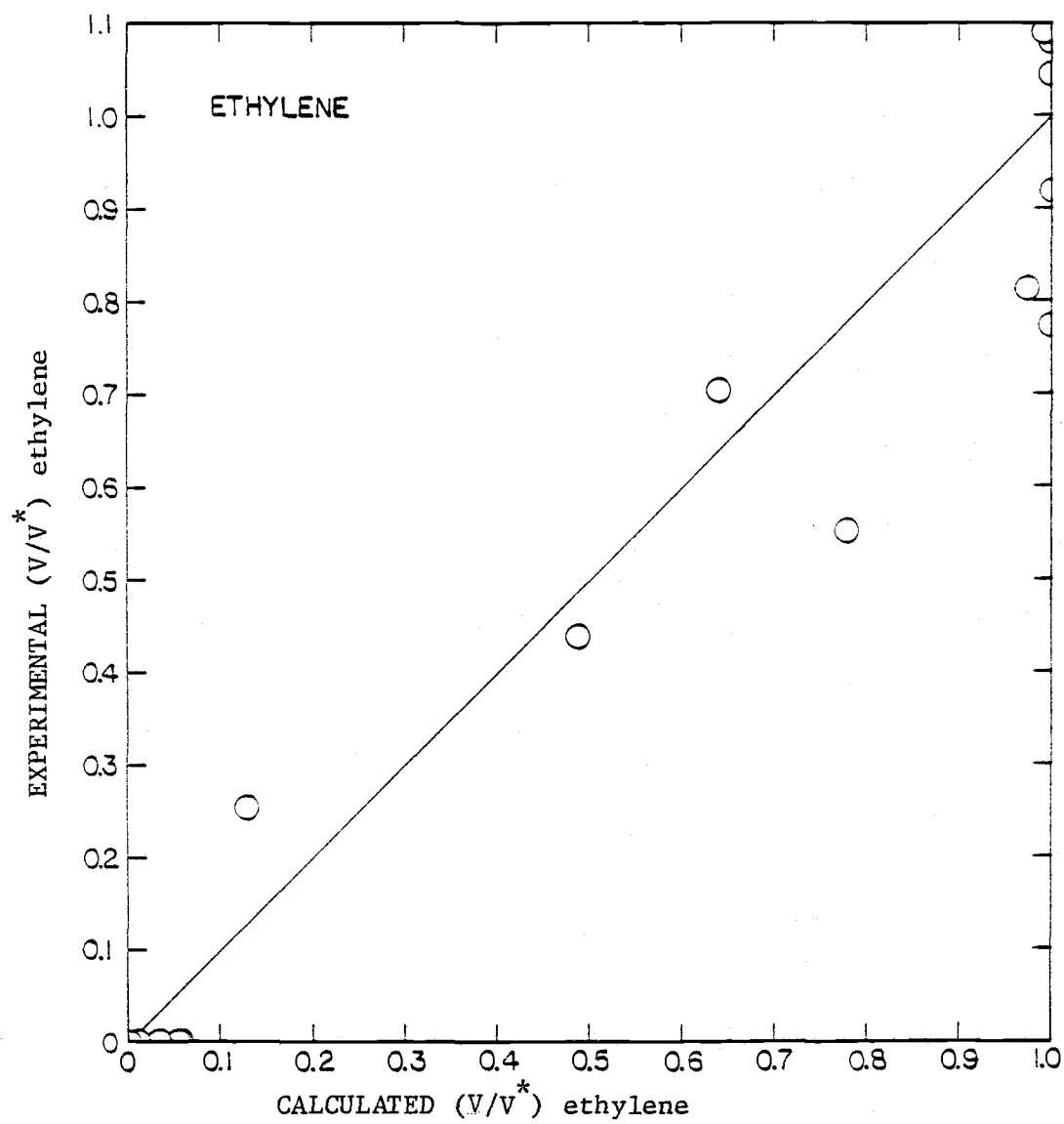


Figure 10

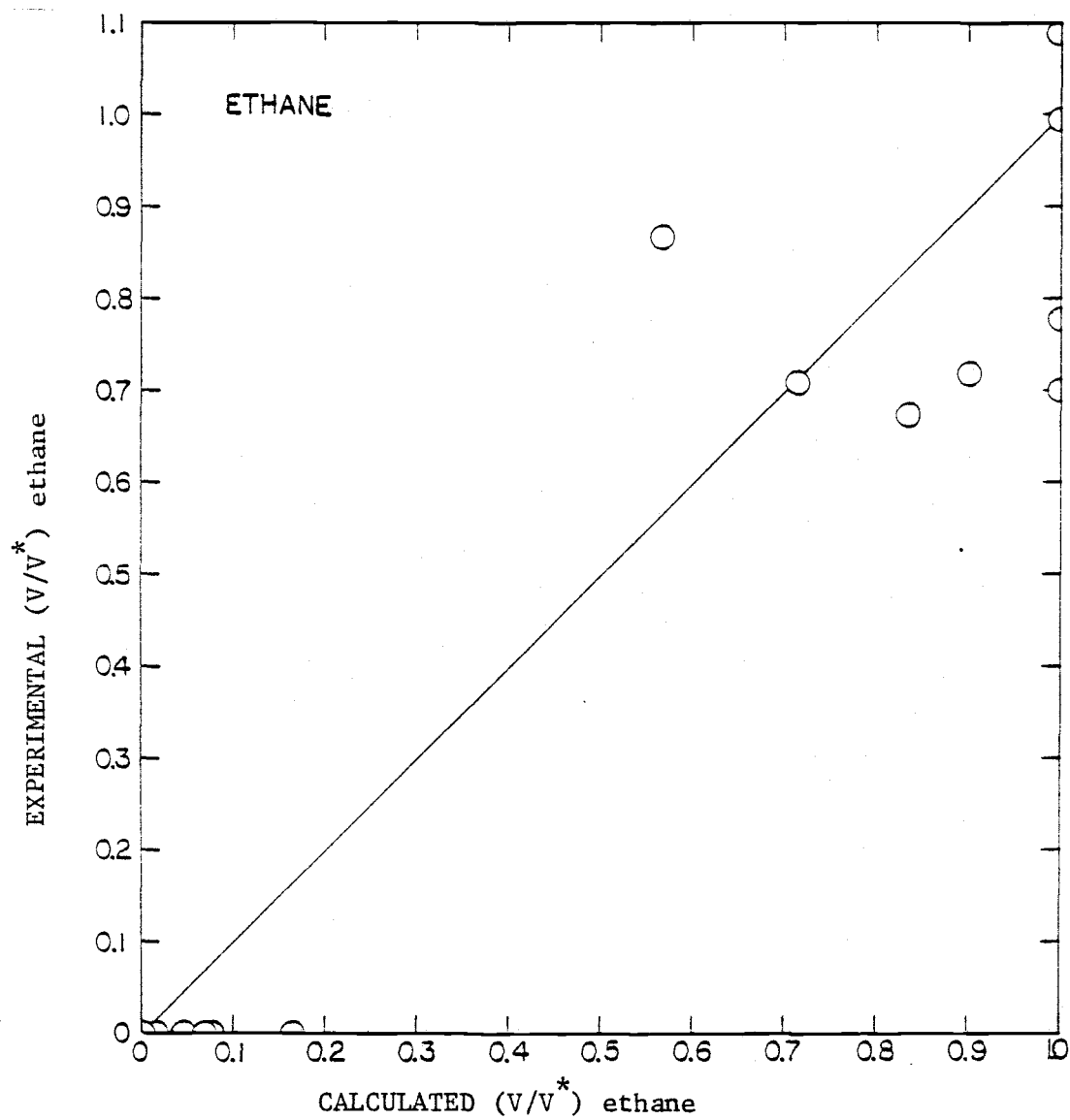


Figure 11

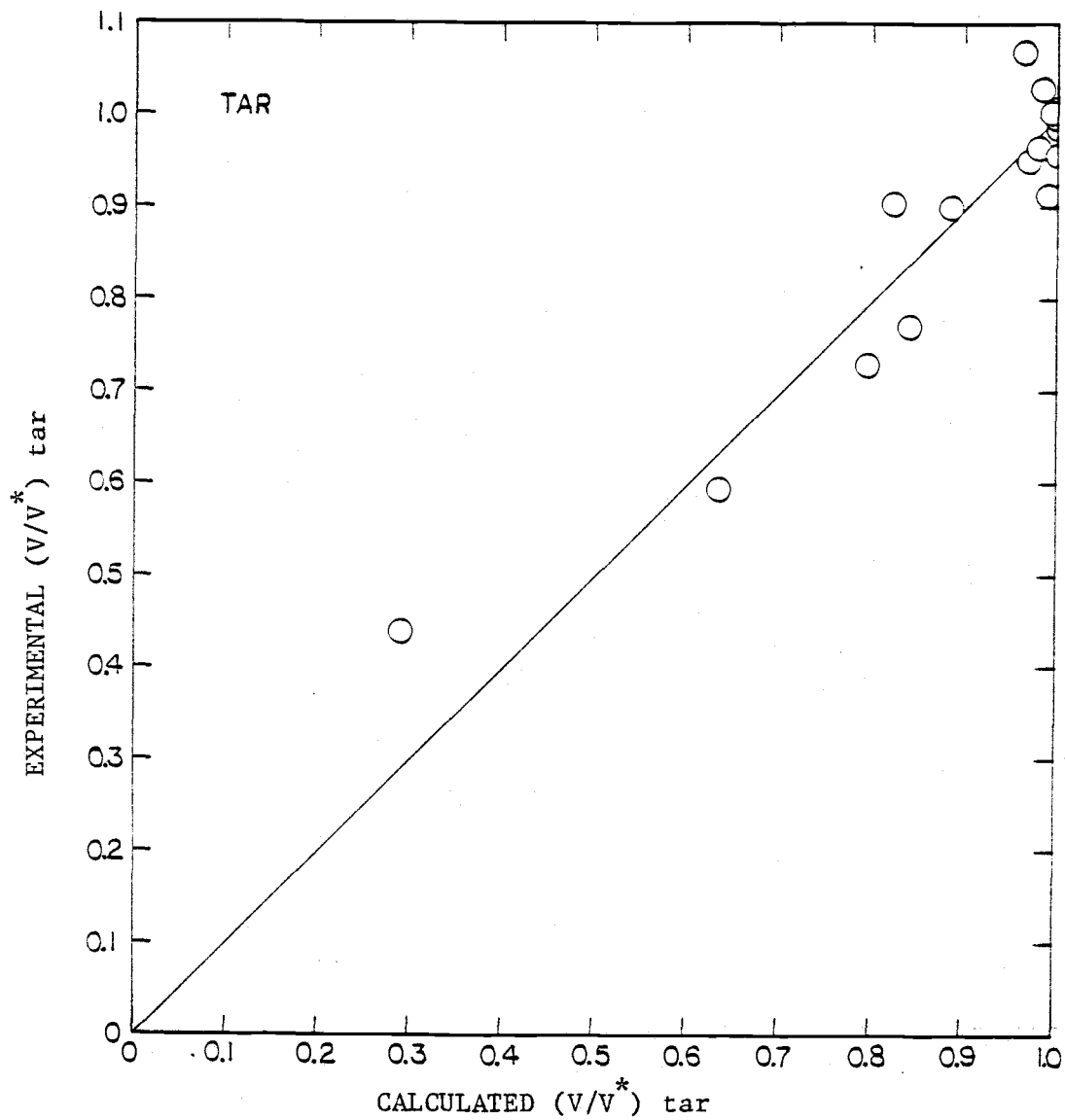


Figure 12

adequate over the temperature range 300-1100°C to correlate the data.

Effect of Heating Rate

Heating rates of approximately 100, 500 and 1000°C/s were studied to obtain peak temperatures in the range 300-1100°C to study cellulose pyrolysis. At a given peak temperature and zero holding time, more volatilization takes place for sample heated at 100°C/s than for those heated at 500°C/s or 1000°C/s. This expected result arises because at lower heating rates, more time is available for conversion during the heat-up period. As an example, values from Tables 4 and 5 indicate that for a peak temperature of approximately 400°C the total volatiles obtained for different heating rates are as follows: 7.87 percent at 1000°C/s; 13.15 percent at 500°C/s; and 32 percent at 100°C/s. Amounts of tar and other products formed at 100°C/s and 500°C/s were not determined and, hence, no comments can be made on the mechanism of the process at these heating rates. Once again, values of 90 percent and higher for total volatiles, exhibited at high temperature, are due to very fine carbon particles being carried away from the hot screen by the gases evolved.

The kinetic parameters for the above-mentioned heating rates and zero holding time are listed in Table 6. Plots of experimental

versus calculated values in Figure 13, 15 and 17, show good fits to the data using the single reaction model. An interesting fact that emerged was the significant differences in kinetic parameters obtained for different heating rates. Attempts at obtaining a fit for all the heating rates combined resulted in a poorer fit of data to the single reaction model, as seen in Figure 19. The possible reasons for this are discussed later in this chapter.

Effects of Solids Residence Time

With the electric grid apparatus used, solids residence time or holding time is defined as the total period, including heat-up time and the time for which the solid sample is maintained at a desired peak temperature before letting the sample cool down. The effect of holding times on the overall volatilization is shown in Tables 4 and 5 for different heating rates. The magnitude of the effect of holding time at lower temperatures is more pronounced. This is due to the fact that at lower peak temperatures and zero holding time pyrolysis of cellulose is essentially incomplete. Any holding time provided at these temperatures shows a significant increase in the yields of volatiles produced. At higher temperatures, with zero holding time, the reaction is rapid enough to yield the maximum volatiles obtainable at that temperature and above, during the heat-up period itself, providing holding times at these

temperatures show no further change in the total volatiles yielded.

The kinetic parameters obtained for the different heating rates and for zero and non-zero holding times are shown in Table 6. Plots of experimental versus calculated values are shown in Figures 14, 16 and 18. For a particular heating rate, the kinetic parameters obtained are nearly identical for zero holding time and for combined zero and non-zero holding times. This seems to indicate that the reaction mechanism is the same during heat up and the isothermal holding period, though perplexingly different for each heating rate.

The V^* values obtained lie between 86.7-88.8 percent. Approximate analysis indicates volatile matter (VM) to be equal to 83 percent. The greater-than-one ratio of V^*/VM is reasonable since char formation is inhibited at high heating rates and temperatures.

A possible explanation for the difference in kinetic parameters obtained at various heating rates could be the presence of a heat transfer resistance between the cellulose particle and the screen being heated. This heat transfer resistance would play an important role as the heating rate is increased tenfold from 100°C/s to 1000°C/s. It is, therefore, possible that the sample does not see the same temperature-time history as the screen, there being a significant time lag. Since the temperature time history plays an important role in fitting data to the pyrolysis model, any errors in it would introduce significant errors in the kinetic parameters

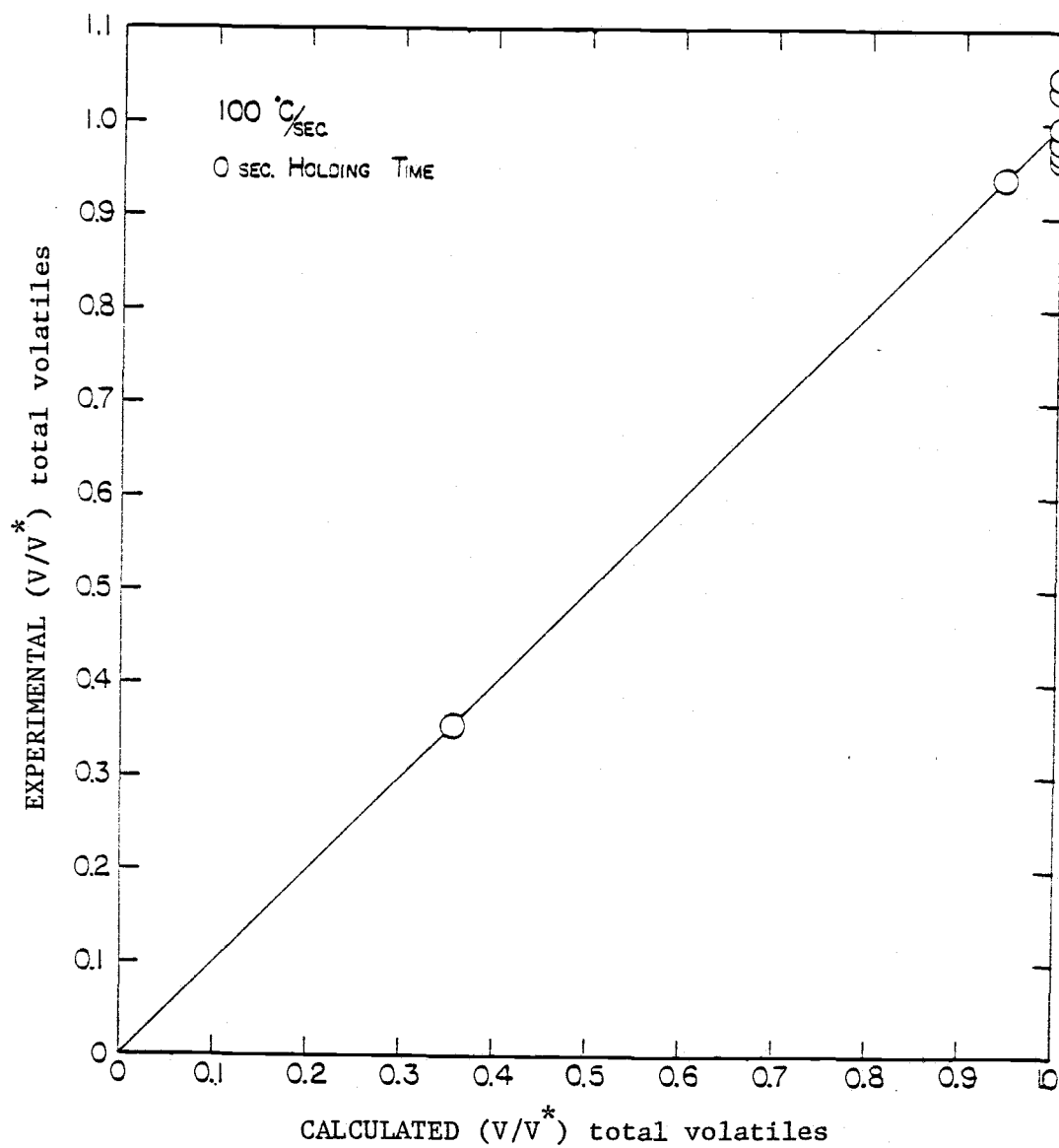


Figure 13

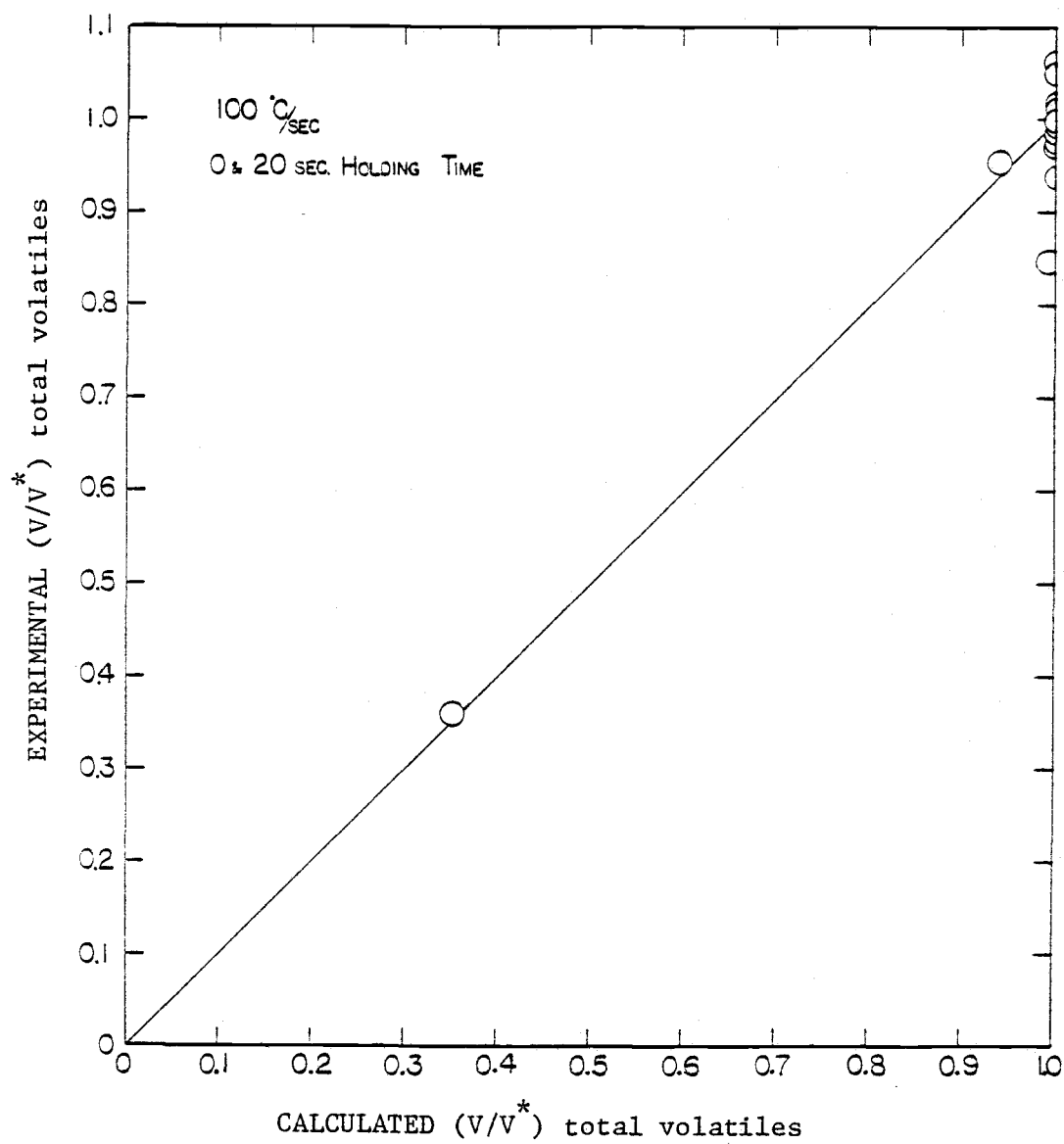


Figure 14

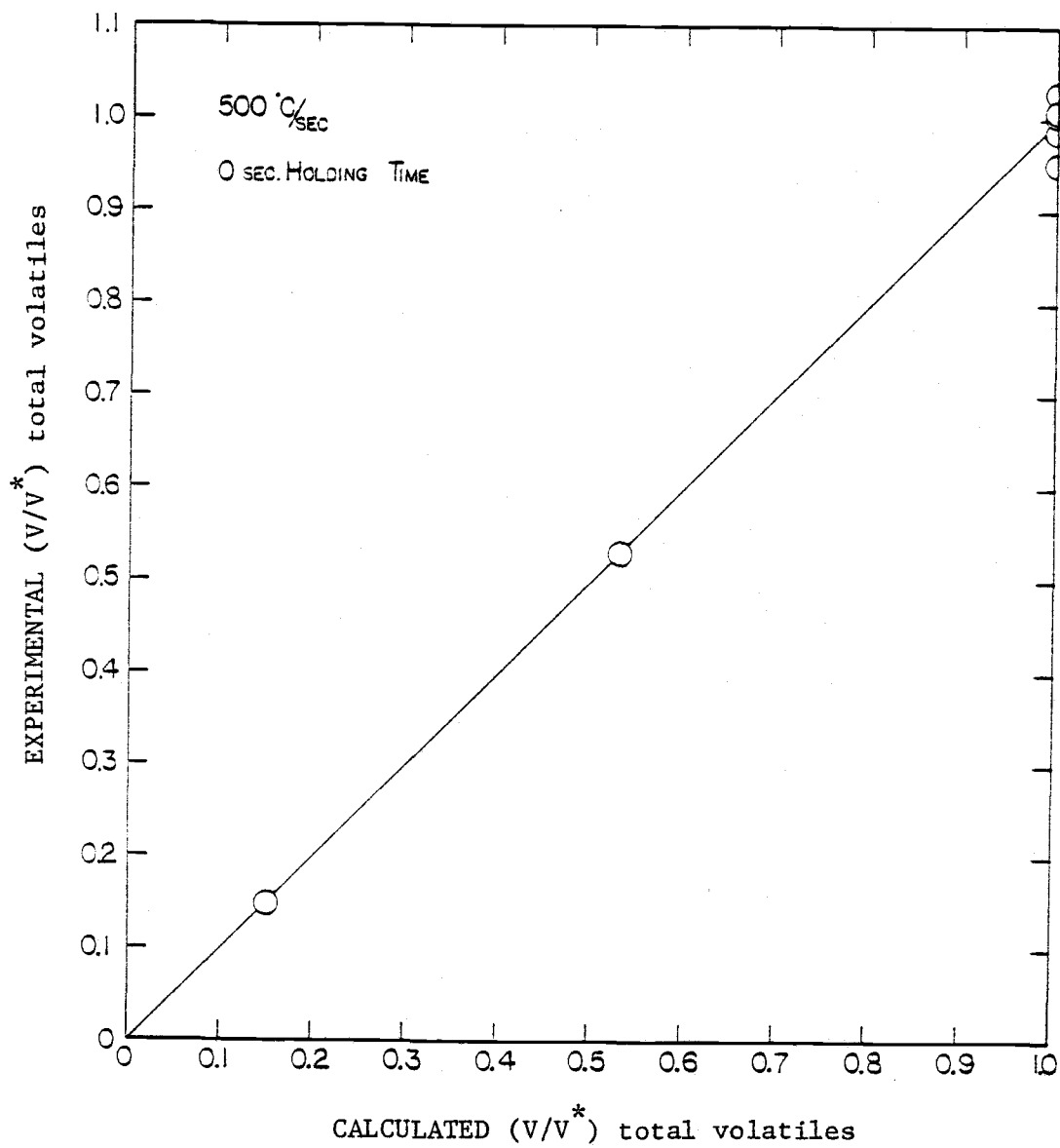


Figure 15

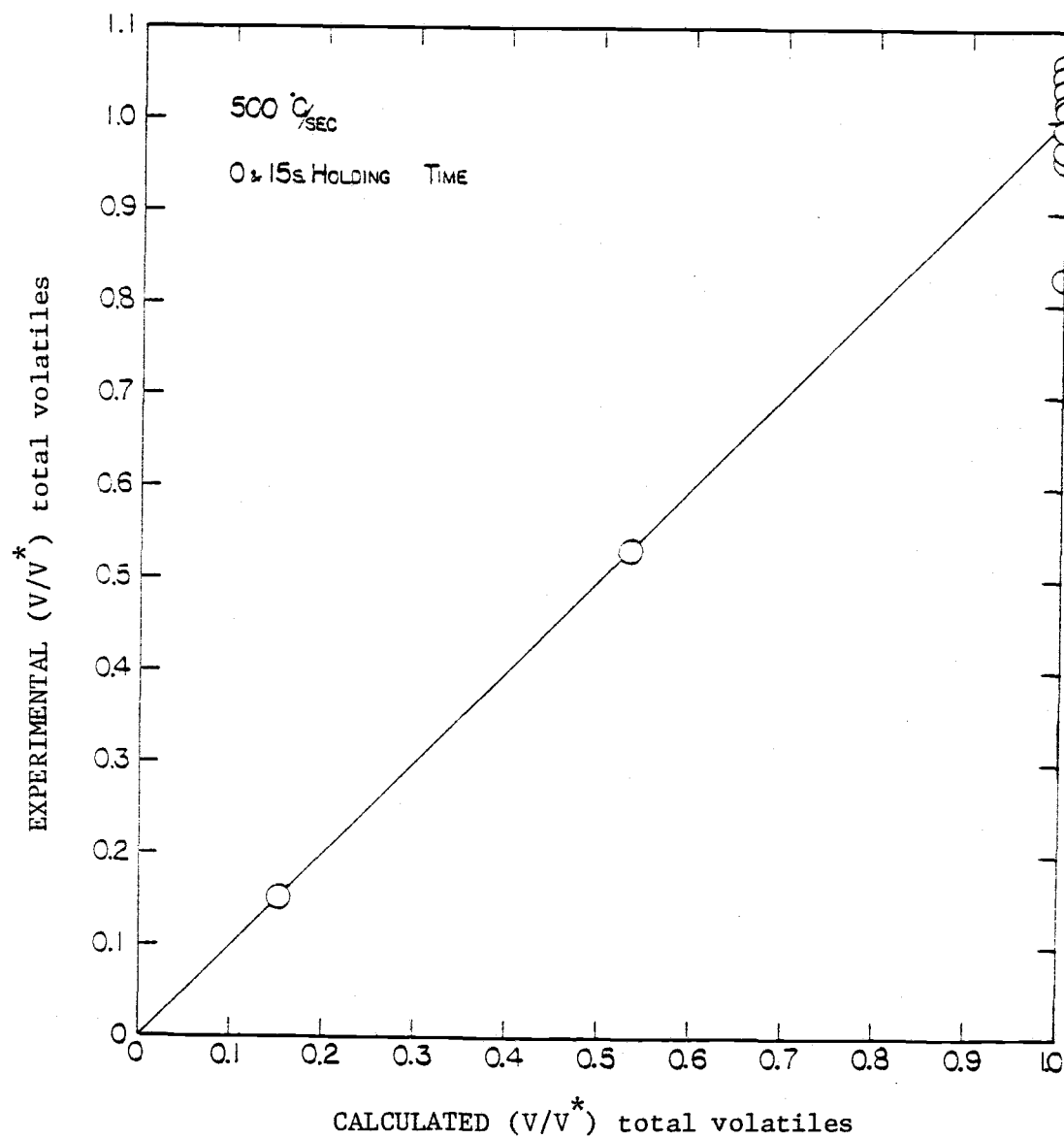


Figure 16

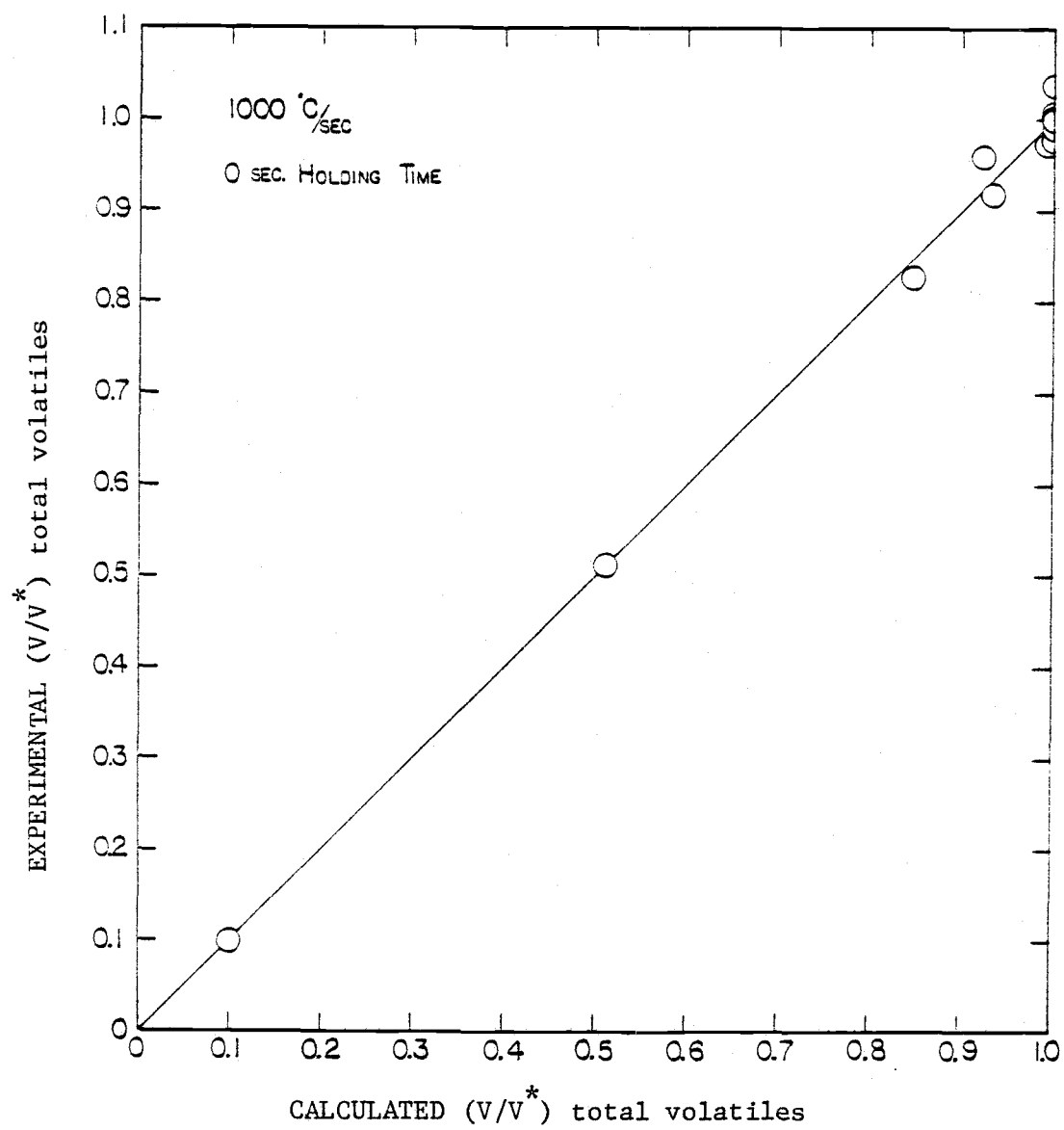


Figure 17

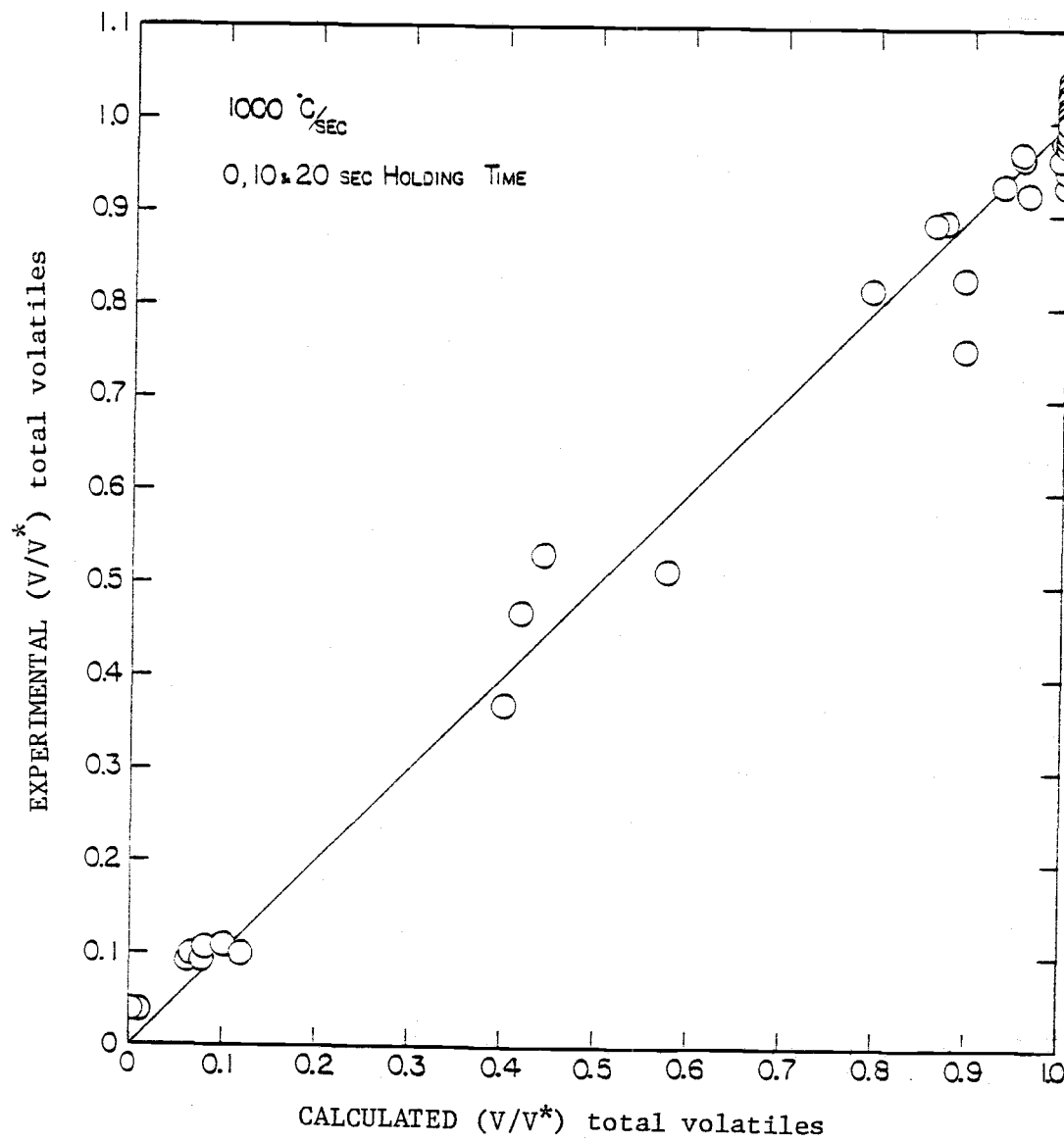


Figure 18

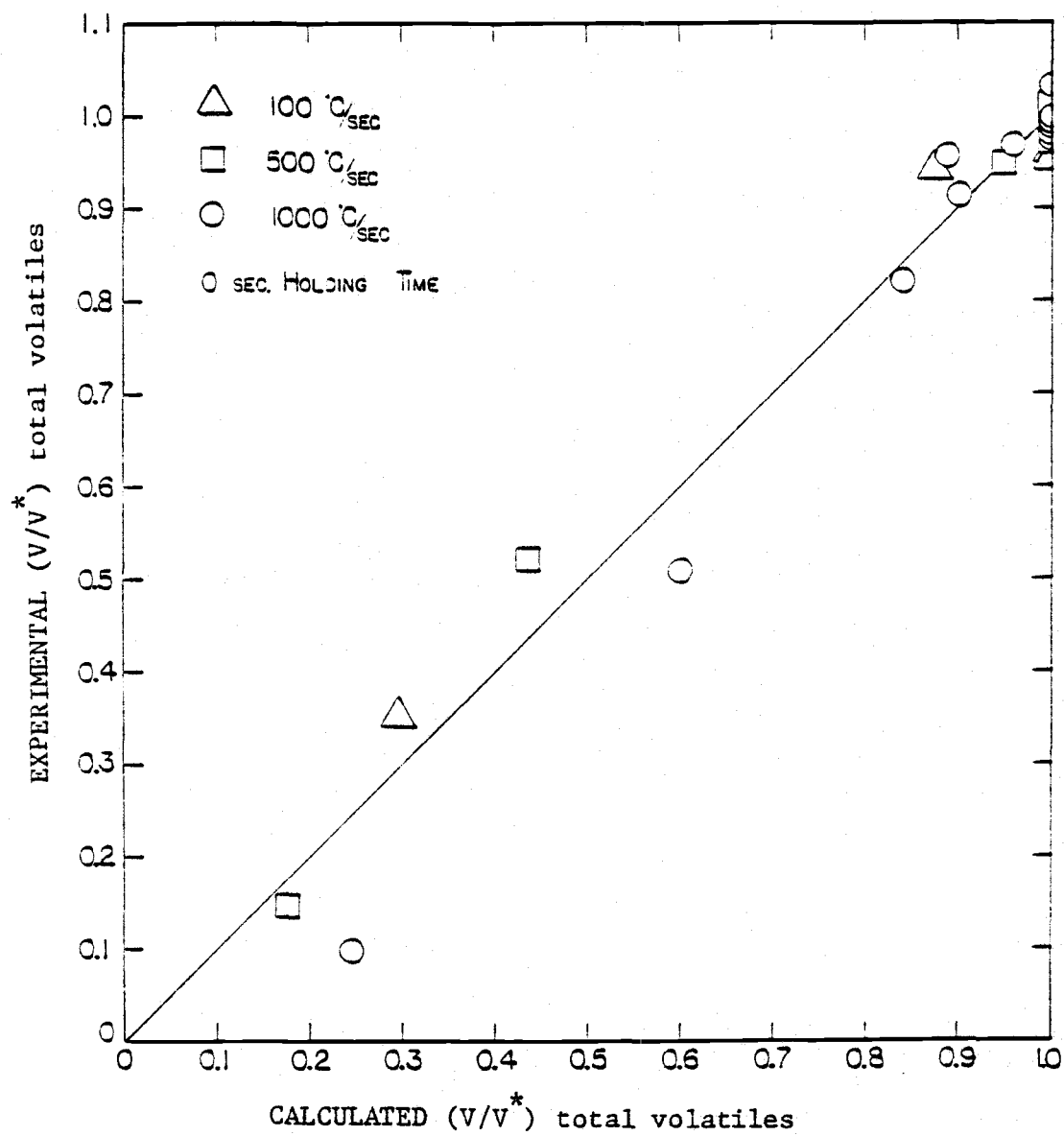


Figure 19

obtained. This, in turn, would question the ability and limits of the electric grid system regarding heating rates and sample sizes permissible.

Another possible explanation could be that the reaction mechanism is truly different at different heating rates, resulting in the wide variation in kinetic parameters. The difference in mechanism could be arising due to competition between mass transfer and secondary cracking, but the small particle size precludes that possibility.

The third explanation questions the experiments carried out at low temperatures with zero holding time, since at low temperatures, most of the volatilization takes place during the initial period of the cooling curve (where the cooling rate is approximately 100°C/s) and not during heat up where the heating rate is 100, 500 or 1000°C/s . The kinetic parameters shown for each heating rate would therefore be a misrepresentation. An improvement in experimental method would involve carrying out experiments at different heating rates, but having large holding times at lower peak temperatures till further increments in holding times show no changes in volatile yield. This would eliminate or minimize the effects of the cooling curve where the initial cooling rate varies from 100°C/s for a peak temperature of 400°C , to about 300°C/s for a peak temperature of 1000°C/s . The amount of volatilization taking place in the initial

part of the cooling curve, for low peak temperatures, is verified by simulating volatile formation as a function of time for different heating rates and their respective kinetic parameters. The cooling portion of the temperature-time profiles used for simulation were similar to those observed during experimental runs for different peak temperatures. Figures 22, 23 and 24 show the effects of zero and non-zero holding time.

Figures 20 and 21 show the poor fits obtained when an attempt was made at grouping the different heating rates together. The kinetic values appear to be an average for the combination of all heating rates, there being a greater bias towards the kinetic parameters obtained for 1000°C/s alone. The reason for this bias is due to the fact that 50 experiments were conducted at 1000°C/s, whereas only 14 experiments were conducted at 500°C/s and 100°C/s, respectively. The logarithmic plots of rate constant versus reciprocal absolute temperature, and simulated volatile formation as function of time are shown in Figures 25 and 26. The differences in kinetic values then become apparent.

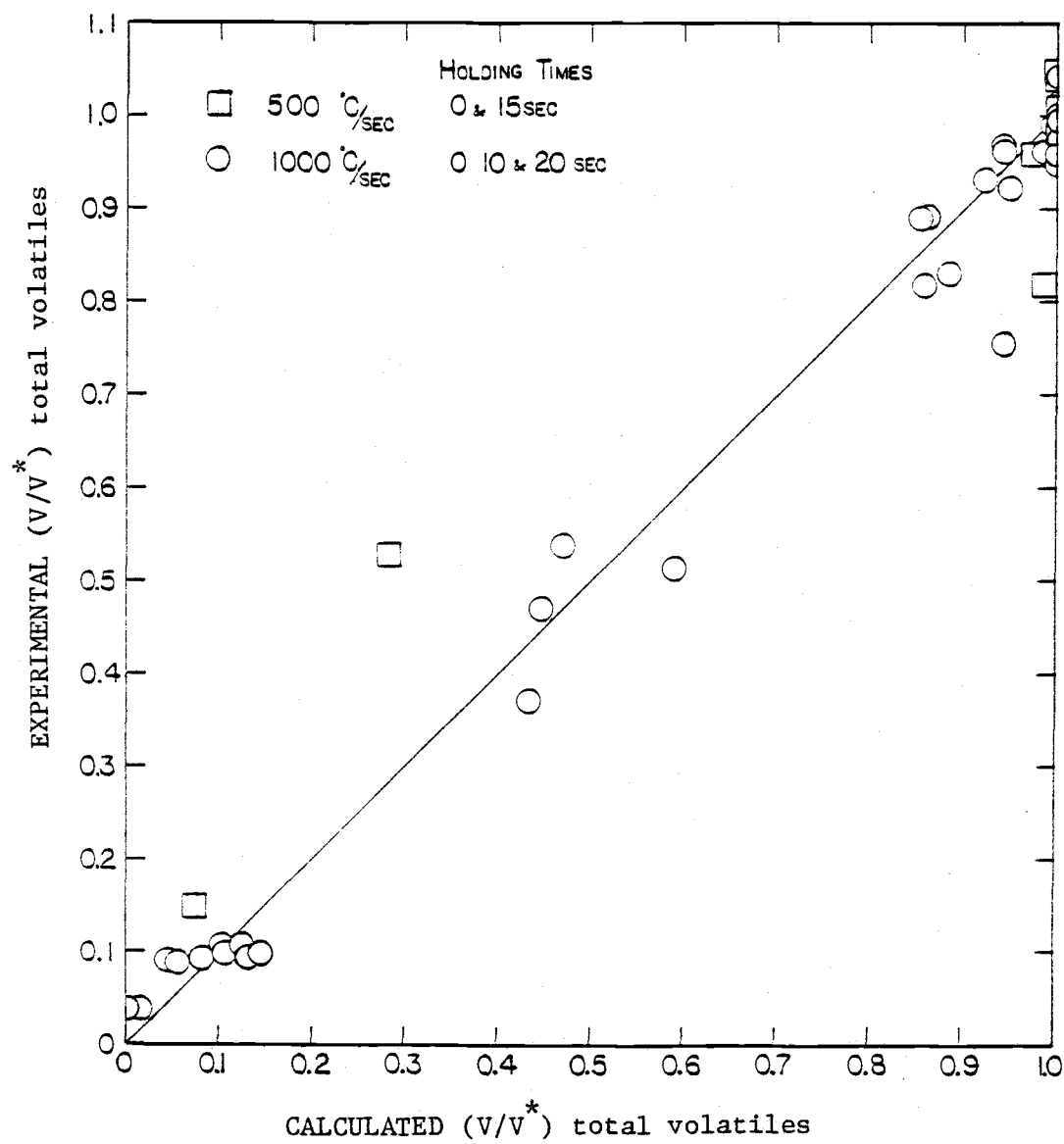


Figure 21

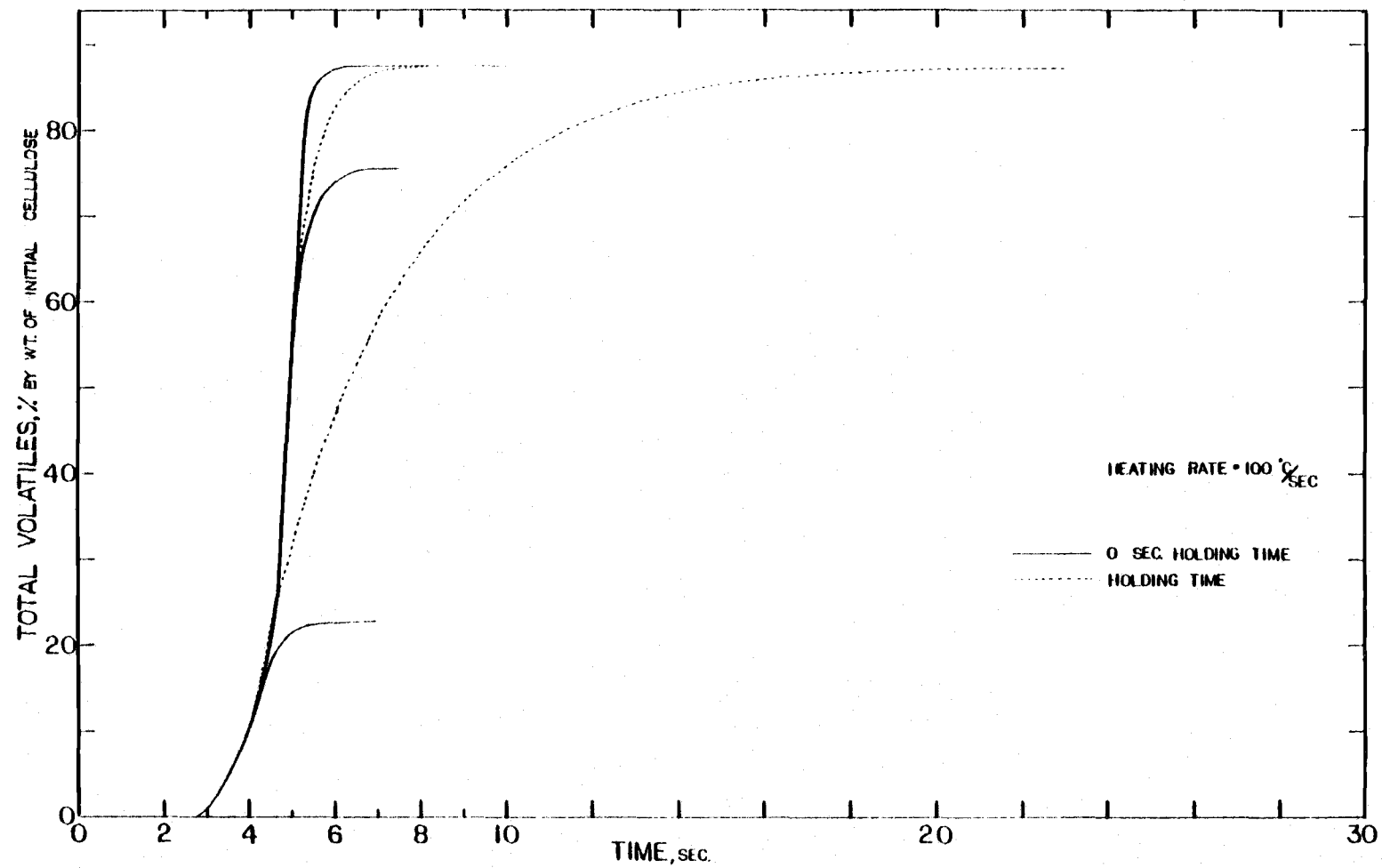


Figure 22

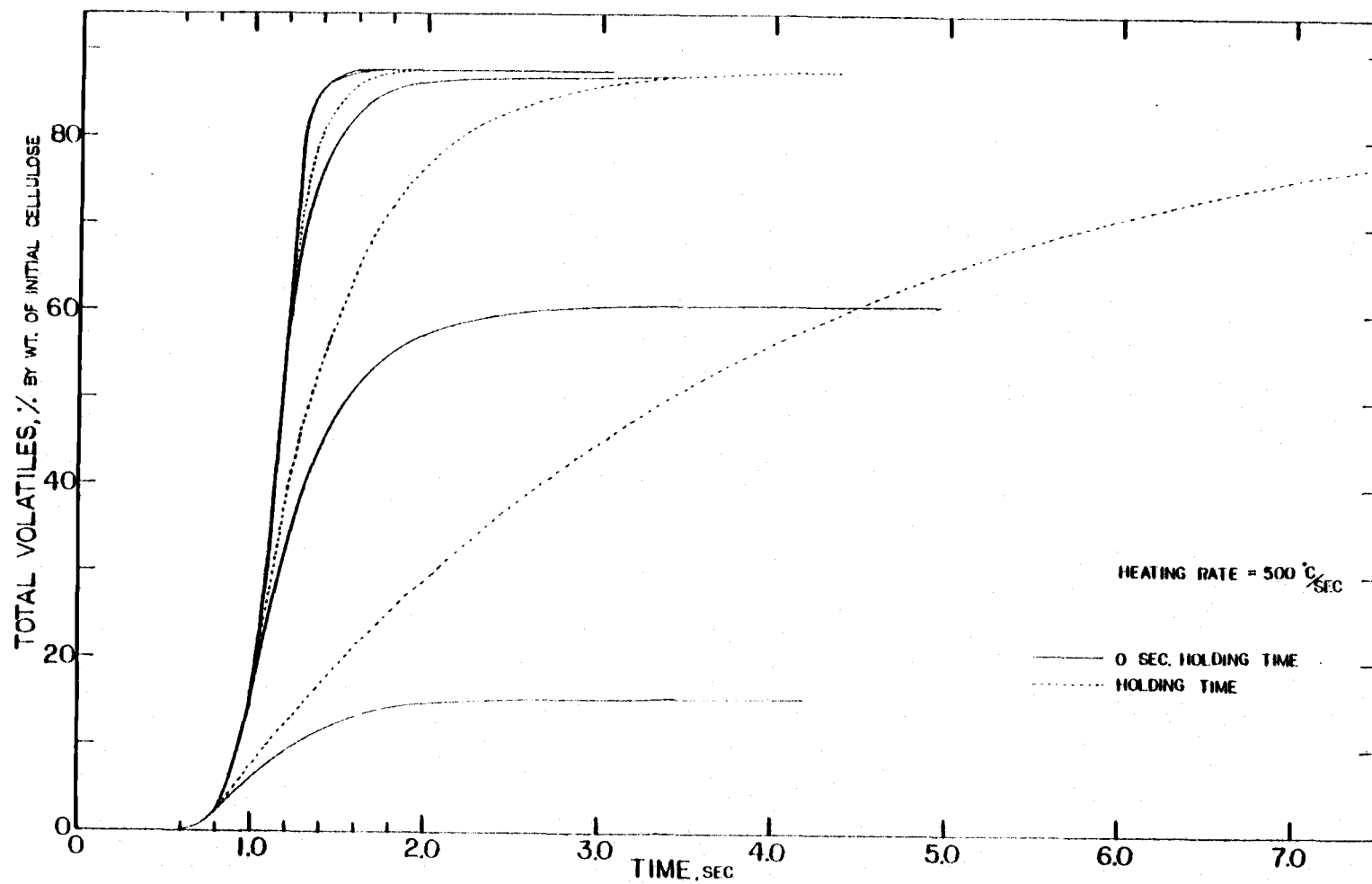


Figure 23

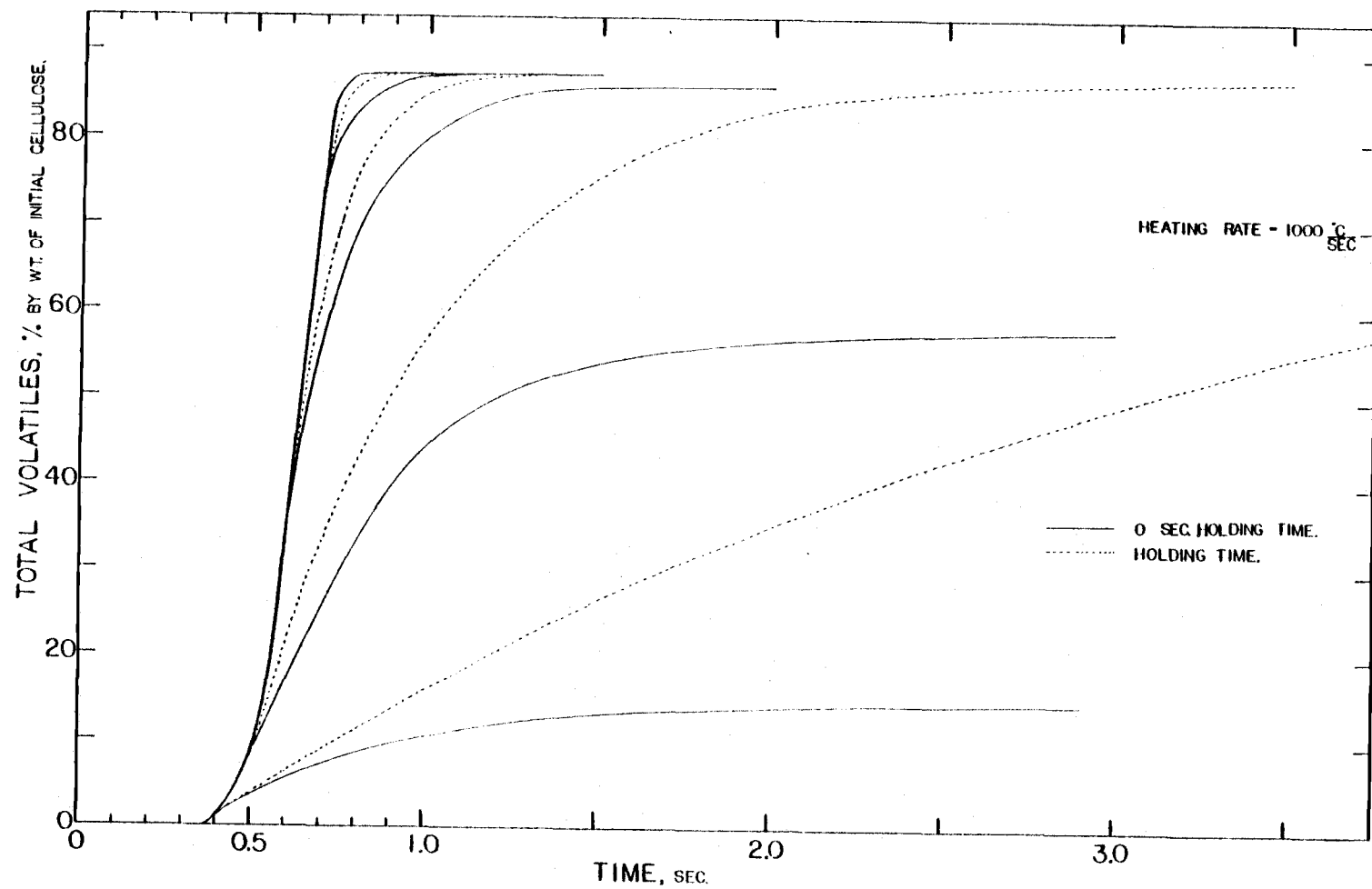


Figure 24

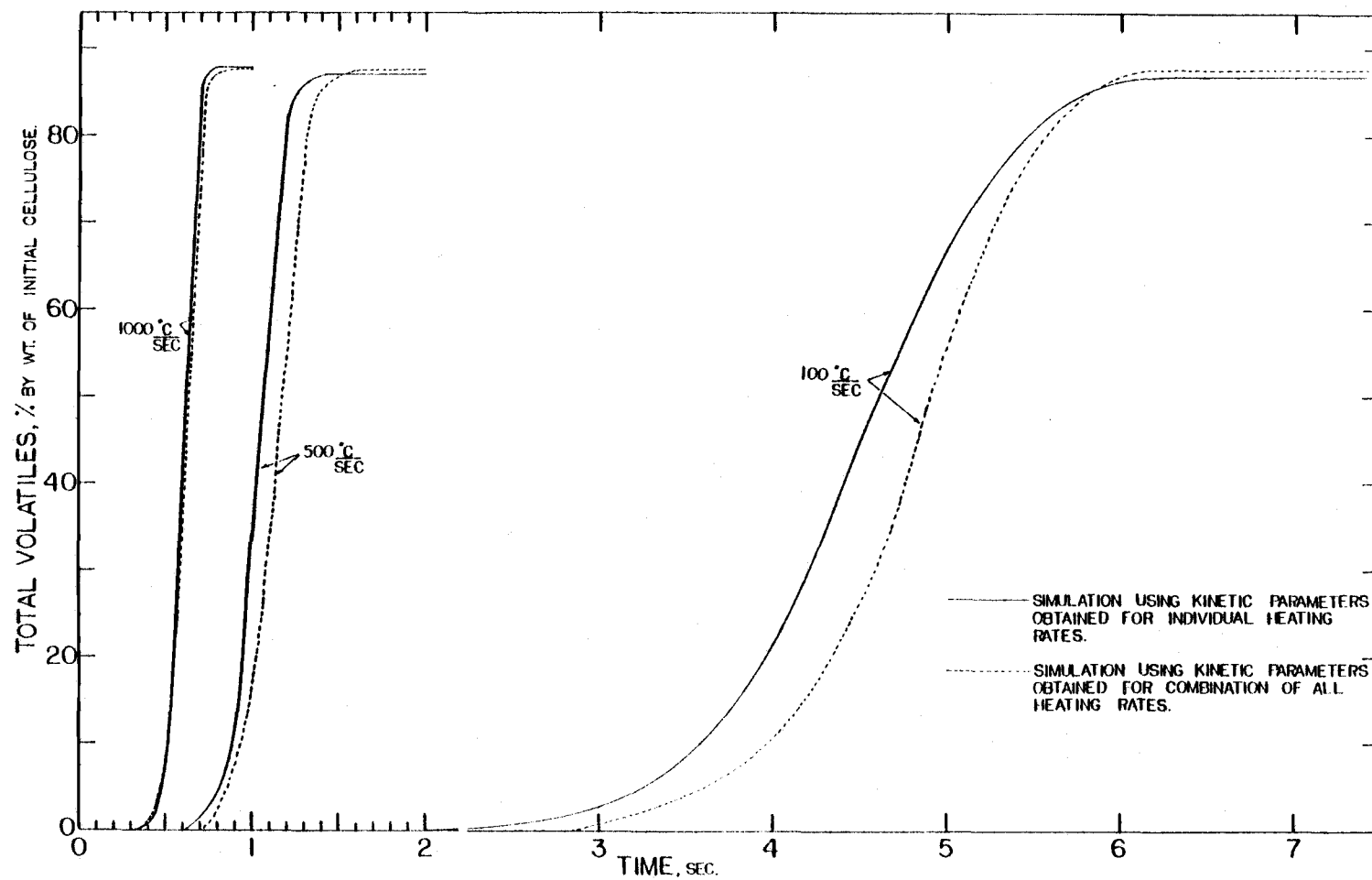


Figure 25

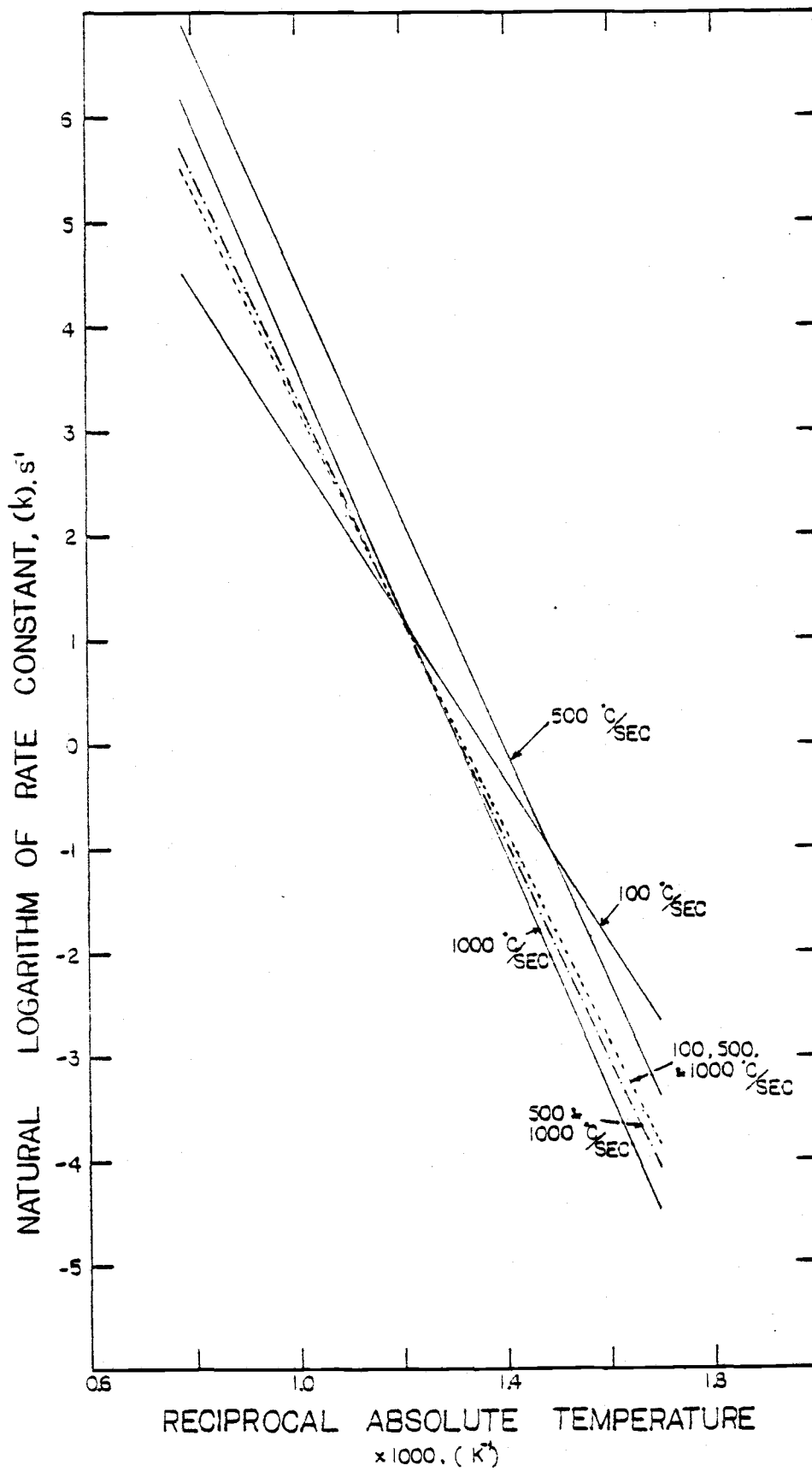


Figure 26

VI

CONCLUSIONS

Results from this study indicate the important role played by temperature on the yields and composition of the product gases. Lower temperatures favor tar and char formation along with small quantities of CO and CO₂. Higher temperatures favor secondary cracking of tar yielding more CO and resulting in the formation of CH₄, C₂H₄, and C₂H₆. The effect of solids residence time is more pronounced at lower temperatures. Thus, for a fixed solids residence time, volatile yields always increase with an increase in temperature until some asymptotic value is attained. Therefore, the possibility of an optimum temperature and residence time of solids to obtain maximum rate of volatilization exists; the asymptotic values achieved by the different products further strengthens this belief.

For the heating rate of approximately 1000°C/s and zero holding time, appreciable decomposition of cellulose begins between 350-400°C, tar and char formation being most dominant. There is a "step-like" change in volatile yield occurring between 500°C and 650°C until an asymptotic value of approximately 88 percent is reached at temperatures above 650°C. CO starts forming at about 550°C while CO₂ formation occurs around 450°C. Both these products increase with increase in temperature, CO₂ reaching an asymptotic value of 7.7 percent at 750°C while CO keeps increasing to 14.5

percent till a temperature of 1000°C is reached. Tar, which is one of the main products at low temperatures, increases with temperature reaching an asymptotic value of 23 percent at 750°C. Water along with the other unidentified products, formed, goes through a maxima of approximately 52 percent at 600°C and then decreases to an asymptotic value of 43 percent with any further increase in temperature. CH_4 and C_2H_4 start forming at 650°C, while C_2H_6 does not start forming till a temperature of 750°C is reached. The amounts of these gases formed is small, showing asymptotic values at higher temperatures; approximate amounts being 1 percent for CH_4 , 0.6 percent for C_2H_4 , and 0.16 percent for C_2H_6 .

The difference in kinetic parameters obtained for sets of experiments carried out at different heating rates suggests either a difference in devolatilization mechanism or the presence of heat transfer resistance between the particles and the screen being heated. This heat transfer resistance would become significant as heating rate is increased, thus setting a limit on the particle size and range of heating rates that can be studied by this method.

VII

RECOMMENDATIONS

The kinetic parameters obtained in this study do not represent the reaction mechanism but serve only as a useful tool to correlate the data. Also, in this method of study a captive sample is subjected and forced to "see" a particular heating rate. The question arises: What happens when cellulosic materials are suddenly introduced into an inert atmosphere heated to a particular temperature? The heating rate observed by the sample would then be controlled by the following factors: (a) temperature of the inert atmosphere surrounding the particle; (b) particle size; (c) the change in particle size and its physical characteristics as reaction proceeds; (d) properties, such as specific heat and thermal conductivity of the solids and the gaseous surrounding; (e) the heat of reaction; and (f) the anisotropic properties exhibited by various cellulosic materials. The usefulness of the different heating rates between $10^{\circ}\text{C}/\text{min}$ - $10000^{\circ}\text{C}/\text{s}$, studied by various workers, becomes questionable for practical application to process design. Before covering a wide range of heating rates mentioned above, a means of predicting the rate at which the temperature (namely, the heating rate) of the particle surface changes when suddenly introduced into a uniformly hot inert atmosphere, needs to be investigated. Different temperatures and particle sizes need to be studied.

This, then, would narrow down the range of heating rates that would be of practical interest.

A representative and practical study of cellulose pyrolysis should involve the combined effects of heat transfer, mass transfer and reaction kinetics without having to make drastic assumptions that either one or more of these factors is unimportant. A continuous reactor, such as a fluidized bed, free fall or entrained flow reactor, would serve the purpose. Wide ranges of operating variables, such as temperature, solids residence time, gas flow rate, pressure and sample sizes, need to be covered to study their effects on the rate of devolatilization and the yield and composition of the product gases. Effects of other gases, such as nitrogen, hydrogen, carbon dioxide, etc., or a combination of these gases, need to be investigated also. If all these factors are taken into consideration, there is no doubt that the model will become more complex, but it would be more accurate in predicting the results.

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APPENDICES

APPENDIX A

Listing of Computer Programs used for Data Analysis

```

PROGRAM CELLU(DATA3,OUTPUT,TAPES=DATA3,TAPE6=OUTPUT)
C      INSL ROUTINE "ZXSSQ" MINIMIZES THE SUM OF SQUARES OF M
C      FUNCTIONS IN N VARIABLES USING A FINITE DIFFERENCE LEVENBERG-
C      MARQUARDT ALGORITHM.
C      SUBROUTINE DIFF: EVALUATES THE RESIDUAL VECTOR F(1),F(2)....,F(N)
C      FOR GIVEN PARAMETER VALUES A(1),A(2).....,A(N).
C      SUBROUTINE ZINTG: EVALUATES SUM OF INTEGRALS OVER LINEAR SEGMENTS
C      OF THE RECORDED TEMPERATURE-TIME HISTORY.
      EXTERNAL DIFF
      INTEGER M,N,IXJAC,NSIG,MAXFN,IOP,T,I,INFER,
      IER,L(85),KK
      REAL PARM(4),A(3),F(17),XJAC(17,3),XJTJ(6),WORK(55),
      EPS,DELTA,SSQ,XJTJ,TEMP(20,25),SLOPE(20,25),
      VOLA(20,25),G(25),PHI(25),THETA(25),B(25)
      COMMON/C1/TEMP,SLOPE,L,R
      COMMON/C3/VOLA,G,KK,B
C      NUMBER OF EXPERIMENTAL DATA SETS TO BE READ IS M..
      M=17
      R=1.9872
C      VOLA: % OF EACH VOLATILE SPECIES FORMED
      READ(5,15) ((VOLA(I,J),I=1,7),J=1,M)
15    FORMAT(2X,7F10.5)
      READ(5,20) (L(K),K=1,M)
20    FORMAT(2X,6I6/2X,6I6/2X,5I6)
      DO 55 K=1,M
      NN=L(K)
      READ(5,25) (TEMP(I,K),SLOPE(I,K),I=1,NN)
25    FORMAT(3X,F7.2,3X,F11.4)
55    CONTINUE
C      SELECT VOLATILE SPECIES BY CHOOSING KK=1 TO 7; CO,CH4,CO2,
C      C2H4,C2H6,TAR AND WATER RESPECTIVELY.
      KK=1
C      SUPPLY APPROPRIATE PARAMETER VALUES FOR INSL ROUTINE USAGE.
      M=17
      N=3
      IXJAC=17
      NSIG=4
      EPS=0.0
      DELTA=0.0
      MAXFN=1000
      IOP=1
      PARM(2)=1.5
C      SUPPLY INITIAL GUESSES FOR ACTIVATION ENERGY,EI(A(1));INITIAL
C      RATE CONSTANT ZK0I(A(2));AND VSTAR VALUE A(3).
      A(1)=10000.
      A(2)=5000.
      A(3)=14.00
      CALL ZXSSQ(DIFF,M,N,NSIG,EPS,DELTA,MAXFN,IOP,PARM,A,
      N SSQ,F,XJAC,IXJAC,XJTJ,WORK,INFER,IER)
      WRITE(6,30) A(1),A(2),A(3),SSQ,(F(I),I=1,M)
30    FORMAT(2X,*EI=*,E10.4/2X,*ZK0I=*,E12.4/2X,*VSTAR=*,F8.4/2X,
      N *SSQ=*,E10.4/2X,*MINIMISED FUNCTION VALUES*/(12X,E10.4))
      WRITE(6,35) (WORK(I),I=1,5),INFER,IER
35    FORMAT(2X,*WORK=*,E10.4/4(7X,E10.4/),2X,*INFER=*,IS/2X,*IER=*,IS)
50    CONTINUE
      DO 40 K=1,M
      BB=B(K)*A(3)
      CC=VOLA(KK,K)/A(3)
      WRITE(6,45) VOLA(KK,K),BB,CC,B(K)
45    FORMAT(5X,F10.5,5X,F10.5,5X,F10.3,5X,F10.3)

```



```

40  CONTINUE
60  STOP
    END

```

C
C

```

SUBROUTINE DIFF(A,N,N,F)
  INTEGER M,N,I,KK
  REAL A(N),F(N),VOLA(20,25),G(25),PHI(25),THETA(25),B(25)
  COMMON/C2/PHI,THETA
  COMMON/C3/VOLA,G,KK,B
  DO 45 K=1,N
    CALL ZINTG(A(1),A(2),K)
    IF(THETA(K).LT.-50.) GO TO 80
    G(K)=1.-EXP(THETA(K))
    B(K)=G(K)
    GO TO 50
80  G(K)=1.
    B(K)=G(K)
50  CONTINUE
    J=K
    F(J)=VOLA(KK,K)/A(3)-B(K)
45  CONTINUE
    RETURN
    END

```

C
C

```

SUBROUTINE ZINTG(EI,ZK0I,K)
  INTEGER L(25),K
  REAL TEMP(20,25),SLOPE(20,25),R,PHI(25),THETA(25)
  COMMON/C1/TEMP,SLOPE,L,R
  COMMON/C2/PHI,THETA
  NN=L(K)
  PHIS=0.0
  DO 40 J=2,NN
    IF(TEMP(J,K).EQ.TEMP(J-1,K)) GO TO 45
    PHI(J)=R/(EI*SLOPE(J-1,K))*(TEMP(J,K)**2.*(1.-2.*R*
N TEMP(J,K)/EI)*EXP(-EI/(R*TEMP(J,K)))-TEMP(J-1,K)**2.
N *(1.-2.*R*TEMP(J-1,K)/EI)*EXP(-EI/(R*TEMP(J-1,K))))
    GO TO 50
45  DEL=SLOPE(J-1,K)
    PHI(J)=DEL*EXP(-EI/(R*TEMP(J,K)))
50  PHIS=PHIS+PHI(J)
40  CONTINUE
    THETA(K)=-ZK0I*PHIS
    RETURN
    END

```

```

C PROGRAM PYROL1(DATA3,OUTPUT,TAPE5=DATA3,TAPE6=OUTPUT)
C
C THIS PROGRAM IS USED IN FITTING DATA TO THE STATISTICAL DISTRIBUTION MODEL.
C
EXTERNAL GAUSS
INTEGER M,N,IXJAC,NSIG,MAXFN,I,INFER,
N IER,L(25),KK
REAL PARM(4),A(3),F(17),XJAC(17,3),XJTJ(6),WORK(55),
N EPS,DELTA,SSQ,XJTJ,TEMP(20,25),SLOPE(20,25),
N VOLA(20,25)
COMMON/C1/TEMP,SLOPE,L,R
COMMON/C3/VOLA,KK,USTAR,B(25)
C NUMBER OF EXPERIMENTAL DATA SETS,M.
N=17
R=1.9872
READ(5,15) (VOLA(I,J),J=1,M)
15 FORMAT(2X,F10.5)
READ(5,20) (L(K),K=1,M)
20 FORMAT(2X,6I6/2X,6I6/2X,6I6)
DO 55 K=1,M
NN=L(K)
READ(5,25) (TEMP(I,K),SLOPE(I,K),I=1,NN)
25 FORMAT(3X,F7.2,3X,F11.4)
55 CONTINUE
C TO SELECT VALUES FOR TOTAL VOLATILES ONLY,SPECIFY KK=1
C & SUPPLY USTAR VALUE FOR THE SAME.
KK=1
USTAR=87.641
C SUPPLY APPROPRIATE PARAMETER VALUES FOR INSL USAGE.
N=17
N=3
IXJAC=17
NSIG=4
EPS=0.0
DELTA=0.0
MAXFN=1000
IOPT=1
PARM(2)=1.5
C SUPPLY INITIAL GUESSES FOR ACTIVATION ENERGY,EI(A(1));
C INITIAL RATE CONSTANT ZK0I(A(2)); AND SIGMA(A(3)) FOR
C GAUSSIAN DISTRIBUTION FUNCTION OF EI VALUES.
A(1)=.1974E05
A(2)=.4831E06
A(3)=500.
CALL ZXSSQ(GAUSS,M,N,NSIG,EPS,DELTA,MAXFN,IOPT,PARM,A,
N SSQ,F,XJAC,IXJAC,XJTJ,WORK,INFER,IER)
WRITE(6,30) A(1),A(2),A(3),SSQ,(F(I),I=1,M)
30 FORMAT(2X,*EI=*,E10.4/2X,*ZK0I=*,E12.4/2X,*SIGMA=*,E10.4/
N 2X,*SSQ=*,E10.4/2X,*MINIMISED FUNCTION VALUES*/(12X,E10.4))
WRITE(6,35) (WORK(I),I=1,5),INFER,IER
35 FORMAT(2X,*WORK=*,E10.4/4(7X,E10.4/),2X,*INFER=*,15/2X,*IER=*,15)
DO 40 K=1,M
BB=USTAR*B(K)
WRITE(6,50) VOLA(KK,K),BB
50 FORMAT(5X,F10.5,5X,F10.5)
40 CONTINUE
STOP
END
C

```

```

C
SUBROUTINE GAUSS(A,N,M,F)
  INTEGER M,N,I,KK
  REAL A(N),F(M),VOLA(20,25),AVAL(10,25),G(10,25),Y(25)
  COMMON/C2/PHI(25),THETA(20,25)
  COMMON/C3/VOLA,KK,VSTAR,B(25)
  WRITE(6,10) A(1),A(2),A(3)
10  FORMAT(4X,E12.4,3X,E12.4,3X,E12.4)
  EI=A(1)
  ZK0I=A(2)
  SGMA=A(3)
  EMIN=EI-2.*SGMA
  EMAX=EI+2.*SGMA
  H=.5*SGMA
  SGMA2=.5/(SGMA*SGMA)
  SGMA3=1./(SGMA*2.50663)
  DO 45 K=1,M
  DO 55 J=1,9
    E=EMIN+H*(J-1)
    CALL ZINTG(E,ZK0I,K,J)
    AVAL(J,K)=THETA(J,K)-(E-EI)*(E-EI)*SGMA2
    IF(AVAL(J,K).LT.-50.) GO TO 50
    G(J,K)=EXP(AVAL(J,K))
    GO TO 55
50  G(J,K)=0.0
55  CONTINUE
45  CONTINUE
  DO 85 K=1,M
    Y(K)=(G(1,K)+2.*(G(3,K)+G(5,K)+G(7,K))+4.*(G(2,K)+G(4,K)+
      G(6,K)+G(8,K))+G(9,K))*H*.33333*SGMA3
    F(K)=VOLA(KK,K)/VSTAR-1.+Y(K)
85  B(K)=1.-Y(K)
  RETURN
  END

```

```

C
C
SUBROUTINE ZINTG(EA,ZK,K,J)
  INTEGER K,L(25),J
  REAL TEMP(20,25),SLOPE(20,25),R
  COMMON/C2/PHI(25),THETA(20,25)
  COMMON/C1/TEMP,SLOPE,L,R
  NN=L(K)
  PHIS=0.0
  DO 10 I=2,NN
    IF(TEMP(I,K).EQ.TEMP(I-1,K)) GO TO 15
    PHI(I)=R/(EA*SLOPE(I-1,K))*(TEMP(I,K)**2.*(1.-2.*R*
      TEMP(I,K)/EA)*EXP(-EA/(R*TEMP(I,K)))-TEMP(I-1,K)**2.
      *(1.-2.*R*TEMP(I-1,K)/EA)*EXP(-EA/(R*TEMP(I-1,K))))
    GO TO 20
15  DEL=SLOPE(I-1,K)
    PHI(I)=DEL*EXP(-EA/(R*TEMP(I,K)))
20  CONTINUE
    PHIS=PHI(I)+PHIS
10  CONTINUE
    THETA(J,K)=-ZK*PHIS
  RETURN
  END

```

APPENDIX B

**Listing of Total Volatile Yields and the Temperature-Time History
Recorded for each Experiment**

DATA SET NUMBER: 1
TOTAL VOLATILE % = 91.77

TIME	TEMP	SLOPE
0.000	297.00	1361.667
.600	1114.00	527.500
1.000	1325.00	-689.583
1.480	994.00	-235.294
2.500	754.00	-105.250
4.100	585.60	-47.782
7.120	441.30	-17.378
12.100	354.76	-6.665
17.150	321.10	-2.000
29.200	297.00	1.000

DATA SET NUMBER: 2
TOTAL VOLATILE % = 89.28

TIME	TEMP	SLOPE
0.000	296.00	1371.167
.600	1118.70	483.250
1.000	1312.00	-654.375
1.480	997.90	-268.472
2.200	804.60	-108.750
4.200	587.10	-48.333
7.200	442.10	-16.900
12.200	357.60	-6.020
20.240	309.20	-1.325
30.200	296.00	1.000

DATA SET NUMBER: 3
TOTAL VOLATILE % = 87.65

TIME	TEMP	SLOPE
0.000	295.00	964.000
1.000	1259.00	-491.346
1.520	1003.50	-333.562
2.250	760.00	-121.714
3.650	589.60	-55.200
5.900	465.40	-23.750
9.900	370.40	-9.850
13.900	331.00	-3.071
20.900	309.50	1.000

DATA SET NUMBER: 4
TOTAL VOLATILE % = 89.10

TIME	TEMP	SLOPE
0.000	296.00	962.000
1.000	1258.00	-542.714
1.700	878.10	-152.895
3.600	587.60	-57.619
5.700	466.60	-28.471

3.250	324.00	-11.388
12.500	345.60	-10.067
15.500	315.40	-1.213
39.500	297.20	1.000

DATA SET NUMBER: 5
TOTAL VOLATILE % = 88.73

TIME	TEMP	SLOPE
0.000	297.00	1266.546
.550	993.60	672.571
.900	1229.00	-578.367
1.390	945.60	-237.778
2.200	753.00	-102.102
3.960	573.30	-45.017
5.950	438.70	-18.667
11.000	363.10	-7.017
17.000	321.00	-2.133
25.000	301.30	1.000

DATA SET NUMBER: 6
TOTAL VOLATILE % = 88.35

TIME	TEMP	SLOPE
0.000	297.00	988.889
.900	1187.00	-539.655
1.480	874.00	-193.036
2.600	657.80	-69.907
5.190	477.44	-25.433
9.200	375.20	-7.729
16.200	321.10	-2.133
25.200	301.90	1.000

DATA SET NUMBER: 7
TOTAL VOLATILE % = 87.20

TIME	TEMP	SLOPE
0.000	295.00	960.000
.900	1159.00	-472.500
1.500	875.50	-310.968
2.120	682.70	-101.831
3.540	538.10	-47.965
5.300	429.70	-19.900
9.800	350.10	-7.225
13.800	321.20	-2.757
20.800	301.90	1.000

DATA SET NUMBER: 8
TOTAL VOLATILE % = 88.50

TIME	TEMP	SLOPE
0.000	295.00	1027.500
.800	1117.00	-447.222
1.340	875.50	-205.106
2.280	682.70	-88.977
4.040	526.10	-38.567
7.040	410.40	-15.375
11.040	348.90	-6.995
15.000	321.20	-1.987
21.040	309.20	1.000

DATA SET NUMBER: 9
TOTAL VOLATILE % = 87.31

TIME	TEMP	SLOPE
0.000	297.00	1007.500
.300	1103.00	-508.409
1.240	879.30	-194.000
2.240	685.30	-82.427
4.300	515.50	-32.789
7.850	399.10	-13.338
11.850	345.75	-6.063
15.850	321.50	-3.033
21.850	303.30	1.000

DATA SET NUMBER: 10
TOTAL VOLATILE % = 88.47

TIME	TEMP	SLOPE
0.000	297.00	945.000
.300	1069.00	-402.051
1.580	755.40	-123.654
3.140	562.50	-45.933
6.140	425.00	-17.921
10.180	352.60	-6.233
16.180	315.20	-1.534
24.200	302.99	1.000

DATA SET NUMBER: 11
TOTAL VOLATILE % = 86.48

TIME	TEMP	SLOPE
0.000	296.00	1047.143
.700	1029.00	-282.778
1.600	774.50	-122.143
3.140	586.40	-46.645
6.150	446.00	-18.024
11.160	355.70	-5.811
17.200	320.60	-1.811
26.200	304.30	1.000

DATA SET NUMBER: 12
TOTAL VOLATILE % = 86.19

TIME	TEMP	SLOPE
0.000	295.00	922.286
.700	940.60	-262.125
1.500	730.90	-108.315
3.280	538.10	-45.200
5.280	447.70	-20.775
9.280	364.60	-8.680
14.280	321.20	-2.900
19.280	306.70	1.000

DATA SET NUMBER: 13
TOTAL VOLATILE % = 81.22

TIME	TEMP	SLOPE
0.000	294.00	996.667
.600	892.00	-208.000
1.400	725.60	-97.850
3.400	529.90	-38.333
6.400	414.90	-17.125

10.400	346.40	-4.300
15.400	321.90	-2.614
22.400	303.50	1.000

DATA SET NUMBER: 14
TOTAL VOLATILE % = 84.95

TIME	TEMP	SLOPE
0.000	296.00	990.000
.600	390.00	-210.444
1.500	700.60	-98.025
3.120	541.80	-46.219
5.500	431.80	-19.020
9.480	356.10	-6.313
14.500	321.90	-2.255
25.540	297.00	1.000

DATA SET NUMBER: 15
TOTAL VOLATILE % = 73.11

TIME	TEMP	SLOPE
0.000	295.00	946.667
.600	363.00	-173.740
1.830	649.30	-72.850
3.830	503.60	-33.167
6.830	404.10	-14.575
10.830	345.80	-6.050
14.830	321.60	-2.614
21.830	303.30	1.000

DATA SET NUMBER: 16
TOTAL VOLATILE % = 45.35

TIME	TEMP	SLOPE
0.000	297.00	1044.000
.500	819.00	-202.222
1.400	637.00	-72.800
3.400	491.40	-32.367
6.400	394.30	-12.725
10.400	343.40	-5.340
15.400	316.70	-2.440
20.400	304.50	1.000

DATA SET NUMBER: 17
TOTAL VOLATILE % = 3.88

TIME	TEMP	SLOPE
0.000	296.00	1065.000
.400	722.00	-151.579
1.350	578.00	-53.561
3.400	468.20	-24.400
7.400	370.60	-9.150
11.400	334.00	-3.486
18.400	309.60	1.000

DATA SET NUMBER: 18
TOTAL VOLATILE % = 90.72

TIME	TEMP	SLOPE
0.000	297.00	908.900
.900	1115.00	2.697

5.349	1127.00	10.380
8.749	1163.00	-373.000
9.749	790.00	-114.170
11.749	561.65	-44.100
14.748	429.40	-16.800
19.762	345.16	-8.020
22.762	321.10	1.000

DATA SET NUMBER: 19
TOTAL VOLATILE % = 89.51

TIME	TEMP	SLOPE
0.000	297.00	962.500
.800	1067.00	-60.000
1.400	1031.00	4.500
9.400	1067.00	-381.000
10.000	338.40	-120.300
12.000	597.92	-44.110
15.000	465.50	-20.000
21.015	345.20	-4.020
33.005	297.00	1.000

DATA SET NUMBER: 20
TOTAL VOLATILE % = 87.93

TIME	TEMP	SLOPE
0.000	297.00	1003.140
.700	999.20	-34.600
2.099	950.80	3.500
9.013	975.00	-207.500
10.413	684.50	-78.680
12.413	527.17	-31.500
17.409	369.80	-6.050
27.407	309.31	1.000

DATA SET NUMBER: 21
TOTAL VOLATILE % = 85.70

TIME	TEMP	SLOPE
0.000	297.00	1018.100
.600	907.63	-44.390
1.695	859.00	7.700
9.395	859.00	-133.710
11.495	578.20	-42.730
15.495	407.30	-12.210
22.495	321.83	1.000

DATA SET NUMBER: 22
TOTAL VOLATILE % = 83.34

TIME	TEMP	SLOPE
0.000	297.00	1078.000
.500	836.00	-23.830
2.834	780.38	-1.950
9.183	768.00	-120.000
10.833	570.00	-40.250
14.833	409.00	-13.600
19.828	341.06	-4.430
26.840	310.00	1.000

DATA SET NUMBER: 23

TOTAL VOLATILE % = 71.82

TIME	TEMP	SLOPE
0.000	295.00	1043.500
.400	712.41	-36.620
1.400	675.79	1.560
9.227	688.00	-77.700
11.426	517.11	-32.000
15.431	388.96	-11.900
19.432	341.35	-4.880
24.432	316.95	1.000

DATA SET NUMBER: 24

TOTAL VOLATILE % = 8.87

TIME	TEMP	SLOPE
0.000	295.00	1130.800
.300	634.25	-48.560
1.540	574.04	-1.560
9.258	562.00	-50.200
11.657	441.58	-20.100
14.652	381.38	-12.050
18.650	333.20	-2.900
28.612	304.31	1.000

DATA SET NUMBER: 25

TOTAL VOLATILE % = 92.00

TIME	TEMP	SLOPE
0.000	298.00	974.730
1.000	1172.73	28.610
2.700	1221.36	2.590
7.395	1233.52	3.040
19.395	1270.00	-668.750
19.795	1002.50	-243.160
20.795	759.34	-89.160
23.795	491.85	-24.300
28.798	370.27	-5.350
38.798	316.77	1.000

DATA SET NUMBER: 26

TOTAL VOLATILE % = 90.43

TIME	TEMP	SLOPE
0.000	297.00	973.330
.700	1173.00	18.600
19.500	1173.00	-392.000
20.400	920.30	-127.710
22.400	564.89	-44.600
25.399	431.11	-15.200
31.401	339.89	-3.800
39.401	309.49	1.000

DATA SET NUMBER: 27

TOTAL VOLATILE % = 88.95

TIME	TEMP	SLOPE
0.000	297.00	990.000
.800	1089.00	18.400
19.200	1089.00	-360.000
20.000	901.00	-120.000
22.000	561.00	-44.000

25.000	429.00	-14.300
31.000	340.20	-3.900
39.000	309.00	1.000

DATA SET NUMBER: 28
TOTAL VOLATILE % = 87.66

TIME	TEMP	SLOPE
0.000	296.00	985.700
.700	986.00	-48.220
1.450	949.83	1.362
19.196	974.00	-181.300
20.796	683.93	-66.100
23.795	485.72	-26.000
27.792	381.78	-12.100
30.832	345.00	1.000

DATA SET NUMBER: 29
TOTAL VOLATILE % = 86.49

TIME	TEMP	SLOPE
0.000	295.00	989.400
.600	988.62	-1.320
19.251	864.00	-128.500
21.551	568.50	-40.000
25.553	408.44	-12.300
32.560	322.25	-1.850
42.544	303.78	1.000

DATA SET NUMBER: 30
TOTAL VOLATILE % = 81.90

TIME	TEMP	SLOPE
0.000	298.00	964.320
.500	780.00	-1.738
18.912	748.00	-89.700
21.311	532.76	-37.110
24.311	421.43	-14.430
30.312	334.84	-3.215
40.312	302.69	1.000

DATA SET NUMBER: 31
TOTAL VOLATILE % = 66.35

TIME	TEMP	SLOPE
0.000	299.00	1022.500
.400	708.00	-59.370
1.200	660.50	.676
19.691	673.00	-62.500
22.891	473.00	-21.250
27.891	366.75	-5.200
39.910	304.25	1.000

DATA SET NUMBER: 32
TOTAL VOLATILE % = 8.32

TIME	TEMP	SLOPE
0.000	298.00	978.330
.300	591.50	-40.830
1.200	554.75	.677
19.295	567.00	-51.450

21.225	434.10	111.940
24.294	389.38	-7.960
36.300	309.75	1.000

DATA SET NUMBER: 33
TOTAL VOLATILE % = 88.39

TIME	TEMP	SLOPE
0.000	297.00	1277.660
.640	1114.70	417.500
1.000	1265.00	-966.070
1.280	994.50	-337.720
1.850	802.00	-160.290
2.900	633.70	-72.150
4.900	489.40	-32.070
7.900	393.20	-13.230
11.868	340.70	-5.650
17.036	311.50	-1.610
26.042	297.00	1.000

DATA SET NUMBER: 34
TOTAL VOLATILE % = 88.07

TIME	TEMP	SLOPE
0.000	297.00	1252.500
.560	998.40	640.000
.900	1216.00	-564.170
1.500	877.50	-193.400
2.500	684.10	-88.480
4.140	539.00	-39.770
7.180	418.10	-14.520
12.180	345.50	-6.040
17.180	315.30	-1.510
25.193	303.20	1.000

DATA SET NUMBER: 35
TOTAL VOLATILE % = 88.00

TIME	TEMP	SLOPE
0.000	295.00	1272.090
.550	994.65	506.710
.900	1172.00	-676.360
1.340	874.40	-207.410
2.500	633.80	-80.190
4.600	465.40	-24.430
7.650	390.90	-10.940
13.701	324.70	-2.700
21.701	303.10	1.000

DATA SET NUMBER: 36
TOTAL VOLATILE % = 87.98

TIME	TEMP	SLOPE
0.000	296.00	1041.430
.700	1025.00	-360.000
1.400	773.00	-126.960
2.790	597.80	-63.210
4.400	495.40	-32.500
7.400	397.90	-11.450
13.400	329.20	-2.610
24.396	300.50	1.000

DATA SET NUMBER: 37
TOTAL VOLATILE % = 84.48

TIME	TEMP	SLOPE
0.000	297.00	1046.920
.600	925.15	-241.540
1.400	731.92	-105.670
3.000	562.85	-44.280
6.000	430.00	-15.970
11.672	339.42	-4.310
18.677	309.23	1.000

DATA SET NUMBER: 38
TOTAL VOLATILE % = 84.60

TIME	TEMP	SLOPE
0.000	297.00	290.000
.600	891.00	-216.300
1.400	717.96	-98.880
3.400	520.20	-38.730
6.400	404.02	-13.840
11.401	334.80	-4.940
16.405	310.08	1.000

DATA SET NUMBER: 39
TOTAL VOLATILE % = 78.44

TIME	TEMP	SLOPE
0.000	296.00	971.670
.600	879.00	-297.700
1.070	739.15	-103.050
3.070	533.06	-37.620
6.069	420.21	-18.400
10.070	346.60	-5.260
17.066	309.90	1.000

DATA SET NUMBER: 40
TOTAL VOLATILE % = 81.98

TIME	TEMP	SLOPE
0.000	297.00	966.670
.600	877.00	-184.900
1.800	655.12	-80.120
3.800	494.88	-32.870
6.800	396.27	-14.790
10.801	337.10	-6.780
14.798	310.00	1.000

DATA SET NUMBER: 41
TOTAL VOLATILE % = 78.19

TIME	TEMP	SLOPE
0.000	295.00	946.670
.600	863.00	-210.710
1.300	715.50	-98.350
3.300	518.80	-34.820
6.300	414.35	-14.750
11.300	340.60	-5.120
17.300	309.88	1.000

DATA SET NUMBER: 42
TOTAL VOLATILE % = 47.40

TIME	TEMP	SLOPE
0.000	296.00	998.000
.500	795.00	-179.520
1.400	633.43	-74.570
3.400	484.29	-29.000
6.400	397.29	-16.570
9.401	347.57	-6.210
15.404	310.29	1.000

DATA SET NUMBER: 43
TOTAL VOLATILE % = 32.63

TIME	TEMP	SLOPE
0.000	296.00	993.000
.500	792.50	-206.150
1.100	668.81	-80.400
3.100	508.01	-33.250
6.076	409.06	-15.460
10.077	347.21	-4.640
18.072	310.11	1.000

DATA SET NUMBER: 44
TOTAL VOLATILE % = 41.40

TIME	TEMP	SLOPE
0.000	297.00	984.000
.500	789.00	-169.330
1.550	611.20	-60.310
3.550	490.59	-31.080
6.550	397.34	-16.580
9.550	347.60	-6.220
15.547	310.30	1.000

DATA SET NUMBER: 45
TOTAL VOLATILE % = 9.62

TIME	TEMP	SLOPE
0.000	295.00	1045.000
.400	713.00	-143.370
1.400	569.63	-46.970
4.400	428.73	-15.660
10.398	334.80	-4.940
15.402	310.08	1.000

DATA SET NUMBER: 46
TOTAL VOLATILE % = 9.48

TIME	TEMP	SLOPE
0.000	296.00	1022.500
.400	705.00	-154.290
1.200	581.57	-45.260
4.200	445.80	-21.600
8.200	359.40	-9.260
12.199	322.37	-4.320
16.196	305.10	1.000

DATA SET NUMBER: 47
TOTAL VOLATILE % = 8.26

TIME	TEMP	SLOPE
0.000	297.00	1005.000
.400	699.00	-168.760
1.300	547.12	-38.940
4.500	422.52	-18.890
8.500	347.76	-6.230
14.516	310.28	1.000

DATA SET NUMBER: 48
TOTAL VOLATILE % = 7.87

TIME	TEMP	SLOPE
0.000	296.00	957.500
.400	679.00	-156.500
1.200	553.80	-42.060
4.200	427.63	-17.010
8.200	359.59	-6.190
16.193	310.11	1.000

DATA SET NUMBER: 49
TOTAL VOLATILE % = 8.11

TIME	TEMP	SLOPE
0.000	293.00	911.000
.400	657.40	-97.430
1.800	521.00	-35.550
4.800	414.36	-16.740
8.300	347.40	-5.310
15.805	310.20	1.000

DATA SET NUMBER: 50
TOTAL VOLATILE % = 3.56

TIME	TEMP	SLOPE
0.000	296.00	1073.330
.300	618.00	-86.520
1.750	492.55	-31.370
4.750	398.45	-13.050
9.748	333.22	-4.520
14.744	310.64	1.000

DATA SET NUMBER: 51
TOTAL VOLATILE % = 3.50

TIME	TEMP	SLOPE
0.000	293.00	906.670
.300	565.00	-81.110
1.200	492.00	-36.500
3.200	419.00	-16.220
6.201	370.33	-6.760
15.199	309.50	1.000

DATA SET NUMBER: 52
TOTAL VOLATILE % = 90.08

TIME	TEMP	SLOPE
0.000	303.00	493.500
2.000	1290.00	-180.080
4.400	857.80	-91.530
9.400	400.13	-8.260

12.404	317.50	-1.967
34.399	303.00	1.000

DATA SET NUMBER: 53
TOTAL VOLATILE % = 88.54

TIME	TEMP	SLOPE
0.000	303.00	472.220
1.800	1153.00	-285.140
3.550	654.00	-53.290
7.550	440.86	-11.191
17.550	328.95	-1.145
37.593	306.00	1.000

DATA SET NUMBER: 54
TOTAL VOLATILE % = 88.13

TIME	TEMP	SLOPE
0.000	301.00	495.000
1.400	1093.00	-281.440
2.850	741.20	-59.370
7.850	444.34	-11.690
17.888	327.00	-1.097
32.510	310.96	1.000

DATA SET NUMBER: 55
TOTAL VOLATILE % = 86.40

TIME	TEMP	SLOPE
0.000	301.00	480.000
1.400	973.00	-183.300
3.650	560.50	-34.500
8.650	388.00	-6.500
18.650	323.00	-1.833
33.656	310.50	1.000

DATA SET NUMBER: 56
TOTAL VOLATILE % = 84.30

TIME	TEMP	SLOPE
0.000	299.00	474.170
1.200	368.00	-114.830
4.200	523.50	-24.680
10.399	358.18	-5.140
20.391	306.92	-1.877
30.391	298.05	1.000

DATA SET NUMBER: 57
TOTAL VOLATILE % = 46.39

TIME	TEMP	SLOPE
0.000	299.00	420.000
1.000	719.00	-66.530
4.750	469.50	-19.910
9.750	369.96	-9.050
14.750	324.71	-2.198
24.750	302.73	1.000

DATA SET NUMBER: 58
TOTAL VOLATILE % = 13.15

TIME	TEMP	SLOPE
0.000	300.00	453.750
.300	363.00	-70.910
3.550	468.00	-20.010
8.551	367.93	-5.644
18.551	311.49	-1.283
29.045	298.00	1.000

DATA SET NUMBER: 59
TOTAL VOLATILE % = 92.01

TIME	TEMP	SLOPE
0.000	301.00	478.760
2.000	1258.52	2.840
8.507	1277.00	6.500
15.007	1277.00	-340.820
16.507	765.76	-98.550
18.507	568.66	-33.260
23.507	402.37	-8.000
33.519	322.27	-1.230
43.495	310.00	1.000

DATA SET NUMBER: 60
TOTAL VOLATILE % = 91.43

TIME	TEMP	SLOPE
0.000	303.00	452.780
1.301	1118.25	1.670
15.004	1140.30	-333.200
16.504	640.50	-65.330
19.504	444.50	-18.370
24.505	352.63	-2.860
39.411	310.00	1.000

DATA SET NUMBER: 61
TOTAL VOLATILE % = 89.44

TIME	TEMP	SLOPE
0.000	301.00	490.250
1.600	1085.40	-22.490
3.000	1053.92	1.050
15.000	1066.52	-277.100
16.300	650.87	-50.380
21.000	424.15	-11.750
28.502	336.00	-1.900
38.502	317.00	1.000

DATA SET NUMBER: 62
TOTAL VOLATILE % = 88.00

TIME	TEMP	SLOPE
0.000	303.00	498.640
1.400	1001.10	-1.916
14.500	976.00	-217.600
16.000	649.60	-62.770
19.000	461.30	-12.550
29.002	335.77	-1.500
44.049	313.20	1.000

DATA SET NUMBER: 63

TOTAL VOLATILE % = 86.33

TIME	TEMP	SLOPE
0.000	299.00	476.830
1.200	871.20	-1.710
14.767	848.00	-142.450
16.767	563.10	-36.100
21.767	382.60	-7.100
31.753	311.70	-1.270
41.753	299.00	1.000

DATA SET NUMBER: 64
TOTAL VOLATILE % = 83.30

TIME	TEMP	SLOPE
0.000	299.00	461.350
1.000	760.35	1.345
14.902	786.00	-122.140
17.002	529.50	-34.200
20.002	426.90	-10.990
30.003	317.89	-1.890
39.998	299.00	1.000

DATA SET NUMBER: 65
TOTAL VOLATILE % = 72.11

TIME	TEMP	SLOPE
0.000	300.00	495.500
.800	696.40	.183
15.000	699.00	-65.410
18.750	453.73	-16.230
25.749	340.13	-3.100
35.743	309.15	1.000

DATA SET NUMBER: 66
TOTAL VOLATILE % = 90.92

TIME	TEMP	SLOPE
0.000	297.00	302.790
3.000	1205.38	6.054
10.000	1247.76	-275.480
11.993	698.81	-50.370
17.782	407.21	-9.183
27.782	315.38	-1.025
42.787	300.00	1.000

DATA SET NUMBER: 67
TOTAL VOLATILE % = 92.21

TIME	TEMP	SLOPE
0.000	297.00	235.320
3.500	1120.62	7.700
9.004	1163.00	-291.370
10.604	696.81	-47.090
16.604	414.27	-8.600
28.103	315.38	-1.538
38.103	300.00	1.000

DATA SET NUMBER: 68
TOTAL VOLATILE % = 87.71

TIME	TEMP	SLOPE
0.000	298.00	253.420
2.750	994.91	37.636
5.250	1094.00	-220.190
7.050	697.66	-44.310
12.800	442.86	-14.518
20.600	329.62	-1.887
35.603	301.31	1.000

DATA SET NUMBER: 69
TOTAL VOLATILE % = 86.15

TIME	TEMP	SLOPE
0.000	298.00	195.000
2.754	835.00	32.100
7.022	972.00	-128.530
10.272	554.29	-25.610
17.521	368.64	-5.345
27.556	315.00	-1.079
42.385	299.00	1.000

DATA SET NUMBER: 70
TOTAL VOLATILE % = 84.52

TIME	TEMP	SLOPE
0.000	299.00	144.040
3.250	767.12	38.500
6.000	873.00	-125.130
8.200	597.71	-36.710
13.200	414.18	-9.036
23.200	323.82	-1.521
38.137	301.10	1.000

DATA SET NUMBER: 71
TOTAL VOLATILE % = 85.11

TIME	TEMP	SLOPE
0.000	298.00	139.650
2.300	619.20	70.586
5.995	880.00	-136.800
8.745	503.80	-19.920
17.145	336.47	-2.498
32.145	299.00	1.000

DATA SET NUMBER: 72
TOTAL VOLATILE % = 82.78

TIME	TEMP	SLOPE
0.000	299.00	97.800
5.000	788.00	-85.780
8.200	513.52	-25.470
13.199	386.19	-6.370
23.194	322.52	-1.226
38.194	304.13	1.000

DATA SET NUMBER: 73
TOTAL VOLATILE % = 31.29

TIME	TEMP	SLOPE
0.000	299.00	90.500
4.000	661.00	-49.840

9.400	441.69	-16.670
13.400	357.35	-4.220
23.435	315.00	-1.466
33.314	301.11	1.000

DATA SET NUMBER: 74
TOTAL VOLATILE % = 86.65

TIME	TEMP	SLOPE
0.000	300.00	171.820
3.250	858.40	41.850
5.250	942.10	1.417
19.999	963.00	-126.520
23.249	551.80	-25.380
30.499	367.80	-5.300
40.495	314.82	-1.380
50.510	301.00	1.000

DATA SET NUMBER: 75
TOTAL VOLATILE % = 85.27

TIME	TEMP	SLOPE
0.000	298.00	126.500
4.000	804.00	28.000
6.000	860.00	-2.000
20.000	832.00	-95.800
23.500	496.70	-18.740
31.702	343.00	-2.800
46.702	301.00	1.000

DATA SET NUMBER: 76
TOTAL VOLATILE % = 85.62

TIME	TEMP	SLOPE
0.000	299.00	121.140
4.400	832.00	26.250
6.000	874.00	-1.000
20.000	860.00	-102.500
23.000	552.50	-24.460
31.001	356.80	-3.720
46.001	301.00	1.000

DATA SET NUMBER: 77
TOTAL VOLATILE % = 81.30

TIME	TEMP	SLOPE
0.000	299.00	115.340
3.500	702.70	52.400
5.250	794.40	-2.332
20.001	760.00	-88.550
22.751	516.50	-25.780
27.751	387.60	-5.770
42.760	301.00	1.000

DATA SET NUMBER: 78
TOTAL VOLATILE % = 84.01

TIME	TEMP	SLOPE
0.000	299.00	97.800
5.000	788.00	-2.917
19.398	746.00	-53.980

24.498	470.70	-19.890
30.748	346.40	-3.010
45.764	301.20	1.000

DATA SET NUMBER: 79
TOTAL VOLATILE %= 73.43

TIME	TEMP	SLOPE
0.000	299.00	88.500
4.000	653.00	.875
20.000	667.00	-50.030
24.500	441.86	-13.980
31.750	340.50	-2.430
46.771	304.00	1.000

APPENDIX CYields and Temperature-Time History Recorded for each Experiment

CO	CH4	CO2	C2H4	C2H6	TAR	WATER
14.330	1.118	7.260	.584	.094	22.310	46.070
15.070	1.086	7.960	.620	.146	23.260	41.140
13.030	.997	7.620	.417	.164	23.000	42.400
13.710	1.108	7.940	.496	.133	23.500	42.200
12.940	.946	8.089	.564	.104	23.500	42.587
13.920	1.164	7.744	.589	.156	23.400	41.380
11.670	.967	8.100	.439	.160	21.310	43.560
12.310	.951	7.201	.607	.096	24.000	43.340
8.980	.693	7.390	.299	.090	22.500	47.450
10.760	.813	8.316	.380	.095	24.910	43.196
9.000	.597	7.340	.238	.116	22.200	46.990
5.830	.321	7.100	.138	0.000	21.000	49.600
3.420	0.000	6.120	0.000	0.000	19.000	53.680
4.560	0.000	6.300	0.000	0.000	21.090	52.500
2.840	0.000	6.095	0.000	0.000	17.000	47.170
.500	0.000	3.330	0.000	0.000	13.850	27.670
0.000	0.000	.590	0.000	0.000	10.250	0.000

DATA SET NUMBER: 1

TIME	TEMP	SLOPE
0.000	297.00	1361.667
.600	1114.00	527.500
1.000	1325.00	-689.583
1.480	994.00	-235.294
2.500	754.00	-105.250
4.100	585.60	-47.782
7.120	441.30	-17.378
12.100	354.76	-6.665
17.150	321.10	-2.000
29.200	297.00	1.000

DATA SET NUMBER: 2

TIME	TEMP	SLOPE
0.000	296.00	1371.167
.600	1118.70	483.250
1.000	1312.00	-654.375
1.480	997.90	-268.472
2.200	804.60	-108.750
4.200	587.10	-48.333
7.200	442.10	-16.900
12.200	357.60	-6.020
20.240	309.20	-1.325
30.200	296.00	1.000

DATA SET NUMBER: 3

TIME	TEMP	SLOPE
0.000	295.00	964.000
1.000	1259.00	-491.346
1.520	1003.50	-333.562
2.250	760.00	-121.714
3.650	589.60	-55.200
5.900	465.40	-23.750
9.900	370.40	-9.850
13.900	331.00	-3.071

20.900 309.50 1.000

DATA SET NUMBER: 4

TIME	TEMP	SLOPE
0.000	296.00	962.000
1.000	1258.00	-542.714
1.700	878.10	-152.895
3.600	587.60	-57.619
5.700	466.60	-28.471
8.250	394.00	-11.388
12.500	345.60	-10.067
15.500	315.40	-1.213
30.500	297.20	1.000

DATA SET NUMBER: 5

TIME	TEMP	SLOPE
0.000	297.00	1266.546
.550	993.60	672.571
.900	1229.00	-578.367
1.390	945.60	-237.778
2.200	753.00	-102.102
3.960	573.30	-45.017
6.950	438.70	-18.667
11.000	363.10	-7.017
17.000	321.00	-2.133
26.000	301.80	1.000

DATA SET NUMBER: 6

TIME	TEMP	SLOPE
0.000	297.00	988.889
.900	1187.00	-539.655
1.480	874.00	-193.036
2.600	657.80	-69.907
5.180	477.44	-25.433
9.200	375.20	-7.729
16.200	321.10	-2.133
25.200	301.90	1.000

DATA SET NUMBER: 7

TIME	TEMP	SLOPE
0.000	295.00	960.000
.900	1159.00	-472.500
1.500	875.50	-310.968
2.120	682.70	-101.831
3.540	538.10	-47.965
5.800	429.70	-19.900
9.800	350.10	-7.225
13.800	321.20	-2.757
20.800	301.90	1.000

DATA SET NUMBER: 8

TIME	TEMP	SLOPE
0.000	295.00	1027.500
.800	1117.00	-447.222
1.340	875.50	-205.106
2.280	682.70	-88.977

4.040	526.10	-38.567
7.040	410.40	-15.375
11.040	348.90	-6.995
15.000	321.20	-1.987
21.040	309.20	1.000

DATA SET NUMBER: 9

TIME	TEMP	SLOPE
0.000	297.00	1007.500
.800	1103.00	-508.409
1.240	879.30	-194.000
2.240	685.30	-82.427
4.300	515.50	-32.789
7.850	399.10	-13.338
11.850	345.75	-6.063
15.850	321.50	-3.033
21.850	303.30	1.000

DATA SET NUMBER: 10

TIME	TEMP	SLOPE
0.000	297.00	965.000
.800	1069.00	-402.051
1.580	755.40	-123.654
3.140	562.50	-45.833
6.140	425.00	-17.921
10.180	352.60	-6.233
16.180	315.20	-1.534
24.200	302.90	1.000

DATA SET NUMBER: 11

TIME	TEMP	SLOPE
0.000	296.00	1047.143
.700	1029.00	-282.778
1.600	774.50	-122.143
3.140	586.40	-46.645
6.150	446.00	-18.024
11.160	355.70	-5.811
17.200	320.60	-1.811
26.200	304.30	1.000

DATA SET NUMBER: 12

TIME	TEMP	SLOPE
0.000	295.00	922.286
.700	940.60	-262.125
1.500	730.90	-108.315
3.280	538.10	-45.200
5.280	447.70	-20.775
9.280	364.60	-8.680
14.280	321.20	-2.900
19.280	306.70	1.000

DATA SET NUMBER: 13

TIME	TEMP	SLOPE
0.000	294.00	996.667
.600	892.00	-208.000
1.400	725.60	-97.856

3.400	529.90	-38.333
6.400	414.90	-17.125
10.400	346.40	-4.900
15.400	321.90	-2.614
22.400	303.60	1.000

DATA SET NUMBER: 14

TIME	TEMP	SLOPE
0.000	296.00	990.000
.600	890.00	-210.444
1.500	700.60	-98.025
3.120	541.80	-46.219
5.500	431.80	-19.020
9.480	356.10	-6.813
14.500	321.90	-2.255
25.540	297.00	1.000

DATA SET NUMBER: 15

TIME	TEMP	SLOPE
0.000	295.00	946.667
.600	863.00	-173.740
1.830	649.30	-72.850
3.830	503.60	-33.167
6.830	404.10	-14.575
10.830	345.80	-6.050
14.830	321.60	-2.614
21.830	303.30	1.000

DATA SET NUMBER: 16

TIME	TEMP	SLOPE
0.000	297.00	1044.000
.500	819.00	-202.222
1.400	637.00	-72.800
3.400	491.40	-32.367
6.400	394.30	-12.725
10.400	343.40	-5.340
15.400	316.70	-2.440
20.400	304.50	1.000

DATA SET NUMBER: 17

TIME	TEMP	SLOPE
0.000	296.00	1065.000
.400	722.00	-151.579
1.350	578.00	-53.561
3.400	468.20	-24.400
7.400	370.60	-9.150
11.400	334.00	-3.486
18.400	309.60	1.000