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THE FLASH PYROLYSIS OF CELLULOSE IN THE PRESENCE OF  $K_2 \mbox{CO}_3$ 

presented by

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has been accepted towards fulfillment of the requirements for

Master of Science degree in Chemical Engineering

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### THE FLASH PYROLYSIS OF CELLULOSE IN THE PRESENCE OF K<sub>2</sub>CO<sub>3</sub>

By

JONATHAN E. TRAUTZ

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

#### ABSTRACT

#### THE FLASH PYROLYSIS OF CELLULOSE IN THE PRESENCE OF K<sub>2</sub>CO<sub>3</sub>

By

JONATHAN E. TRAUTZ

Quantitative analysis of product yields from the high temperature flash pyrolysis of cellulose in the presence of  $K_2CO_3$  have been conducted to determine the effect of the salt on the product yields. Experiments were run on a wire screen pyrolysis reactor.

At elevated temperatures and rapid heating rates the pyrolysis product yields are significantly altered by the presence of  $K_2CO_3$ . Similar product yield trends are found for slow and high temperature flash pyrolysis when  $K_2CO_3$  is present.

Neutron activation of the pyrolysis char reveal that the 1.0 weight percent loaded samples contain all of the  $K_2CO_3$  originally impregnated on to them however, a majority of the  $K_2CO_3$  has been lost from the 5.0 and 10.0 weight percent samples. Experimental results suggest that  $K_2CO_3$ acts like a catalyst at lower concentrations (1.0 percent) and that the excess  $K_2CO_3$  in the higher concentrations (5.0 and 10.0 percent) is lost through a reaction with char. I dedicate this work to Denise; my wife, and my friend. For without her continuous support this endeavor could never have been completed.

#### ACKNOWLEDGMENTS

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#### CHAPTER I

#### INTRODUCTION

#### A. General Introduction

"Flash pyrolsis" are words which for the untrained mind conjure up images of unknown scientific frontiers. These words are in fact not as overwhelming as they appear. "Flash" by definition refers to a process which is occurring rapidly or for a very brief moment; instantaneous. In terms of experimental parameters it indicates heating rates in excess of  $250^{\circ}$ C per second. A definition of pyrolysis is given by T. Milne<sup>1</sup>: "Pyrolysis of carbonaceous materials has been defined as incomplete thermal degradation, resulting in char, condensible liquids, or tars and gaseous products, generally in the absence of air." Therefore, "Flash Pyrolysis" of cellulose is the rapid heating of cellulose in a non-oxygen atmosphere.

Cellulose is a polymer composed of d-glucose units (six carbon sugars) with molecular weights greater than 100,000 in wood.<sup>2</sup> On a weight percent basis cellulose is usually the major component of wood; therefore, any analysis of cellulose can be used as a good representation of wood in general.

The three major product groups resulting from cellulose pyrolysis are shown in Figure 1. The pyrolysis gases are a mixture of several gas compounds: hydrogen, carbon monoxide, carbon dioxide, methane and



several lower molecular weight hydrocarbons. The second major product group is made up of tars and condensible liquids. This group is comprised of mainly levoglucosan (1,6-anhydro- $\beta$ -D glucopyranose) as well as smaller amounts of other anhydroglucose compounds and water.<sup>3,4,5</sup> Char (charcoal), the third major product, is a material consisting mostly of carbon. The actual pyrolysis yields produced for each of the different groups are dependent upon several parameters. These parameters and their influence upon product yields are discussed in the next section.

The various by-products of wood pyrolysis have many applications.<sup>6,7,8</sup> Biomass is a renewable resource; consequently, the potential for wood pyrolysis as a source of energy and chemical feedstocks is in principle unlimited. Because biomass has lower sulfur and ash content than coal, it is also a much cleaner form of energy to use.<sup>2</sup> The tarry liquids can be used as boiler fuels and the char as a home heating material. The gaseous products can be used as a low to medium B.T.U. gas which can be pipelines for home and industrial use. The product gases of pyrolysis contain ethylene and other low molecular weight hydrocarbons. They can be used as starting materials in the petro-chemical and petroleum industries for synthetic rubber, plastics, alcohols and liquid fuels production. One can, therefore, see the need for research in an area which has so many applications.

#### B. Pyrolysis Parameters

Pyrolysis of wood materials has been covered extensively in the literature.  $^{1-20}$  Several recurring trends have appeared in regards to the influence that the external parameters have upon the pyrolysis product composition. The parameters of interest to this study are

heating rate, residence time, peak temperature, sample particle size and reactor design. This section will cover each of these parameters and their influence upon product composition.

Only a few studies were found which addressed the heating rate parameter.  $^{9,10}$  Scientists at the Massachusetts Institute of Technology found that at lower temperature ranges (<600-700<sup>o</sup>C) with decreasing heating rate there is a corresponding decrease in char yields. <sup>9</sup> For the same conditions there is an increase in gas and tar yields. Slow pyrolysis Thermal Gravimetric Analysis (TGA) studies conducted by another group support these same trends for the char production. <sup>10</sup> At higher temperatures (>600-700<sup>o</sup>C) the heating rate appears to have very little influence on the product yields. The predominant factor at high temperatures is peak temperature alone.

The residence time is the duration in which a wood material is in contact with a heat source. The influence of this parameter upon pyrolysis product yields is covered in several papers. <sup>1,7,9,11,12</sup> It is found that as the residence time is increased the amount of tar and total gaseous materials produced increase as well. At the same time there is a corresponding decrease in the amount of char produced. A simple explanation for this phenomena is presented by M. R. Hajaligol<sup>9</sup>: "This behavior is believed to reflect the fact that at zero holding time and lower temperatures, decomposition of the cellulose is incomplete when the final temperature is attained. Holding the sample at the final temperature allows continued decomposition which generates additional tar and gas and less char." As was found for the heating rate parameter, residence time appears to have very little influence upon the product composition above the temperature range 600-700<sup>o</sup>C.

At these high temperatures the peak temperature becomes the dominating parameter.

The final temperature that a sample is pyrolyzed at (peak temperature) is very influential upon product yields. Several studies have shown that as the temperature increases there is a corresponding increase in the total amount of gas produced and decrease in the amount of char produced.<sup>8,9,11,12,13,14</sup> The influence of peak temperature on the individual gases within the total gas yield is also covered in these studies. Only two reports were found to contain information pertaining to temperature effects on tar yields.<sup>9,11</sup> They reported that the tar yields increased with temperature, reaching a maximum between 550-700<sup>o</sup>C and then decreased with further temperature increases. The difference in temperature values at which maximum tar yields are reported in these studies is probably a result of dissimilar heating rates, residence times and wood materials pyrolyzed.

The effect of sample particle size upon product composition was covered in one study.<sup>11</sup> The amount of tar produced for the three different sample sizes used did not appear to be size dependent. The authors felt that residence time of the wood material in the reactor might be the deciding factor on tar production. In general the char yields increased as the particle size decreased, and gas yields were slightly higher for larger particles except at the highest temperature  $(700^{\circ}C)$ .

The final parameter of pyrolysis is reactor design. There have been many different types of pyrolysis reactors used, varying from batch bench top to pilot plant continuous feed reactors. These reactor designs include micro-wave induced pyrolysis, <sup>15</sup> wire-mesh,<sup>9,16</sup> solar

furnaces,<sup>5</sup> continuous feed with fluidized bed,<sup>11,13</sup> fixed bed,<sup>4,17</sup> introduced sample bed,<sup>7,18</sup> continuous feed entrained flow,<sup>6,12,19</sup> as well as commercially available Thermal Gravimetric Analyzers (TGA).<sup>10,20</sup> Because the design of these reactors is so varied they inherently have different heating rates (slow versus flash pyrolysis), residence times, peak temperatures, and wood particle sizes used in them. Therefore the reactor design determines the types of parameters as well as their settings. This in turn determines the pyrolysis product yields.

The trends are well established for the parameters discussed in the preceding paragraphs. Another important parameter which has been shown to significantly influence the pyrolysis product yields is the presence of additives. These materials and their influence will be covered in the next section.

C. The influence of additives on the slow pyrolysis of wood material.

The previous section covered the influence that various parameters have on pyrolysis product composition. Completion of a literature survey on wood pyrolysis revealed several studies which used additives when pyrolyzing samples.<sup>4,17,18,20,21,22</sup> In these studies the cellulose samples are impregnated by soaking in aqueous solutions containing known concentrations of the additives. The samples are then removed and dried. The type of additives used are varied, ranging from acids to alkali salts. These materials are shown to significantly alter the pyrolysis product yields.

One of the more frequently used additives is potassium carbonate  $(K_2CO_3)$ . The affect that  $K_2CO_3$  has upon slow pyrolysis product yields is well established. 17,20,21,22 Research experiments have shown that

the presence of  $K_2CO_3$  increases char yields while significantly decreasing tar formation. Two reports demonstrated over a ten-fold decrease by weight in tar formation for samples containing one weight percent  $K_2CO_3$  when compared to unloaded samples.<sup>21,22</sup> A study by D. L. Pyle<sup>17</sup> disclosed that char yields increase as the weight percent of  $K_2CO_3$  in the samples is increased. This study also shows that for twenty weight percent  $K_2CO_3$  samples there is a 2.4-fold weight increase in char production. Gas yield were shown to increase by twenty-five percent as a result of  $K_2CO_3$  being present.

Another major influence of additives is that they lower the initial decomposition (pyrolysis) temperature of cellulose.  $^{4,17,20,21}$  Economically this might prove to be important in that it lowers the amount of energy required to pyrolyze a given amount of cellulose.

It is obvious that the presence of additives such as  $K_2CO_3$  in cellulose influence the product yield from pyrolysis. All the referenced studies pertaining to additives are for slow pyrolysis only. Pyrolysis of cellulose in the presence of additives has brought many questions to the surface which should be addressed in more detail. These questions and the means to finding their solution are presented in the next section.

#### D. Research Objective

The pyrolysis of wood materials in the presence of additives shows a great deal of promise for selectively altering product yields. The influence that  $K_2CO_3$  has on slow pyrolysis product yields is well established; therefore, this would be a desirable additive to use when conducting further pyrolysis research. As is suggested in the previous

section, many questions remained unanswered after conducting a literature survey of pyrolysis. These questions will be addressed in the following paragraphs.

A large scale continuous feed pyrolysis unit would more than likely be designed to run at high temperatures and rapid heating rates. <sup>6,19</sup> Consequently, research conducted in the area of flash pyrolysis of cellulose at high temperatures with additives present would help to better define the product yields expected from full scale pyrolysis units. The influence that heating rate or peak temperatures have upon product yields is covered in Section B. It was shown that the peak temperature becomes the predominant parameter at high temperatures; therefore, one has to question whether  $K_2CO_3$  has any influence upon pyrolysis product yields at elevated temperatures (>700°C). Restated: are product yields from the flash pyrolysis of cellulose at high temperatures altered by the presence of  $K_2CO_3$  or is the high peak temperature the predominant factor influencing product yields?

Another question resulting from the previous paragraph is brought to mind. If the yields are altered because  $K_2CO_3$  is present, do they follow the same trends as were shown for slow pyrolysis?

Nowhere in the literature was it questioned what becomes of the  $K_2CO_3$  after pyrolysis. Does the  $K_2CO_3$  remain on the char? Also, does the  $K_2CO_3$  act as a catalyst or a reactant when pyrolyzing cellulose?

In order to attempt to answer these questions an experimental scale pyrolysis reactor was constructed which is capable of both rapid heating rates and elevated peak temperatures. Neutron activation studies of the char were also conducted to help clarify the question of  $K_2CO_3$  location. The next three chapters will cover experimental

apparatus, experimental technique, and sample calculations/experimental results.

### Research Objective

Conduct experimental research to determine:

- 1. If product yields from the flash pyrolysis of cellulose at elevated temperatures are altered by the presence of  $K_2CO_3$ .
- 2. If the yields are altered, do they follow the same trends as shown for slow pyrolysis?
- 3. Does the  $K_2CO_3$  remain on the char?
- 4. Does  $K_2CO_3$  act as a catalyst or a reactant?

#### CHAPTER II

#### EXPERIMENTAL APPARATUS

#### A. Pyrolysis Reactor

The reactor used in the experiments is a screen type as shown in Figure 2. By passing a high voltage and amperage between the copper electrodes (denoted f) in Figure 2, the two 325 mesh stainless steel screens (g) become red hot because of their resistance to electrical conduction. In this way the cellulose sample placed between the screens is pyrolyzed.

The reactor consists of a 2" 0.D. stainless steel tube 6" in length (d). One end is closed off except for a Swagelock fitting connected to a  $\frac{1}{4}$ " copper tube (i). This is the gas outlet which is in line with the gas collection system. The opposite end of the stainless steel tube is swaged to a 2" Swagelock fitting (j). The inner lining of the reactor (h) is a hollow tube of 99.99 percent alumina 5" in length by 1 and 3/4" 0.D. This liner acts as a support for the electrodes. Because the resistance to electrical conduction is large in this ceramic material, all electrical current passes through the electrodes and screens only. The calculation of resistance in alumina is given in Appendix 1, Part A.

The power supply leads (b) are insulated 8 gauge copper wire which are introduced into the reactor through air tight Conax fittings. These power leads connect to the electrodes. Two thermocouples are run into

Figure 2. Pyrolysis Reactor

- a. Helium Inlet
- b. Electrical Wire Inlets
- c1. Thermocouple Inlets
- c2. Thermocouples in Reactor
  - d. Reactor Wall
  - e. Reactor Support
  - f. Copper Electrodes
  - g. 325 Mesh Wire Screens
  - h. Alumina Inner Reactor Lining
  - i. Product Gas Outlet
  - j. 2" Swagelock Fitting
  - k. Brass Cross Fitting



Figure 2. Pyrolysis Reactor

the reactor through another Conax fitting (c1). One thermocouple is placed between the screens and is connected to the temperature controller. This thermocouple is an exposed junction Chromel-Alumel (K type) thermocouple designed for fast response times. It provides a signal to the temperature controller which controls the maximum temperature that the screens reach. This will be discussed in more detail in the electrical system section. The second thermocouple is an ungrounded junction Chromel-Alumel (K type) which is placed above the screens close to the inside wall of the reactor. This thermocouple is used to indicate the wall temperature. During pyrolysis the levoglucosan is dispersed onto the reactor wall which reaches a maximum temperature of  $120^{\circ}$ C. Because levoglucosan does not begin to decompose until  $280^{\circ}$ C it is safe to assume further decomposition is minimal.

Helium is introduced through a Swagelock fitting connected to a 1/8" copper tube (e). The Swagelock fitting (a) and the Conax fittings (b) and C1) are connected to a brass cross fitting (k) which is threaded into the 2" Swagelock fitting (j).

The approximate volume of the reactor which includes inlet and outlet tubing is 197 cubic centimeters. Through the use of Swagelock and Conax fittings an air tight reactor was constructed. This is an essential criterion for conducting pyrolysis experiments.

#### B. Electrical System

The electrical systems used in the pyrolysis experiments are outlined in Figures 3 and 4. Figure 3 is the electrical system for the pyrolysis reactor. Figure 4 is the electrical system for gas analysis. The pyrolysis reactor system will be discussed first.

Because of the rapid heating rate required for flash pyrolysis, in excess of  $250^{\circ}$ C per second, it was predicted that a large power requirement would be needed. Before an available power supply was used, calculations were made to estimate the electrical power required. The extreme case was analyzed in order to determine the maximum power requirement. This was the case where the screens were almost instantly heated to 1,000°C and were then maintained at this temperature.

An energy balance around the screens gives

As outlined in Part B of Appendix 1, there are three methods of energy loss from the screens; conduction, radiation and free convection. Thus,

Total energy lost to surroundings	=	Energy lost due to conduction	+	Energy lost due to radiation		+	Energy lost due to free convection	
н	Ξ	(26.49 +	222.39	+	99.05)	Joule	s/sec	
11	=	347.93 Joule	s/sec					(2-2)

The arithmetic average of resistance  $R_{\mbox{AA}}$  in the screens is 0.3292 ohms. Therefore

I (current) =  $(power/resistance)^{0.5}$  = 32.51 Amps (2-3)

and Volts = I x  $R_{AA}$  = 10.70 (2-4)

The actual power needed when conducting the experiments was approximately 40 amps and 9 volts. The difference between the theoretical and actual power requirements was possibly due to the inability to calculate an accurate value for the resistance of the screens. The Electron Arc Division power supply used is depicted as (a) in Figure 3.

Figure 3 shows an enlargement (i) of the copper electrodes (g) and the wire mesh screens (h) located within the reactor. As described

Figure 3. Electrical System: Pyrolysis Reactor

- a. Electron Arc Division Power Supply
- b. Magnetic Contactor
- c. Omega 4001 Single Set Point Proportional and On-Off Controller
- d. Omega Model 650 Thermocouple Thermometer
- e. Exposed Junction Chromel-Alumel (K Type) Thermocouple
- f. Ungrounded Junction Chromel-Alumel (K Type) Thermocouple
- g. Copper Electrode
- h. 325 Mesh Wire Screens
- i. Enlargement of Electrical System Inside Reactor





in the previous section, the exposed junction Chromel-Alumel (k type) thermocouple (e) is placed between the wire screens. This is connected to an Omega 4001 Single Set Point Proportional and On-Off Controller (c). This controller is interphased with a magnetic contactor (b) which when activated opens the curcuit coming from the power supply.

The undergrounded junction Chromel-Alumel (K type) thermocouple (f) is connected to an Omega Model 650 Thermocouple Thermometer (d) which provides a digital read out of the temperature.

The operation of the electrical system in the pyrolysis experiment is as follows:

1. The Omega 4001 controller is preset at 900<sup>0</sup>C so that above this temperature the controller signals the magnetic contactor to open.

2. The power supply is then turned on resulting in current flowing through the screens. The high resistance screens heat up and become glowing hot. The heating rate obtained in running experiments is in excess of  $300^{\circ}$ C per second.

3. Once the set point temperature is reached (as detected by the thermocouple placed between the screens) the controller signals the magnetic contactor to break the power supply curcuit. This results in the screens cooling down until the temperature is again below the controller set point.

4. Once this occurs the magnetic contactor controlled by the Omega controller opens the circuit again to the screens. The heating process then starts over again.

Because of the delay in response from the thermocouple, controller and contactor, the temperature of the screens was found to oscillate around the set point of  $900^{\circ}$ C. This resulted in temperature variations of  $50-60^{\circ}$ C above the set point and  $80-120^{\circ}$ C below.

Figure 4 shows a schematic of the electrical system used for gas analysis. The Model 154L Perkin-Elmer Vapor Fractometer gas chromatograph (b) has two separate electrical systems. The first system is powered by a 110 volt AC output (c). This provides power to a blower fan and a heating element.

The second system requires a 9 volt DC supply which is provided by the Power/Mate Corporation power supply (a). This provides the power required to run the bridge curcuit of the thermal conductivity detector used to analyze the gas products. For a more in-depth understanding of this circuitry see the manual for the Model 154L Vapor Fractometer or the gas collection system section.

The signal generated by the detector located in the gas chromatograph drives the Model XKR Sargent-Welch Recorder (d) in Figure 4. From the recorder a qualitative analysis of the gas components is obtained. The recorder is interphased with a Sargent-Welch Electronic Integrator (e) which provides a quantitative analysis of the gases. By using this electrical system a qualitative and quantitative analysis of the gaseous products are obtained.

#### C. Gas Collection System

A schematic of the gas system used in the pyrolysis experiments is shown in Figure 5. A description of the various equipment or materials used as well as their corresponding function are discussed in this section. Small letters surrounded by parentheses refer to equipment shown in Figure 5.

# Figure 4. Electrical System: Gas Analysis

- a. Power/Mate Corporation Power Supply
- b. Model 154L Perkin-Elmer Vapor Fractometer
- c. 110 Volt AC Power Source
- d. Model XKR Sargent-Welch Recorder
- e. Sargent-Welch Electronic Integrator



Figure 4. Electrical System: Gas Analysis

Figure 5. Gas Collection System

- a. Helium Gas Tank
- b. Liquid Nitrogen Trap
- c. Whitey Sample Cylinder
- d. T-Connector
- e. 3-Way Whitey Ball Valve
- f. Atmospheric Vent in G.C. Line
- g. Model 154L Perkin-Elmer Vapor Fractometer
- h. Bubble Flow Meter
- i. 2-Way Whitey On-Off Ball Valve
- j. T-Connector and Pressure Gauge
- k. Pyrolysis Reactor
- 1. 3-Way Whitey Ball Valve
- m. Atmospheric Vent for Pyrolysis Reactor
- n. Dry Ice/Acetone Trap
- o. 6-Port Valve
- p. Atmospheric Outlet for Reactor Line
- q. Sample Collection Loop
- rl and r2. 3-Way Whitey Ball Valves
- s. Liquid Nitrogen Trap
- t. Connecting Tube
- u. 6-Way Whitey Sample Valve
- v. Sample Loop
- w. Calibration Gas Tank
- x. Calibration Gas Atmospheric Outlet





(a) <u>Helium Gas Tank</u> - A 99.999 percent pure source of helium was used in the pyrolysis experiments. This helium was utilized to flush the reactor, collect the gaseous products preceding pyrolysis of the cellulose sample and as a carrier gas in the gas chromatograph.

(b) <u>Liquid Nitrogen Trap</u> - This trap consists of a 14" by  $\frac{1}{4}$ " O.D. U-shaped stainless steel tube. Inside the tube is 0.5 grams of silica gel desiccant (6-16 mesh) used to absorb any impurities which might be present in the helium. The U-shaped tube is placed in a Dewar flask of liquid nitrogen (-196<sup>0</sup>C).

(c) <u>Whitey Sample Cylinder</u> - This 500 cc sample cylinder is filled with Linde 3A molecular sieves (1/8" pellets). These molecular sieves further absorb any impurities missed by the upstream nitrogen cold trap. By passing the helium through the liquid nitrogen trap and then the sample cylinder, the gas will have had all moisture and other impurities removed to a level undetectable in the gas chromatograph.

(d) <u>T-Connector</u> - The purified helium is split into two lines at this point. The first line runs to the gas chromatograph (G.C.); the second to the reactor.

(e) <u>3-Way Whitey Ball Valve</u> - This 3-way valve in the G.C. line allows the helium gas to be directed to the G.C. or to be vented to the atmosphere at (f).

(f) <u>Atmospheric Vent in G.C. Line</u> - This vent is used to vent impurities to the atmosphere when the sample cylinder molecular sieves are being regenerated by heating at  $200^{\circ}$ F.

(g) <u>Model 154L Perkin-Elmer Vapor Fractometer</u> - This gas chromatograph is used to analyze the product gases from the pyrolysis experiments. Figure 6 shows the flow schematic of the G.C. The difference





between the thermal conductivities of the carrier gas (helium) and components of interest are detected in the detector cell using thermistors. This difference is converted to an electrical signal which is relayed to the chart recorder described in the gas analysis electrical system section. The injection block shown in Figure 6 could not be made air tight subsequently, it was removed.

The column used in the G.C. was a 60/80 mesh Carbosieve S-II. The dimensions of this stainless steel column are 5 feet in length by 1/8 inch O.D. It was used successfully to separate carbon monoxide, carbon dioxide, methane and the C<sub>2</sub> hydrocarbons.

(h) <u>Bubble Flow Meter</u> - This meter is used to determine the flow rate through the G.C. The flow meter is connected to the outlet of the G.C. downstream from the column side of the detector.

(i) <u>2-Way Whitey On-Off Ball Valve</u> - This valve regulates the helium flow rate through the pyrolysis reactor. It may also be put in an off position while batch pyrolysis of the sample is taking place or to check for air leaks in the reactor.

(j) <u>T-Connector and Pressure Gauge</u> - This gauge is used to detect pressure changes from leakage in the reactor before running each sample.

(k) <u>Pyrolysis Reactor</u> - Discussed in detail in the two preceding sections.

(1) <u>3-Way Whitey Ball Valve</u> - This valve has three different positions. The first is the off position and is used for the same reasons as outlined for the 2-way valve (i). The second position allows gases passing through the reactor to be vented to the atmosphere at (m). After the cellulose sample is in place and the reactor sealed, this position is used to initially purge the reactor with helium, thus
removing a majority of the air present in the reactor. The final setting allows product gases from the reactor to be diverted to collection traps whose description will be forthcoming.

(m) <u>Atmospheric Vent for the Pyrolysis Reactor</u> - Discussed in the preceding paragraph.

(n) <u>Dry Ice/Acetone Trap</u> - This trap consists of a 22" length of  $\frac{1}{4}$ " O.D. U-shaped stainless steel tube with fiberglass packed inside. The tube is placed in a Dewar flash containing dry ice and acetone (-77<sup>o</sup>C). The purpose of this trap is to collect any water or particulate matter which is a product of the pyrolysis reaction.

(o) <u>6-Port Valve</u> - This valve has two positions. The first position (down) allows the reactor gases coming from the dry ice/acetone trap to go through the sample-collection loop (q) and eventually be vented to the atmosphere at (p). In this position gaseous products from the reactor are collected in the sample-collection loop. Simultaneously, helium from the reference side of the G.C. passes through the valve and goes directly to the column where it is eventually vented to the atmosphere (h). See Figure 6 for more detail. There is at no time any direct connection between the G.C. and reactor gas lines.

In the second position (up) the reference side helium from the G.C. goes through the sample-collection loop (q), then returns to the column as previously discussed. In this way the gaseous products from the pyrolysis reactor which were collected in the sample-collection loop are flushed into the G.C. for qualitative and quantitative analysis. The reactor line in this position is diverted directly to the atmosphere at (p).

(p) <u>Atmospheric Outlet for Reactor Line</u> - Discussed in the preceding paragraph.

(q) <u>Sample-Collection Loop</u> - This loop has two important sections.

1. Liquid Nitrogen Trap (s)

2. 6-Way Whitey Sample Injection Valve (u)

(r1 and r2) <u>3-Way Whitey Ball Valve</u> - These two 3-way valves are used in combination for two purposes. In the first position gases flowing through the sample-collection loop pass through the liquid nitrogen trap (s). The second position allows the same gases to by-pass the liquid nitrogen trap through a connecting tube (t) located between the valves.

(s) Liquid Nitrogen Trap - This trap consists of a 22" length by "4" O.D. U-shaped stainless steel tube placed in a Dewar flask filled with liquid nitrogen. As the product gases from the reactor pass through this cooled tubing they condense and are retained. The trap contains 0.1 grams of silica gel, added to the inside of the tube to insure complete collection of carbon monoxide which has a boiling point close to liquid nitrogen. Once all the gases are collected, the trap is placed in boiling water so the liquids become gases again. These gases are then flushed into the G.C. for analysis.

(t) <u>Connecting Tube</u> - Tube used to by-pass the liquid nitrogen trap (s).

(u) <u>6-way Whitey Sample Valve</u> - This six port valve is used to inject known volumes of calibration gas used in calibrating the experimental results. Like the six port valve (o), this valve has two positions. The first position allows the gases coming from the calibration gas tank (w) to flow through the 2 cc sample loop (v) and exit to the atmosphere at the calibration gas atmospheric outlet (x). While this is occurring the gases flowing through the samplecollection loop (q) are entering the valve and exiting without coming in contact with the calibration gases. When the valve is switched to the second position the sample-collection loop flows into the sample loop (v). In this way a 2 cc sample of the calibration gas is injected into the sample-collection loop (q) which will eventually be analyzed in the gas chromatograph (g). Also in this position the gas coming from the calibration gas tank (w) is vented directly to the atmosphere at (x).

(v) <u>Sample Loop</u> - This 36.8" length by 1/8" O.D. copper tube has a volume of 2 cc. Its use is described in the preceding paragraph.

(w) <u>Calibration Gas Tank</u> - This tank contains a gas of known composition. This composition is 5.33 percent carbon monoxide, 5.26 percent carbon dioxide, 5.20 percent methane, and the balance Helium. All percents are by volume.

(x) <u>Calibration Gas Atmospheric Outlet</u> - Discussed in the preceding paragraphs.

## D. Gas Plug Dispersion

Because the distance from the liquid nitrogen trap (s) to the G.C. (g) in Figure 5 is so long (107" of 1/8" copper tubing) it was suspected that a plug of gas might disperse before reaching the G.C. column. If this occurred then good separation in the column would not be achieved.

By modeling the concentration of a plug of gas as it flows through the tubing as a function of both time and distance, the following equation is obtained.

$$\frac{\partial C}{\partial t} = \frac{D_{AB}}{\partial x^2} \frac{\partial^2 C}{\partial x^2}$$
(2-5)

As outlined in Part C of Appendix 1, given the appropriate boundary conditions the solution to equation (2-5) is

$$C = C_0 (1 - erf (x/\sqrt{4tD_{AB}}))$$
 (2-6)

where

$$C_0$$
 = original concentration of the plug of gas  
x = distance from the original plug boundary  
 $D_{AB}$  = diffusion coefficient = 1.397 (cm)<sup>2</sup>/second

If the most extreme dilution of the plug of gas which can be tolerated is defined as  $C = 0.01C_0$  at x = 11" (one-half the original plug length when it leaves the liquid nitrogen trap), then equation (2-6) can be rearranged to solved for the time t.

$$t = \frac{x^2}{16D_{AB}}$$
(2-7)

t = 122.9 seconds

The actual time required for the plug to reach the column at a flow rate of 30  $(cm)^3$ /minute was calculated to be 11.64 seconds. Because the difference between these two values was so large it was safe to assume that the plug of gas would reach the G.C. column intact with only minimal dilution occurring.

Figure 7 shows a schematic of the three main components of the experimental apparatus combined; pyrolysis reactor, electrical system, gas collection system.

Figure 7. Experimental Apparatus

- a. Electron Arc Division Power Supply
- b. Magnetic Contactor
- c. Omega 4001 Single Set Point Proportional and On-Off Controller
- d. Omega Model 650 Thermocouple Thermometer
- e. Helium Gas Tank
- f. Pyrolysis Reactor
- g. Gas Collection System (simplified)
- h. Model 154L Perkin-Elmer Vapor Fractometer
- i. Model XKR Sargent-Welch Recorder
- j. Sargent-Welch Electronic Integrator





E. Sample Preparation

The cellulose used in the experiments was #4 Whatman filter paper. It was chosen because of its purity and thinness. It has been shown. that ash can act as a catalyst<sup>26</sup>; therefore this low ash content filter paper, less than 0.06 percent by weight, is an excellent source of pure cellulose. The advantage of using these thin samples (0.008 inch) is that the formation of a thick layer of char during the pyrolysis reaction is avoided. Therefore it is less likely that the product materials formed inside the sample will react appreciably with the hot char surfaces as they travel to the surface of the sample.

In running the experiments it was desired to make 0.0, 1.0, 5.0 and 10.0 weight percent  $K_2CO_3$  in cellulose samples. Weight percent is defined as

Weight = 
$$\frac{(gms of K_2CO_3 in the cellulose) x 100}{(gms of cellulose + gms of K_2CO_3 in cellulose)}$$
 (2-8)

The samples were impregnated with  $K_2CO_3$  by placing the cellulose paper in distilled water which contained a known concentration of alkali salt. After the water evaporates the  $K_2CO_3$  remains on the sample. The method for preparing the samples is as follows.

Samples of Whatman filter paper (17mm by 35mm) were prepared with an average weight of 0.05376 grams. Knowing the desired weight percent and the average weight of each cellulose sample, the average weight of  $K_2CO_3$  required per sample could be calculated using equation (2-8). These values are presented in Table 1.

Ten of the precut/preweighed cellulose samples were placed in distilled water then weighed immediately to determine their water up-take. The average water up-take was determined to be 0.12575 grams/

cellulose sample. Knowing the density of water at  $25^{\circ}$ C to be 0.996077 grams/ml the average water up-take per sample was converted to 0.126245 ml/cellulose sample. Since it was desired to use 80 ml of solution to place the samples in for impregnation, the following equation was used to calculate the weight of K<sub>2</sub>CO<sub>3</sub> required in 80 ml of water.

Grams of 
$$K_2CO_3$$
 =   
(grams of  $K_2CO_3$ /sample) x 80 ml water  
(2-9)
(ml of distilled water/sample)

The calculated values are presented in Table 1.

Once the sample were prepared, they were dryed in a furnace for 24 hours at  $80^{\circ}$ C. After this they were placed in a glass desicator for an additional 30 days before experiments were conducted. As a control the 0.0 weight percent samples were run through the procedure of impregnation and drying, except of course no  $K_2CO_3$  was present in the distilled water. By knowing the original weight and the weight after impregnating each sample, the difference between these values would give the grams of  $K_2CO_3$  absorbed in that particular cellulose sample. Equation (2-8) could then be used to calculate the actual weight percent for each sample. Ten samples were prepared for each desired weight percent. Their average values are given in Table 1.

Desired Weight %	Average grams of K <sub>2</sub> CO <sub>3</sub> Cellulose Sample	<u>Gms of K<sub>2</sub>CO<sub>3</sub> 80 ml water</u>	Actual Average Weight Percent
0.0	0.000	0.000	0.00
1.0	5.4307 x 10 <sup>-4</sup>	0.344	1.38
5.0	$2.8295 \times 10^{-3}$	1.793	6.49
10.0	5.9733 x 10 <sup>-3</sup>	3.785	13.05

Table 1. Cellulose Sample Preparation Values

### CHAPTER III

## EXPERIMENTAL TECHNIQUE

A. Preparation for Gas Collection and Analysis.

This section will cover three topics of experimental preparation. They are preparing the G.C. and other recording instruments for use, purging the collection traps and gas lines, and running a daily control sample gas.

Before the pyrolysis experiments can be conducted the G.C. and recording instruments must be adjusted. The flow rate in the G.C. column is established at 30 cc per minute by regulating the column pressure control to a setting of 14 psig. This flow rate can be confirmed by using the bubble flow meter (h) of Figure 5. Both the Power/Mate Power Supply (a) in Figure 4 and the detector voltage switch on the G.C. are turned on and adjusted to 9 volts. The G.C. temperature control is turned to the blower setting which activates the oven fan. Other settings which should be preset on the G.C. are power control at 100 percent power and recorder range control at an attenuation of 32. The temperature control is now adjusted to  $175^{\circ}$ C. The heating of the column removes any impurities which may have collected while the column was not being used. Subsequently the temperature control is readjusted to the blower setting and the column cooled to room temperature. The G.C. is now ready for gas analysis.

During the initial heating of the column to  $175^{\circ}C$  the cold traps and gas lines are also purged of impurities. While the 6-port valve (o) of Figure 5 is in the up position, the liquid nitrogen traps (b) and (s) are placed in boiling water. This removes any impurities which may have collected on the silica gel inside the traps. After five minutes the boiling water is removed and the first trap (b) is placed in liquid nitrogen. The second trap (s) is removed from the flowing helium of the sample collection loop (q) by adjusting the 3-way valves (r1 and r2). The gas collection system is now ready to be used.

The power setting on the Model XKR Sargent-Welch Recorder is adjusted to the "on" position. Other controls which should be preset are chart speed at two centimeters per minute, variable span in the "off" position, and span set at 50 millivolts.

The Sargent-Welch Electronic Integrator (e) in Figure 4 is placed on the stand-by power setting. The span should be preset at 50 millivolts.

A control sample gas is used each day an experiment is run to allow evaluation of the pyrolysis gaseous products both qualitatively and quantitatively. The volume percent of CO,  $CH_4$ , and  $CO_2$  in the calibration gas tank is 5.33, 5.20, and 5.26, respectively. With the 6-port valve (o) of Figure 5 in the up position and the 6-way valve (u) in the first position, the trap (s) is opened and placed in liquid nitrogen. After purging the sample loop (v) for 1-2 minutes with gas from the calibration gas tank (w), the 6-way valve (u) is switched to the second position. This injects a two cc sample of the calibration gas into the sample-collection loop (q). Because the sample loop

is upstream of the liquid nitrogen trap (s) the sample gas is collected in this trap. The recorder and integrator are now set on the record position. After five minutes the liquid nitrogen is removed and the trap is placed in boiling water. The sample gas is now flushed into the G.C. for analysis. For details on gas analysis see Chapter III, Section C.

#### B. Sample Loading.

This section covers the details of preparation for sample loading. The chronological order in which they are presented coincide with the actual experimental approach used.

The electrodes (f) and thermocouples (c2) in Figure 2 are first cleaned with acetone. This is done in order to remove any levoglucosan which may still be present from the previous experiment. All handling of electrodes, thermocouples, screens and samples are done with plastic gloves in order to prevent contamination with body oils. The screens are put in place and heated in air for 10 seconds at 900<sup>o</sup>C. This burns off any residue from screens that have been previously used. It also prevents further oxidation of the metal screens during experimental runs.

A 14.5 milligram cellulose sample is cut and weighted from the previously prepared samples outlined in Chapter II, Section E. The approximate size of these 14.5 milligram samples is one centimeter by one centimeter. The prepared sample and the exposed junction Chromel-Alumel (K type) thermocouple are then placed between the screens using acetone cleaned forcepts.

One of the alumina tube liners (h) in Figure 2 is slipped into place around the electrodes and screens. A clean alumina tube, prepared by heating in a furnace at  $700^{\circ}$ C for one hour, is used for each experiment. The outer reactor wall (d) is put in place and swaged with the 2" Swagelock fitting (j) to form an air tight seal. Finally the product gas outlet tube (i) is swaged to its appropriate fitting. The pyrolysis reactor is now completely sealed.

C. Purging and Flash Pyrolysis.

This section covers the details of preparation for purging the reactor and flash pyrolysis of the cellulose sample. Once again the chronological order given coincides with the actual experimental approach used.

By placing the 3-way valve (1) of Figure 5 in the vent position (m) and 2-way valve (i) open at a flow rate of 300 cc per minute, the reactor is flushed with helium for 3 minutes to remove air. After this time the 3-way valve (1) is put in the off position and the reactor is pressurized to 40 psig. The 2-way valve (i) is then closed and the reactor is checked for pressure leaks using the pressure gauge (j). If a leak is detected then a soap solution is used to locate it and appropriate measures are taken to eliminate the problem. If there is no change in pressure for a period of 30 minutes then the reactor is considered air tight and the pressure is released through the atmospheric vent (m).

With the 6-port valve (o) in the second position, the 3-way valve (1) is switched to the third position. This allows gases from the reactor passing through the dry ice/acetone trap (n) to be vented to the atmosphere at (p). The 2-way valve (i) is adjusted to allow a flow rate of 30 cc per minute for 25 minutes. This further helps purge both the reactor and the gas line of any air. Two minutes before purging is complete, trap (s) is opened and placed in liquid nitrogen. Trap (n) at this time is placed in dry ice/acetone. The 6-port valve (o) is moved to the first position (down) so that gases coming from the reactor will now pass through the sample-collection loop (q).

After the 25 minute purge is complete the reactor is sealed at both ends by putting valves (i) and (l) in the closed position. The sample is then pyrolyzed for 15 seconds at atmospheric pressure as outlined in Chapter II, Section B.

### D. Gas Collection and Analysis.

After pyrolysis the reactor is allowed to cool for five minutes. The 3-way valve (1) is opened to the third position again and the flow rate through the reactor is established at 30 cc per minute using the 2-way valve (i). In this way the product gases from pyrolysis are collected in the liquid nitrogen trap (s) for 25 minutes.

When this time period has expired the liquid nitrogen trap (s) is closed off and the Dewar flask containing liquid nitrogen removed. The 6-port valve (o) is placed in the up position so that helium from the reference side of the G.C. is now flowing through the samplecollection loop (q) and into the G.C. column. The liquid nitrogen trap is opened again and placed in boiling water. The product gases collected in the trap are now flushed into the G.C. for analysis. The dry ice/acetone trap is also placed in boiling water to remove any moisture which may have collected.

The preceding techniques are used to prepare the reactor for pyrolysis, to pyrolyze the sample, to collect the product gases, and to flush the gases into the G.C. for qualitative and quantitative analysis.

E. Collection of Data.

1. Gas

In the preceding sections the methods used to collect the pyrolysis product gases were covered. This section will cover how these gases are analyzed both qualitatively and quantitatively.

The control sample gas or pyrolysis product gases are released from the liquid nitrogen trap (s) and flushed into the G.C.'s column. After two minutes from the time of release, the temperature control on the G.C. is adjusted to  $175^{\circ}$ C. The ramping of the temperature to  $175^{\circ}$ C allows better separation of the gaseous components in the Carbosieve S-II column. As is described in the manual for the 154L Vapor Fractometer, "Qualitative analysis is based on the times at which components emerge from the column. For a particular column and a given set of operating conditions, the retention time for each component is characteristic of the substance and serves to identify it." As each component elutes from the column, its thermal conductivity is measured against the reference gas (helium). This difference in thermal conductivities is converted into an electrical signal which drives the Model XKR Sargent-Welch Recorder and produces a graphic display as shown in Figure 8. This readout shows a peak for each component as a function of time (qualitative) and concentration (quantitative).

The amount of each component is directly proportional to the area under its curve. This curve is electronically integrated using the





Sargent-Welch Electronic Integrator. The integrator records the results in the form of lines on the margin of the recorder chart as shown in Figure 8.

Each day an experiment is conducted a control sample gas is run as outlined in Chapter III, Section A. Since this sample gas is of a known volume, it can be used to calibrate the pyrolysis product gases of that day both qualitatively and quantitatively. For details on data manipulation, see Chapter IV, Section A. The actual integrated values obtained for the daily controls and experimental runs are presented in Tables 4 and 6, respectively.

2. Char

After the gaseous products are analyzed, both ends of the reactor are closed off using valves (i) and (1) in Figure 5. The product gas outlet tube (i) of Figure 2 is removed, followed by the outer reactor wall (d) and alumina liner (h). Using acetone-cleaned forceps the char sample found between the screens is removed and weighed. The weighed values for the various experimental runs are given in Table 9.

3. Tar

Although actual quantitative weight measurements for the tar were not conducted, visual observation of the amount of tar condensed on the ceramic tube allowed the trend in tar yield to be determined.

## F. Neutron Activation of Char

As the weight percent of  $K_2CO_3$  was increased in the prepared samples, it was observed that the weight of the remaining char increased as well. Neutron activation studies were conducted to determine whether the increase in weight was a result of an increased amount of  $K_2CO_3$  remaining in the char or whether  $K_2CO_3$  actually produced more char.

Neutron activation was used to determine the amount of potassium (K) remaining in the char samples. An assumption made in this study is that the potassium remaining in the char is still present in the form of  $K_2CO_3$ .

One char sample from each of the weight percent categories along with control samples were irradiated in the nuclear reactor at Michigan State University. The rate (counts per second) were determined for the gama-ray emission from the radioactive decay of  $^{42}$ K. The control samples consisted of weighed amounts of pure K<sub>2</sub>CO<sub>3</sub> in quantities comparable to those found in the 1.0, 5.0 and 10.0 weight percent categories. Table 2 shows the control sample weights and their corresponding rates. Table 3 gives the rates for the various char samples used.

Figure 9 is a graph constructed by plotting the rate versus weight of  $K_2CO_3$  using control sample values. Knowing the rate of the various char samples, this graph can be used to find the grams of  $K_2CO_3$  for that corresponding sample. These values are presented in Table 3.

Weight of K <sub>2</sub> CO <sub>3</sub> (grams)	Approximate Weight Percent	Rate (Counts per second)
1.45 X 10 <sup>-4</sup>	1.0	0.7
<b>7.25</b> x 10 <sup>-4</sup>	5.0	3.2
1.45 x 10 <sup>-3</sup>	10.0	5.3

Table 2. Neutron Activation: Control Samples

Table 3. Neutron Activation: Char Samples

Experimental Run #	Weight Percent	Rate	Weight of $K_2CO_3$ (grams)
9	1.04	0.9	$2.00 \times 10^{-4}$
15	6.17	0.9	$2.00 \times 10^{-4}$
22	12.80	0.5	$1.05 \times 10^{-4}$

.



Figure 9. Neutron Activation Graph: Rate Versus Weight of  $K_2 CO_3$ .

## CHAPTER IV

## SAMPLE CALCULATIONS AND EXPERIMENTAL RESULTS

## A. Data Manipulation

The methods used to collect the experimental data were covered in Chapter III, Section C. This section will show how the rough data is converted to meaningful quantitative values. Experimental Run #14 will be used as an example for all data manipulations. All tabular data referred to in this section are presented in the second section of this chapter.

## 1. Weight of CO, $CH_4$ , and $CO_2$ in the control sample gas.

The volume percentage of CO,  $CH_4$ , and  $CO_2$  in the calibration gas tank is 5.33, 5.20 and 5.26, respectively. There is a dead space of 0.045 cc's in the 6-way Whitey sample valve; therefore a 2 cc injected sample will contain 2.045 cc. Each of the components are treated as an ideal gas at atmospheric pressure. By correcting to room temperature the weight of each component is calculated in the following manner:

Weight = 
$$\frac{0.0533 \times 2.045 \text{ cm}^3 \times 1 \text{ mole } \times 28 \text{ grams } \times 273^{\circ}\text{K}}{22,400 \text{ cm}^3 1 \text{ mole } 298^{\circ}\text{K}} = (4-1)$$

 $1.2482 \times 10^{-4}$  grams

Weight = 
$$\frac{0.0520 \times 2.045 \text{ cm}^3 \times 1 \text{ mole } \times 16 \text{ grams } \times 273^{\circ}\text{K}}{22,400 \text{ cm}^3 \text{ l mole } 298^{\circ}\text{K}} = (4-2)$$

 $6.9585 \times 10^{-5} \text{ grams}$ 

Weight = 
$$\frac{0.0526 \times 2.045 \text{ cm}^3 \times 1 \text{ mole } \times 44 \text{ grams } \times 273^{\circ}\text{K}}{22,400 \text{ cm}^3 1 \text{ mole } 298^{\circ}\text{K}} = (4-3)$$

 $1.9357 \times 10^{-4}$  grams.

2. Integrated area (A) for the control sample components.

The integrated area is given by the following relationship:

$$A = \frac{\text{number of counts x recorder chart speed}}{750 \text{ counts / centimeter - minute}}$$
(4-4)

A recorder chart speed of two centimeters per minute were used for all control samples and experimental runs. Run #14 was conducted on 10-25-84, therefore the sample control counts from this same date will be used for calibration purposes. These values are given in Table 4. The integrated areas are calculated using equation (4-4) as follows:

$$A(CO) = \frac{26.25 \text{ counts x 2 centimeters/minute}}{750 \text{ counts / centimeters - minute}} = 7.000 \times 10^{-2} \text{ cm}^2 (4-5)$$

$$A(CH_{4}) = \frac{23.8 \text{ counts x 2 centimeters/minute}}{750 \text{ counts / centimeters - minute}} = 6.347 \times 10^{-2} \text{ cm}^{2} \quad (4-6)$$

$$A(CO_2) = \frac{28.83 \text{ counts x } 2 \text{ centimeters/minute}}{750 \text{ counts / centimeters - minute}} = 7.688 \text{ x } 10^{-2} \text{ cm}^2 \quad (4-7)$$

The calculated values for the sample control integrated areas are given in Table 4.

3. Weight per integrated area for each sample component.

Both the weight and integrated area are known for each component of the sample gas for the day Run #14 was conducted. The weight per integrated area can now easily be calculated.

$$\frac{\text{Weight of CO}}{A(CO)} = \frac{1.2482 \times 10^{-4} \text{ grams}}{7.000 \times 10^{-2} \text{ cm}^2} = 1.7831 \times 10^{-3} \frac{\text{grams}}{\text{cm}^2} \quad (4-8)$$

$$\frac{\text{Weight of CH}_{4}}{A(CH_{4})} = \frac{6.9585 \times 10^{-5} \text{ grams}}{6.347 \times 10^{-2} \text{ cm}^{2}} = 1.0963 \times 10^{-3} \frac{\text{grams}}{\text{cm}^{2}}$$
(4-9)

$$\frac{\text{Weight of } CO_2}{A(CO_2)} = \frac{1.9357 \times 10^{-4} \text{ grams}}{7.688 \times 10^{-2} \text{ cm}^2} = 2.5178 \times 10^{-3} \frac{\text{grams}}{\text{cm}^2}.$$
 (4-10)

The calculated values for the various sample runs are presented in Table 5. These values are important in that they given a relationship between the weight of each component and a particular chart area. These values can then be used to calibrate the experimental data which is collected the same day.

# 4. <u>Calculate the integrated area</u> (A exp) <u>for pyrolysis Experimental</u> Run #14.

The integrated areas of the experimental runs can be calculated using equation (4-4). The integrated counts presented in Table 6 for Experimental Run #14 are 625.85 for CO, 88.25 for  $CH_4$ , and 191.15 for CO<sub>2</sub>. Therefore

$$A(CO)_{exp} = \frac{625.85 \text{ counts x } 2 \text{ cm./min.}}{750 \text{ counts/ cm.-min.}} = 1.6689 \text{ cm}^2$$
 (4-11)

$$A(CH_4)_{exp} = \frac{88.25 \text{ counts x } 2 \text{ cm./min.}}{750 \text{ counts/ cm.-min.}} = 0.2353 \text{ cm}^2$$
 (4-12)

$$A(CO_2)_{exp} = \frac{191.15 \text{ counts x } 2 \text{ cm./min.}}{750 \text{ counts/ cm.-min.}} = 0.5097 \text{ cm}^2$$
. (4-13)

The integrated areas for all experimental runs are given in Table 7.

## 5. <u>Calculate the weight of each component produced for pyrolysis</u> <u>Experimental Run #14</u>.

Knowing the area  $(A_{exp})$  of each experimental component as calculated in equations (4-11) to (4-13) and its corresponding weight per area of the sample component as presented in equations (4-8) to (4-10), the weight of each component produced from the pyrolysis of cellulose can be found using the following relationship:

Weight of each  
component produced = 
$$A_{exp} \times \frac{grams \ calibration \ sample}{area \ of \ calibration \ sample}$$
 (4-14)  
For the three components of interest from Run #14 one finds the  
Weight of CO = (1.6689 cm<sup>2</sup>) x (1.7831 x 10<sup>-3</sup> grams/cm<sup>2</sup>) = (4-15)  
2.9759 x 10<sup>-3</sup> grams  
Weight of CH<sub>4</sub> = (0.2353 cm<sup>2</sup>) x (1.0963 x 10<sup>-3</sup> grams/cm<sup>2</sup>) = (4-16)

 $2.5801 \times 10^{-4} \text{ grams}$ 

Weight of 
$$CO_2 = (0.5097 \text{ cm}^2) \times (2.5178 \times 10^{-3} \text{ grams/cm}^2) = (4-17)$$
  
1.2834 x 10<sup>-3</sup> grams.

The various weights for each of the experimental runs are given in Table 7. Before the weight percent of product (with respect to cellulose) can be calculated for each component, the weights of both  $K_2CO_3$  and cellulose present in the 14.5 milligram sample must be determined. The next two sections will cover how these weights are calculated. 6. Weight of  $K_2CO_3$  present in the 14.5 milligram sample for Run  $\frac{\#14}{14}$ .

Equation (2-8) of Chapter II, Section E can be rearranged to solve for the weight of  $K_2CO_3$  since both weight percent and original weight of the sample are known for each experimental run.

Weight of   

$$K_2CO_3$$
 = (weight percent) x (gms of cellulose + gms of  $K_2CO_3$ )  
100 (4-18)

since

(gms of cellulose + gms of  $K_2CO_3$ ) = 14.5 milligrams

therefore

weight of  $K_2CO_3 = (14.5 \times 10^{-5} \text{ grams}) \times (\text{weight percent}).$  (4-19)

Run #14 has a weight percent of 6.3 therefore, using equation (4-19) the calculated value is:

weight of 
$$K_2CO_3 = (14.5 \times 10^{-5}) \times 6.3 = 9.1350 \times 10^{-4}$$
 grams.  
(4-20)

See Table 8 for calculated values.

7. Weight of cellulose in the 14.5 milligram sample for Run #14.

This value is easily computed using the following relationship:

Weight of \_ weight of original \_ weight of  $K_2CO_3$ cellulose \_ sample (14.5 mg) \_ present in sample (4-21)

For Run #14 this value is:

weight of cellulose =  $(14.5 \times 10^{-3} \text{ grams}) - (9.135 \times 10^{-4} \text{ grams}) = (4-22)$  $1.35865 \times 10^{-2} \text{ grams}.$  The calculated values for the different experimental runs are presented in Table 8.

It is important to recognize that this weight percent is with respect to cellulose only, where as the weight percent defined by equation (2-8) is with respect to cellulose and  $K_2CO_3$ . As the amount of  $K_2CO_3$  in the 14.5 milligram sample is increased, the amount of cellulose present decreases. This new weight percent takes into consideration the changing weight of cellulose present for the various weight percent samples. In this way the quantity of each component produced for a given amount of cellulose and the effect that  $K_2CO_3$  has on it is better defined.

Weight percent with   
respect to cellulose = 
$$\frac{\text{weight of pyrolysis component x 100}}{\text{weight of cellulose in the sample}}$$
. (4-23)

For Experimental Run #14 the weight percent for each of the components calculated using equation (4-23) are:

Weight percent = 
$$\frac{2.97589 \times 10^{-3} \text{ grams } \times 100}{1.35865 \times 10^{-2} \text{ grams}}$$
 = 21.90 (4-24)

Weight percent = 
$$\frac{2.58014 \times 10^{-4} \text{ grams } \times 100}{1.35865 \times 10^{-2} \text{ grams}} = 1.90$$
 (4-25)

Weight percent = 
$$\frac{1.28339 \times 10^{-3} \text{ grams } \times 100}{1.35865 \times 10^{-2} \text{ grams}} = 9.45$$
 (4-26)

See Table 8 for the calculated values.

9. Weight percent of char with respect to cellulose.

This can be easily computed using equation (4-23).

Weight percent = 
$$\frac{\text{grams of char x 100}}{\text{grams of cellulose in the sample}}$$
 (4-27)

The weights of the char samples are given in Table 9. For Run #14 the char weight is 1.7 milligrams, thus

Weight percent = 
$$\frac{1.7 \times 10^{-3} \text{ grams } \times 100}{1.35865 \times 10^{-2} \text{ grams}} = 12.51$$
 (4-28)

Table 9 gives the calculated values of weight percent of char.

## 10. Weight of $K_2CO_3$ lost from the cellulose sample during pyrolysis.

In conducting the neutron activation studies it was observed that not all of the original  $K_2CO_3$  was still present in the 5.0 and 10.0 weight percent char samples. The estimated weight of  $K_2CO_3$  remaining in these char samples is given in Table 3. If these weights can be used as a rough estimate for the amount of  $K_2CO_3$  remaining in the other char samples then the grams of  $K_2CO_3$  lost as a result of pyrolysis can easily be calculated as follows:

Weight of 
$$K_2CO_3$$
 grams of  $K_2CO_3$  originally grams of  $K_2CO_3$ .  
lost during = present in 14.5 mg - remaining in  
pyrolysis sample char (Table 3)  
(4-29)

For Experimental Run #14 (approximately 5.0 weight percent) the

Weight of 
$$K_2CO_3$$
 lost =  $(9.135 \times 10^{-4}) - (2.0 \times 10^{-4}) =$   
during pyrolysis 7.135 x  $10^{-4}$  grams. (4-30)

If calculating a 10.0 percent sample then the value used from Table 3 would be  $1.05 \times 10^{-4}$  grams. The computed values are shown in Table 10.

The amount of  $K_2CO_3$  remaining in the 1.0 weight percent char samples are approximately equal to the amount originally present. Therefore these calculations do not apply for the 0.0 percent and 1.0 percent samples.

11. Weight of CO produced from the reaction of  $K_2CO_3$  with char.

It has been shown that the following reaction takes place between  $K_2CO_3$  and carbon (char).<sup>27,28,29</sup>

$$K_2CO_3 + 2C(char) = 2K + 3CO$$
 (4-31)

In the event that the  $K_2CO_3$  lost during the pyrolysis of cellulose reacts in this way, the amount of CO produced from this reaction can easily be calculated. Since the weight of  $K_2CO_3$  lost during pyrolysis has been determined by the neutron activation study and for every mole of  $K_2CO_3$  lost there are three moles of CO produced, the following relationship can be used to calculate the desired quantity.

grams of 
$$K_2CO_3$$
 lost x  $\frac{1 \text{ mole } K_2CO_3 \times 3 \text{ moles } CO \times 28 \text{ grams } CO}{138.18 \text{ gms } K_2CO_3 \times 1 \text{ mole } K_2CO_3 \times 1 \text{ mole } CO}$ 

For Run #14 this value is calculated to be:

Weight of CO produced from 
$$K_2CO_3$$
 reaction =  

$$\frac{7.135 \times 10^{-4} \text{ gms } K_2CO_3 \times 1 \text{ mole } K_2CO_3 \times 3 \text{ moles } CO \times 28 \text{ grams } CO}{138.18 \text{ gms } K_2CO_3 \text{ 1 mole } K_2CO_3 \text{ 1 mole } CO} =$$

4.3374 x  $10^{-4}$  grams.

Table 10 gives calculated values for the experiments performed.

12. Calculate the actual weight of CO produced from cellulose.

The actual weight of CO produced from cellulose, excluding that which is a result of the  $K_2CO_3$  reaction of equation (4-31) is calculated using the following equation:

The calculated value for Experimental Run #14 is:

Actual weight = 
$$(2.9759 \times 10^{-3} \text{ grams}) - (4.3374 \times 10^{-4} \text{ grams}) = 2.5422 \times 10^{-3} \text{ grams}.$$
 (4-35)

See Table 11 for the calculated values of the various experimental runs.

## 13. Calculate the corrected weight percent of CO.

This weight percent refers to the actual grams of CO calculated in the preceding section. This excludes the CO which was a result of the reaction with  $K_2CO_3$ . Therefore:

$$\begin{array}{rcl} \text{Corrected weight} &=& \frac{\text{actual grams of CO produced x 100}}{\text{weight of cellulose in the sample}} & (4-36) \end{array}$$

For Run #14 the corrected weight percent of CO is:

$$\begin{array}{rcl} \text{Corrected weight} &=& \frac{2.5422 \times 10^{-3} \text{ grams} \times 100}{1.35865 \times 10^{-2} \text{ grams}} &=& 18.71 \quad (4-37) \end{array}$$

Table 11 gives the calculated values for the experiments performed.

14. Weight of  $C_2H_4$  in the control sample.

At a later time it was decided to evaluate the  $C_2H_4$  (ethylene) and  $C_2H_2$  (acetylene) produced in the pyrolysis experimental runs. A new 0.56 cc sample loop was put in place of the 2.0 cc loop. A tank of pure  $C_2H_4$  was used to purge the sample loop. The weight of  $C_2H_4$  can be calculated in the following manner using the same constraints as found in Part 1 of this section.

Weight of 
$$C_2H_4 = \frac{0.56 \text{ cm}^3 \times 1 \text{ mole} \times 28 \text{ grams} \times 273^{\circ}K}{22,400 \text{ cm}^3 1 \text{ mole} 298^{\circ}K} = (4-38)$$

6.4128 x  $10^{-4}$  grams.

15. Integrated area (A) for the  $C_2H_4$  control sample.

Only one  $C_2H_4$  control sample was run to use as a standard for all experimental runs. The number of integrated counts procured from this run using the 0.56 cc sample was 122.25. Using equation (4-4) the integrated area is calculated to be:

$$A(C_2H_4) = \frac{122.25 \text{ counts x } 2 \text{ cm./min.}}{750 \text{ counts/cm.-min.}} = 0.3260 \text{ cm}^2$$
 (4-39)

16. Weight per integrated area for the  $C_2H_4$  control sample.

Both the weight and integrated area for  $C_2H_4$  are known so the desired value can easily be calculated.

$$\frac{\text{Weight of } C_2H_4}{A(C_2H_4)} = \frac{6.4128 \times 10^{-4} \text{ grams}}{0.3260 \text{ cm}^2} = 1.9671 \times 10^{-3} \frac{\text{grams}}{\text{cm}^2}$$
(4-40)

## 17. Calculate the integrated areas for $C_2 H_{\mu}$ and $C_2 H_2$ from Experimental Run #3.

Because of technical difficulties (bases line drift on the recorder, unstable G.C. electrical system at high temperatures) only a limited number of integrated counts were obtained for  $C_2H_4$  and  $C_2H_2$ . The integrated counts and their corresponding  $K_2CO_3$  weight percents are presented in Table 12. The integrated counts from Run #3 are 59.25 for  $C_2H_4$  and 23.80 for  $C_2H_2$ . Equation (4-4) is used to calculate the desired values.

$$A(C_2H_4) = \frac{59.25 \text{ counts } \times 2 \text{ cm./min.}}{750 \text{ counts } / \text{ cm.-min.}} = 1.580 \times 10^{-1} \text{ cm}^2$$
 (4-41)

$$A(C_2H_2) = \frac{23.80 \text{ counts } \times 2 \text{ cm./min.}}{750 \text{ counts } / \text{ cm.-min.}} = 6.347 \times 10^{-2} \text{ cm}^2$$
 (4-42)

The integrated areas for the selected experimental runs are given in Table 13.

18. Calculate the weights of  $C_2H_4$  and  $C_2H_2$  for Experimental Run #3.

Since the thermal conductivities of  $C_2H_4$  and  $C_2H_2$  are very similar, the weight per integrated area calculated for  $C_2H_4$  can be used for  $C_2H_2$  with little resulting error. Utilizing equation (4-14) one finds:

Weight of  

$$C_2H_4$$
 = (1.580 x 10<sup>-1</sup> cm<sup>2</sup>) x (1.9671 x 10<sup>-3</sup> grams/cm<sup>2</sup>) =  
3.1081 x 10<sup>-4</sup> grams (4-43)

Weight of  

$$C_2H_2$$
 = (6.347 x  $10^{-2}$  cm<sup>2</sup>) x (1.9671 x  $10^{-3}$  grams/cm<sup>2</sup>) =  
1.2485 x  $10^{-4}$  grams (4-44)

Table 13 shows the calculated weights of  $C_2H_4$  and  $C_2H_2$  for the selected experimental runs.

# 19. Calculate the weight percent (with respect to cellulose) of $C_2H_4$ and $C_2H_2$ for Experimental Run #3.

For Run #3 the weight of cellulose in the sample was 14.5 milligrams therefore using equation (4-23) the desired values can easily be calculated.

Weight Percent  
of 
$$C_2H_4$$
 =  $\frac{3.1081 \times 10^{-4} \text{ grams} \times 100}{1.45 \times 10^{-2} \text{ grams}}$  = 2.14 (4-45)  
Weight Percent  
of  $C_2H_4$  =  $\frac{1.2485 \times 10^{-4} \text{ grams} \times 100}{1.45 \times 10^{-2} \text{ grams}}$  = 0.86 (4-46)

The calculated values for the various experimental runs are presented in Table 13.

## B. Tabulated Data and Calculated Results

Date	Inte CO	grated CH <sub>4</sub>	Counts CO <sub>2</sub>	Integrated A(CO)	Areas (x10 <sup>-2</sup> A(CH <sub>4</sub> )	<sup>2</sup> cm <sup>2</sup> ) A(CO <sub>2</sub> )
9-25- <b>8</b> 4	29.00	25.40	30.00	7.733	6.773	8.000
9-25-84	29.40	25.00	29.60	7.840	6.667	7.893
9-25-84	29.00	25.60	32.00	7.733	6.827	8.533
10-10-84	27.00	24.45	26.90	7.200	6.520	7.173
10-11-84	28.10	25.50	29.30	7.493	6.800	7.813
10-15-84	31.00	26.90	26.0*	8.267	7.173	
10-16-84	28.53	24.80	29.45	7.608	6.613	7.853
10-17-84	28.35	25.30	29.65	7.560	6.747	7.907
10-23-84	26.50	26.00	32.00	7.067	6.933	8.533
10-25-84	26.25	23.80	28.83	7.000	6.347	7.688
10-30-84	26.65	24.75	29.73	7.107	6.600	7.928
10-31-84	26.00	24.25	29.55	6.933	6.467	7.880
11-05-84	27.75	25.10	30.00	7.400	6.693	8.000
11-07-84	27.93	25.08	30.24	7.493	6.680	8.128
11-08-84	28.10	25.05	30.48	7.448	<b>6.6</b> 88	8.064

Table 4. Control Values: Integrated Counts and Areas.

\*Recorder pen drifted below base line, data not valid.

Date	<u>Grams CO</u> A(CO)	Grams CH <sub>4</sub> A(CH <sub>4</sub> )	$\frac{\text{Grams } CO_2}{A(CO_2)}$
9-25-84	1.6141	1.0273	2.4196
9-25-84	1.5921	1.0438	2.4523
9-25-84	1.6141	1.0193	2.2684
10-10-84	1.7336	1.0673	2.6984
10-11-84	1.6657	1.0233	2.4774
10-15-84	1.5099	0.9701	
10-16-84	1.6406	1.0522	2.4649
10-17-84	1.6510	1.0314	2.4481
10-23-84	1.7663	1.0036	2.2684
10-25-84	1.7831	1.0964	2.5178
10-30-84	1.7563	1.0543	2.4416
10-31-84	1.8003	1.0761	2.4564
11-05-84	1.6867	1.0396	2.4196
11-07-84	1.6657	1.0417	2.3815
11-08-84	1.6756	1.0404	2.4004

Table 5. Control Values: Weight/Area (x 10<sup>-3</sup> grams/cm<sup>2</sup>)

Experimental Run #	Date of Experiment	Weight % of K <sub>2</sub> CO <sub>3</sub>	Int CO	egrated C CH <sub>4</sub>	ounts CO <sub>2</sub>
1	9-26-84	0.00	843.40	196.60	111.5*
2	9-28-84	0.00	769.00	188.15	123.95
3	10-02-84	0.00	777.00	162.50	109.10
4	10-02-84	0.00	753.50	187.40	119.30
5	10-04-84	0.00	825.00	193.00	107.50
6	10-04-84	0.00	640.25	125.50	92.0
7	11-05-84	1.74	<b>6</b> 15.50	119.50	187.50
8	11-05-84	1.43	546.45	106.75	184.45
9	11-07-84	1.04	<b>490.</b> 00	89.00	179.00
10	11-08-84	1.57	694.60	150.30	200.10
11	11-08-84	1.43	575.45	125.00	186.95
12	11-08-84	1.45	<b>569.</b> 25	118.25	180.50
13	10-25-84	6.30	574.55	110.18	225.85
14	10-25-84	6.30	625.85	88.25	191.15
15	10-30-84	6.17	621.15	100.50	232.50
16**	10-30-84	6.37	723.65	74.25	377.25
17	10-30-84	6.37	<b>6</b> 89.00	105.00	203.00
18	10-31-84	6.36	651.90	91.75	252.00
19	11-05-84	<b>6.</b> 80	682.20	74.40	405.90
20	10-10-84	13.30	711.25	102.60	194.3(
21***	10-11-84	13.65	540.10	94.75	285.80
22	10-15-84	12.80	710.50	96.00	201.00
23***	10-16-84	12.80	587.38	91,43	272.65

Table 6. Experimental Values: Integrated Counts.

Table 6 (continued)

Experimental Run #	Date of Experiment	Weight % of K <sub>2</sub> CO <sub>3</sub>	Int CO	egrated Co CH <sub>4</sub>	ounts CO <sub>2</sub>	
24***	10-16-84	13.40	456.75	68.00	270.00	
25	10-16-84	13.40	758.25	101.48	189.05	
26	10-17-84	13.30	754.38	83.65	289.99	
27	10-23-84	12.60	660.75	108.00	195.25	
28****	10-23-84	12.60	341.00	49.00	303.00	

\* Recorder pen drifted below the base line, data not valid.

**\*\*** Possible air lead in reactor, data not valid.

\*\*\* Sample fused to screen, data not valid.

\*\*\*\* Sample fell out of screen, data not valid.
Experimental Run #	Integ	rated Ar	reas (cm <sup>2</sup> )	Weight ( Produce	of Pyrolys ed (x10 3	is Gases grams)
1	2.2491	0.5243		3.6137	0.5401	
2	2.0507	0.5017	0.3305	3.2949	0.5169	0.7867
3	2.0720	0.4333	0.2909	3.3292	0.4464	0.6924
4	2.0093	0.4997	0.3181	3.2285	0.5148	0.5772
5	2.2000	0.5147	0.2867	3.5349	0.5302	0.6823
õ	1.7073	0.3347		2.7433	0.3448	
7	1.6413	0.3187	0.5000	2.7685	0.3313	1.2098
3	1.4572	0.2847	0.4919	2.4579	0.2959	1.1091
9	1.3067	0.2373	0.4773	2.1765	0.2472	1.1368
10	1.8523	0.4008	0.5336	3.1036	0.4170	1.2808
11	1.5345	0.3333	0 <b>.49</b> 85	2.5712	0.3468	1.1967
12	1.5180	0.3153	0.4813	2.5435	0.3281	1.1554
13	1.5321	0.2938	0.6023	2.7320	0.3221	1.5164
14	1.6689	0.2353	0.5097	2.9759	0.2580	1.2834
15	1.6564	0.2680	0.6200	2.9092	0.2826	1.5138
16						
17	1.8373	0.2800	0.5413	3.2270	0.2952	1.3217
18	1.7384	0.2447	0.6720	3.1297	0.2633	1.6507
19	1.8192	0.1984	1.0824	3.0685	0.2063	2.6190
20	1.8967	0.2736	0.5181	3.2880	0.2920	1.3981
21						
22	1.8947	0.2560	0.5360	2.8607	0.2483	1.3245

Table 7. Experimental Values: Integrated Areas and Weight of Pyrolysis Gases Produced.

Table 7 (continued)

Experimental	Integ	rated Ar	eas (cm²)	Weight ( Produce	of Pyrolys ed (x10 <sup>-3</sup>	is Gases grams)
	C0	CH4	C0 <sub>2</sub>	CO	СН <sub>4</sub>	C0 <sub>2</sub>
23						
24						
25	2.0220	0.2706	0.5041	3.3173	0.2847	1.2426
26	2.0468	0.2231	0.7733	3.3213	0.2301	1.8932
27	1.7620	0.2880	0.5207	3.1122	<b>0.28</b> 90	1.1811
28						

Experimental Run #	Wei K <sub>2</sub> CO <sub>3</sub> (x10 <sup>-4</sup> )	ght (grams) cellulose (x10 <sup>-2</sup> )	Weight CO	% of Pi CH <sub>4</sub>	roducts CO <sub>2</sub>
1	0,0000	1 4500	24 92	3 72	
2	0.0000	1.4500	24.32	2.56	 - AD
2	0.0000	1.4500	22.72	3.50	5.43
3	0.0000	1.4500	22.96	3.08	4./8
4	0.0000	1.4500	22.27	3.55	5.22
5	0.0000	1.4500	24.38	3.66	4.71
6	0.0000	1.4500	18.92	2.38	
7	2.5230	1.4248	19.43	2.33	8.49
8	2.0735	1.4293	17.20	2.07	8.33
9	1.5080	1.4349	15.17	1.72	7.92
10	2.2765	1.4272	21.75	2.92	8.97
11	2.0735	1.4293	17.99	2.43	8.37
12	2.1025	1.4290	17.80	2.30	8.09
13	9.1350	1.3587	20.11	2.37	11.16
14	<b>9.13</b> 50	1.3587	21.90	1.90	9.45
15	8.9465	1.3605	21.38	2.08	11.13
16					
17	9.2365	1.3576	23.77	2.17	9.74
18	9.2220	1.3578	23.05	1.94	12.16
19	9.8600	1.3514	22.71	1.53	19.38
20	19.2850	1.2572	26.15	2.32	11.12
21					
22	18.5600	1.2644	22.63	1.96	10.48

Table 8.	Experimental Values: Weight of $K_2CO_3$ and Cellulose in t	the
	14.5 Milligram Sample, Weight Percent (with respect to	
	cellulose) of Products.	

Table 8 (continued)

Experimental Run #	Weight K <sub>2</sub> CO <sub>3</sub> (x10 <sup>-4</sup> )	(grams) cellulose (x10 <sup>-2</sup> )	Weight CO	% of Pı CH4	roducts CO <sub>2</sub>
23					
24					
25	19.4300	1.2557	26.42	2.27	9.90
26	19.2850	1.2572	26.42	1.83	15.06
27	18.2700	1.2673	24.56	2.28	9.32
28					

Experimental Run #	Milligrams of Char	Weight % of Char
1*		
2*		
3*		
4*		
5	0.10	0.689
6	0.30	2.068
7	1.10	7.721
8	1.10	7.696
9	1.10	7.666
10	1.20	8.408
11	1.10	7.696
12	1.10	7.698
13	2.40	17.665
14	1.70	12.512
15	1.80	13.230
16	0.80	
17	1.70	12.522
18	1.60	11.783
19	1.00	7.400
20	2.40	19.091
21	3.80	
22	1.80	14.236

Table 9. Experimental Values: Char Weights and Weight Percents.

Experimental Run #	Milligrams of Char	Weight % of Char
23		
24		
25	1.60	12.742
26	1.40	11.136
27	2.20	17.360
28		

\*Sample not collected.

Experimental Run #	Weight of K <sub>2</sub> CO <sub>3</sub> Lost During Pyrolysis (x10 <sup>-3</sup> grams)	Weight of CO Produced From K2CO <sub>3</sub> Reaction (x10 <sup>-4</sup> grams)
1		
2		
3		
4		
5		
6		
7	NC	NC
8	NC	NC
9	NC	NC
10	NC	NC
11	NC	NC
12	NC	NC
13	0.7135	4.3374
14	0.7135	4.3374
15	0.6947	4.2228
16		
17	0.7237	4.3991
18	0.7222	4.3903
19	0.7860	4.7781
20	1.8235	11.0851
21		

Table 10.	Experimental Values: Weight of $K_2CO_3$ Lost and $CC$
	Produced from the $K_2CO_3$ Reaction.

Experimental Run #	Weight of K <sub>2</sub> CO <sub>3</sub> Lost During Pyrolysis (x10 <sup>-3</sup> grams)	Weight of CO Produced From K <sub>2</sub> CO <sub>3</sub> Reaction (x10 <sup>-4</sup> grams)
22	1.7510	10.6444
23		
24		
25	1.8380	11.1733
26	1.8235	11.0851
27	1.7220	10.4681
28		

Table 10 (continued)

NC - No Change

Experimental Run #	Actual Weight of CO Produced (x10 <sup>-3</sup> grams)	Corrected Weight Percent of CO
1		
2		
3		
4		
5		
6		
7	NC	NC
8	NC	NC
9	NC	NC
10	NC	NC
11	NC	NC
12	NC	NC
13	2.2982	16.92
14	2.5422	18.71
15	2.4869	18.28
16		
17	2.7871	20.53
18	2.6907	19.82
19	2.5907	19.17
20	2.1795	17.34
21		
22	1.7963	14.21

Table 11.	Experimental	Values:	Corrected	Weight	and	Weight	Percent
	of CO.						

Table 11 (continued)

Experimental Run #	Actual Weight of CO Produced (x10 <sup>-3</sup> grams)	Corrected Weight Percent of CO
23		
24		
25	2.1999	17.52
26	2.2128	17.60
27	2.0654	16.30
28		

NC - No Change

Experimental	Date of	Weight %	Integrated	Integrated Counts		
Run #	Experiment	of $\tilde{k}_2 CO_3$	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>		
3	10-02-84	0.00	59.25	23.80		
4	10-02-84	0.00	48.00	28.75		
7	11-05-84	1.74	28.18	5.00		
8	11-05-84	1.43	32.13	14.75		
15	10-30-84	6.17	28.65	5.45		
19	11-05-84	6.80	18.68	6.90		
22	10-15-84	12.80	13.25	23.50		
26	10-17-84	13.30	18.70	21.30		

Table 12. Experimental Values: Integrated Counts of  $\rm C_2H_2$  and  $\rm C_2H_4$  .

Table 13. Experimental Values: Integrated Area, Weight and Weight Percent of  $C_2\,H_2$  and  $C_2\,H_4$ .

Experimental Run #	Integra (x10 <sup>-2</sup> C <sub>2</sub> H <sub>4</sub>	ted Area cm <sup>2</sup> ) C <sub>2</sub> H <sub>2</sub>	Weight of Pyrolysis Gases (x10 <sup>-4</sup> grams) C <sub>2</sub> H <sub>4</sub> C <sub>2</sub> H <sub>2</sub>		Weight % of Products C <sub>2</sub> H <sub>4</sub> C <sub>2</sub> H <sub>2</sub>	
3	15.8000	6.3467	3.1081	1.2485	2.14	0.86
4	12.8000	7.6667	2.5179	1.5081	1.74	1.04
7	7.5147	1.3330	1.4782	0.2623	1.04	0.18
8	8.5680	3.9333	1.6854	0.7737	1.18	0.54
15	7.6400	1.4533	1.5029	0.2859	1.10	0.21
19	4.9813	1.8400	0.9799	0.3620	0.73	0.27
22	3.5333	6.2667	0.6950	1.2330	0.55	0.98
26	4.9867	5.6800	<b>0.9</b> 809	1.1173	0.78	0.89

C. Summary of Experimental Results.

Tables 14 and 15 give the averaged product weight percent values for the flash pyrolysis of cellulose at different  $K_2CO_3$  weight percents. It is quite evident that the presence of  $K_2CO_3$  in the cellulose samples influences the product yields.

Table 14 shows the char yields for various  $K_2CO_3$  weight percents. It is observed that as the amount of  $K_2CO_3$  is increased in the cellulose sample, the amount of char remaining after pyrolysis increases as well. Neutron activation studies of the char show that the 1.0 percent samples contain approximately the same amount of  $K_2CO_3$  as was originally impregnated in the samples. This results in a 0.0 weight fraction loss of  $K_2CO_3$  for the 1.0 percent samples. The weight fraction of  $K_2CO_3$ lost for the 5.0 percent and 10.0 percent char samples are 0.78 and 0.95, respectively. Therefore a majority of the  $K_2CO_3$  originally present in these samples is in some way lost.

An important conclusion was reached from the neutron activation study. The amount of  $K_2CO_3$  remaining in the 1.0, 5.0 and 10.0 weight percent char samples is comparably equal to or less than that originally impregnated in the 1.0 percent samples. This indicates that the increase in the weight of the char samples with increased loading of  $K_2CO_3$  in some way increases the amount of char produced just by its presence when pyrolysis of cellulose takes place.

Table 15 gives the gas yields for various  $K_2CO_3$  weight percents. The weight percent of CO declines then increases to a value slightly above that of the unloaded sample for the 10.0 weight percent sample. If the  $K_2CO_3$  reaction with char (equation 4-31) is taken into consideration then the CO yield declines and reaches a minimum at the 10.0

percent sample. There is a continuous decline in methane  $(CH_4)$  and ethylene  $(C_2H_4)$  as the loading of  $K_2CO_3$  is increased. Methane yields decline by nearly 50 percent and ethylene by 67 percent when comparing the unloaded and 10.0 percent samples. Acetylene  $(C_2H_2)$  yields decline as  $K_2CO_3$  loading increases until the 10.0 percent sample. At this weight percent the yield is approximately equal to the unloaded samples.

The total gas yields are given in the two farthest columns to the right in Table 15. The following trends are observed when comparing the loaded to the unloaded samples for the uncorrected total gas yield. There is a 13.0 percent decline in gas yields for the 1.0 percent samples. The 5.0 percent samples show a 3.3 percent increase in gas yields. The most significant change is found in the 10.0 percent samples, where a 12.3 percent increase in gas yields is observed when compared to the unloaded samples. For the corrected total gas weight precents one finds a decline in yield for all  $K_2CO_3$  catagories in comparison to the unloaded samples. This shows the significant influence that the  $K_2CO_3$  reaction can have upon the total product gas yields.

Some of the experimental runs were not used in analysis of gas yields for various physical reasons: recorder pen drifting below the base line, possible air leak in the reactor, and sample fused to or falling out of the screens. Other than samples rejected for these reasons, a majority of the integrated values were found to be very close to one another (within 15 percent of the averaged value) for a given  $K_2CO_3$  loading category. Occasionally a sample run or even a particular gas within a run would be noticeably different when compared to other values in the same weight percent category. Such is the case

for Experimental Run #6 and  $CO_2$  values from Run #19 and #26. Because of the large discrepancy these values were not used in calculating the averaged numbers given in Table 15.

When a sample is pyrolyzed in the reactor the tar materials collect on the copper electrodes and the inside wall of the alumina liner. Although actual quantitative analysis of tar yields were not conducted, the following trend was observed. It was visually observed that as  $K_2CO_3$  loading of the samples increased, there was a proportionate decline in tar yields. At 10.0 percent loading there was very little tar produced compared to the unloaded samples.

In conclusion the tar and char yields of pyrolysis appear to be the most influenced by  $K_2CO_3$  loading of cellulose. The gas yields are shown to vary depending upon the weight percent of  $K_2CO_3$ .

Weight % of K <sub>2</sub> CO <sub>3</sub>	Weight % Char	Weight of K Initial	<sub>2</sub> CO <sub>3</sub> (grams) Final	Weight Fraction ** of K <sub>2</sub> CO <sub>3</sub> Lost
0.0	1.38	0.00	0.00	0.00
1.0	7.81	2.09 x 10 <sup>-4</sup>	$2.00 \times 10^{-4}$	0.00***
5.0	12.52	9.26 x 10 <sup>-4</sup>	$2.00 \times 10^{-4}$	0.78
10.0	14.91	18.97 x 10 <sup>-4</sup>	$1.05 \times 10^{-4}$	0.95

Table 14. Char Yields and Neutron Activation Study  $({}^{42}K)$ .\*

\* All table data are averaged values from six experimental runs in each  $K_2CO_3$  weight percent category.

\*\* Weight fraction of  $K_2CO_3$  lost = (initial-final)/initial.

\*\*\* 0.00 within experimental error.

Table 15. Average Gas Weight Percent Values.

Weight %		Av	erage	Weight Per	cent Va	lues		Corrected #
of K <sub>2</sub> CO <sub>3</sub>	CO <sub>3</sub> CO	C0 <sup>*</sup>	CH4	C0 <sub>2</sub>	$C_2H_4$	$C_2H_2$	Total	Total
0.0	23.45**	23.45	3.51*	* 5.04**	1.94	0.95	34.89	34.89
1.0	18.22	18.22	2.30	8.36	1.11	0.36	30.35	30.35
5 <b>.0</b>	22.15	18.91	2.00	10.73***	0.92	0.24	36.04	32.80
10.0	25.24	16.59	2.13	10.21 <sup>@</sup>	0.67	0.94	39.19	30.54

\* Corrected weight percent of CO.

\*\* Experimental Run #6 not used in averaging values.

\*\*\* Experimental Run #19 not used in averaging values.

@ Experimental Run #26 not used in averaging values.

# Corrected Weight Percent of CO used in summing values.

#### CHAPTER V

## CONCLUSION

The pyrolysis of  $K_2CO_3$ -loaded cellulose samples at rapid heating rates (>300°C per second) and high temperatures (900°C) was conducted in order to answer the questions outlined in Chapter I, Section D. This chapter deals with the experimental data collected and the interpretation of the this data so as to attempt to answer the before mentioned questions. The data collected from the pyrolysis experiments, as presented in Chapter IV, was found to be very consistant within the different  $K_2CO_3$ weight percent categories. A summary of the experimental results is given in Chapter IV, Section C.

# A. Comparison of Slow Versus High Temperature Flash Pyrolysis of Cellulose in the Presence of $K_2CO_3$ .

It has been shown that the product yields of pyrolysis are influenced more by elevated peak temperatures (>600-700<sup>o</sup>C) than either residence time or heating rates.<sup>9,10</sup> A number of slow pyrolysis studies have been conducted which use additives to alter product yields,<sup>4,17,18, 20,21,22 Slow pyrolysis of cellulose in the presence of K<sub>2</sub>CO<sub>3</sub> has been shown to increase gas and char yields while at the same time decreasing tar yields.<sup>17, 20, 21, 22</sup> The studies with K<sub>2</sub>CO<sub>3</sub> were conducted at low temperatures and slow heating rates; therefore, it is questioned whether this particular additive has any influence upon product yields at elevated temperatures and rapid heating rates.</sup>

Tables 14 and 15 give the char and gas yields from the flash pyrolysis of cellulose at  $900^{\circ}$ C for varying  $K_2CO_3$  weight percent samples. When comparing samples loaded with  $K_2CO_3$  to those which were not impregnated (unloaded), the influence is obvious. The presence of  $K_2CO_3$ results in increased char yields. The total gas yields appear to vary depending on the weight percent of  $K_2CO_3$  in the sample. Visual inspection of the tar condensing on the inside of the reactor shows a decline in yield as a result of  $K_2CO_3$  being present. Thus all three of the major pyrolysis product groups are influenced by  $K_2CO_3$  at an elevated temperature of  $900^{\circ}$ C and heating rates greater than  $300^{\circ}$ C per second.

As shown in Table 14, the presence of  $K_2CO_3$  increases the yield (weight) of char in comparison to unloaded samples. This same increase in char yield has been observed in low temperature slow pyrolysis studies in which  $K_2CO_3$  or other similar inorganic salts were used. <sup>17,22,23</sup> Table 14 reveals that with increased loading of  $K_2CO_3$  there is a corresponding increase in the char production. This same trend has been demonstrated in a slow pyrolysis study. <sup>17</sup> When comparing the 0.0 and 10.0 percent char sample yields, there is an eleven-fold increase as a result of  $K_2CO_3$  being present.

The uncorrected total gas yields (see Table 15) are found to vary with  $K_2CO_3$  loading. The increased loading of  $K_2CO_3$  favors CO and  $CO_2$ production, at the same time resulting in a decline in hydrocarbon gas yields (CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>). These same gas yield trends have been reported in slow pyrolysis studies.<sup>22,23</sup> The 1.0 percent samples show a decline in total gas yield in comparison to the unloaded samples. The 5.0 and 10.0 percent samples give an increased total gas yield for the same comparison . A general increase in total gas yields have been reported in low temperature slow pyrolysis studies.<sup>22,23</sup> A possible explanation for the decline in total gas yields observed in the 1.0 percent samples is that this study did not take into consideration the water yield as was done in the slow pyrolysis studies.

Table 15 shows that there is a decline in the corrected CO gas yields when compared to the unloaded samples. This results in a corrected total gas yield for loaded samples less than the unloaded samples.

Although quantitative analysis of tar yields were not conducted in this study, visual inspection of the copper electrodes and inside wall of the reactor revealed that as the  $K_2CO_3$  loading increased, there was a continued decline in tar production. This same decline in tar production resulting from  $K_2CO_3$  being present has been reported in several slow pyrolysis studies.<sup>17,22,23</sup>

It is therefore concluded that the additive,  $K_2CO_3$ , continues to alter pyrolysis product yields even at high temperatures and rapid heating rates. This study also shows that the same trends for product yields from slow pyrolysis can be expected for high temperature flash pyrolysis when  $K_2CO_3$  is used as the additive. For both slow and high temperature flash pyrolysis one finds that with increased  $K_2CO_3$  loading there is an increase in both char and total gas yields. At the same time there is a corresponding decline in tar production.

## B. $K_2CO_3$ After the Pyrolysis of Cellulose

A limited number of studies have been conducted which refer to the state of or location of additives after pyrolysis. A slow pyrolysis study of wood bark by Ross and Fong  $^{20}$  used x-ray analysis to detect the presence of K<sub>2</sub>CO<sub>3</sub> on the surface of char samples. Unfortunately this method did not allow a comparison of the initial and final weight of  $K_2 CO_3$  remaining on the char therefore, quantitative loss of  $K_2 CO_3$  due to pyrolysis was not determined. Another slow pyrolysis study of cellulose by Byrne et al.<sup>24</sup> used several different flame-retardants. This study showed that for a majority of the flame-retardants used the amount of retardant originally impregnated in the cellulose was still remaining on the char. Smaller amounts of some of the retardants were however, found in the tars. Unfortunately,  $K_2 CO_3$  was not among the additives used in this study.

One can therefore see the need for experimentation which better defines the location of  $K_2CO_3$  after pyrolysis. Experimentation would also answer the question of whether the observed increases in char yield with increased loading of  $K_2CO_3$  is a result of the additional weight of  $K_2CO_3$  remaining on the char or whether there is an actual altering of the product distribution.

In order to answer the above questions neutron activation of char samples were carried out. For details on the method and results from this activation study see Chapter III, Section F.

Table 14 gives the initial weight of  $K_2CO_3$  impregnated for the various sample weight percents as well as the corresponding final weight of  $K_2CO_3$  remaining in the char determined by neutron activation. Within experimental error it has been determined that the 1.0 percent char samples contain all of the  $K_2CO_3$  originally loaded onto the cellulose. Both the 5.0 and 10.0 percent char samples, however, contain an amount of  $K_2CO_3$  less than or equal to that loaded onto a 1.0 percent sample. This means that for the 5.0 percent samples 78 percent of the  $K_2CO_3$  originally impregnated on the cellulose no longer remained on the char.

For the 10.0 percent samples 95 percent of the  $K_2CO_3$  is lost from the char. This proves that the increase in char weight observed for increased loading of  $K_2CO_3$  is not a result of  $K_2CO_3$  remaining on the char and that the presence of  $K_2CO_3$  actually altered the product yields of char.

Through neutron activation of char samples it is shown that the 5.0 and 10.0 percent char samples contain less  $K_2CO_3$  then was originally impregnated in the cellulose. A possible explanation for the  $K_2CO_3$  not present on the char is covered in the next section.

C.  $K_2CO_3$ : Catalyst or Reactant?

Is  $K_2CO_3$  a catalyst or a reactant? By definition a catalyst is a substance which affects the rate of the reaction, but is recovered from the reaction unchanged. A reactant is a substance which actually changes in the reaction.

In referring to Table 14 it is observed that the presence of 1.0 weight percent  $K_2CO_3$  results in a 5.7-fold increase in char formation in comparison to the 0.0 percent samples. Table 15 shows that there is also an appreciable difference between gas yields for these two weight percents. However, as discussed in the preceding section and as presented in Table 14, there appears to be no loss of  $K_2CO_3$  from the char for the 1.0 percent samples. This suggests that for the 1.0 percent samples  $K_2CO_3$  is not reacting during pyrolysis and is in actuality acting as a catalyst.

Tables 14 and 15 show that the 5.0 and 10.0 percent samples significantly influence both the char and gas yields. However, values from Table 14 show that for these weight percent samples an appreciable amount of  $K_2CO_3$  originally present in the cellulose is no longer present in the char. An equation for the reaction of  $K_2CO_3$  with char was presented in Chapter IV, Section A. This reaction is found to be favored at high temperatures (>800<sup>0</sup>C).

$$K_2 CO_3 + 2C(char) = 2K + 3CO$$
 (4-31)

As observed in Table 15, all of the indivdual gas yields either continually decline or increase as the loading of  $K_2CO_3$  is increased. A slight variation is found for the 10.0 percent samples of acetylene. The obvious exception to this case are the CO yields which first decline at 1.0 percent loading then increase for the 5.0 and 10.0 percent samples. If it is assumed that the  $K_2CO_3$  lost from the char in the 5.0 and 10.0 percent samples is reacting according to equation (4-31), then the CO produced from this reaction can be subtracted from that which is actually produced in pyrolysis. When this is done, as shown in Table 15, there is in actuality a continual decline in CO production. Therefore, one finds the same consistent trends which are observed for the other gas products of pyrolysis. The irregular product yields of CO suggest that  $K_2CO_3$  might in fact be reacting with the char to produce CO. If this is the case then the excess  $K_2CO_3$  is acting as a reactant for the 5.0 and 10.0 weight percent samples.

When comparing the char yields for the 1.0 and 10.0 percent samples there is less than a two-fold increase for a ten-fold increase in  $K_2CO_3$ . However, comparison of the 0.0 and 1.0 percent samples show a 5.7-fold increase in char formation. The corrected total gas yields presented in Table 15 show the same trends as the char yields. That is, the corrected total gas yields are initially more affected by the 1.0 percent samples then the higher  $K_2CO_3$  loaded samples. This further suggests that the 1.0 percent samples have a catalytic influence upon product yields where as the higher  $K_2CO_3$  loaded samples have an excess of  $K_2CO_3$  which most likely acts as a reactant in a reaction such as that given by equation (4-31).

D. Chemistry of Pyrolysis in the Presence of  $K_2CO_3$ .

As discussed in the preceding sections of this chapter, the presence of  $K_2CO_3$  is found to alter pyrolysis product yields. Referring to Figure 1, the presence of  $K_2CO_3$  favors the upper and lower pathways which leads to increased yields of char and gas.

When a cellulose sample is flash pyrolyzed in the screen design reactor used in these experiments, the tar materials produced are almost instantly removed from the area of the hot screens and collect on the inside wall of the reactor. Because of the rapid heating rate and rapid removal of the tarry products, their further chemical breakdown during pyrolysis is unlikely.

Under normal conditions (without additives present) the pyrolysis of cellulose favors the breakage of the bonds labeled (d) in Figure 10.<sup>23</sup> This results in the formation of levoglucosan. Madorsky et al.<sup>25</sup> proposed that additives catalyze the breakdown of cellulose by cleavage of the C-O bond (bonds a,b, and c in Figure 10) and that this results in the destruction of the hexose units. This in turn facilitates the formation of more char and gases. Since the removal of levoglucosan from the area of the hot screens is so rapid, thus removing any likelyhood of secondary reactions, this proposal appears to be a very valid and plausible explanation for the influence of additives on pyrolysis





product yields.

E. Conclusions

Studies on the high temperature flash pyrolysis of cellulose in the presence of  $K_2CO_3$  have been conducted in order to answer the questions outlined in Chapter I, Section D. The experimental research conducted helped answer the questions as is outlined in the following paragraphs.

At elevated temperatures and rapid heating rates the presence of  $K_2CO_3$  when pyrolyzing cellulose has been shown to significantly alter product yields. The same product yield trends observed for slow pyrolysis can be applied to high temperature flash pyrolysis when  $K_2CO_3$  is used. That is, as the loading of  $K_2CO_3$  is increased there is a corresponding increase in char and total gas yields and a continual decline in tar production.

Neutron activation studies of the char products show that the weight increase in char, as  $K_2CO_3$  is increased, is not a result of  $K_2CO_3$  remaining on the char. The majority of the  $K_2CO_3$  originally impregnated on the 5.0 and 10.0 percent samples was lost during pyrolysis. A plausible explanation for the loss of this  $K_2CO_3$  is that at low loading (1.0 weight percent)  $K_2CO_3$  acts as a catalyst; however, at increased loading (5.0 and 10.0 percent samples) experimental data suggest that the excess  $K_2CO_3$  acts as a reactant.

A previously proposed theory is used to help explain on a molecular level the influence of  $K_2CO_3$  on pyrolysis product yields.

A commercial application of these results is possible. A fullscale wood pyrolysis unit could be run at lower heating rates and temperatures when evaluating different additives. Running a large system

at these conditions would result in substantial energy saving as compared to high temperature and heating rates. Once an additive is found which gives a favorable product yield, the system could then be run at elevated temperatures and heating rates where similar product trends could be expected.

F. Suggestions for Future Work.

There are many areas both within this study as well as pyrolysis in general in which further research can be conducted. Most importantly, a more complete material balance on pyrolysis products (including H<sub>2</sub>O, H<sub>2</sub>, and tar weight yields) for the ongoing research at Michigan State University would better define a molecular explanation for the influence of  $K_2CO_3$  on pyrolysis product yields. The use of different additives to determine those which produce increased yields of materials for use in the chemical or petro-chemical industries is another area in which high temperature flash pyrolysis studies might be conducted. The area of biomass pyrolysis has many unanswered questions which may be only resolved through further theoretical and experimental research.

LIST OF REFERENCES

### LIST OF REFERENCES

<sup>1</sup>Milne, T., "Pyrolysis - the thermal behavior of biomass below 600<sup>°</sup>C." "<u>A Survey of Biomass Gasification</u>," <u>2</u>, Chapter 5, Prepared by the Solar Energy Research Institute/TR-33-239 July, 1979.

<sup>2</sup>Graboski, M. and Bain, R., "Properties of biomass relevant to gasification," "<u>A Survey of Biomass Gasification</u>," <u>2</u>, Chapter 5, Prepared by the Solar Energy Research Institute/TR-33-239 July, 1979.

<sup>3</sup>Shafizadeh, F., "Chemistry of pyrolysis and combustion of wood," <u>"Progress in biomass conversion,</u>"(Academic Press, Inc., 1982), pp. 51-76.

<sup>4</sup>Hixson, A.N. and Hsu, C.C., "C<sub>1</sub> to C<sub>4</sub> oxygenated compounds by promoted pyrolysis of cellulose," <u>Ind. Eng. Chem. Prod. Res. Dev.</u>, 20, 1981, pp. 109-114.

<sup>5</sup>DeJenga, C.I., Antal Jr., M.J., and Jones Jr., M., "Yields and composition of sirups resulting from the flash pyrolysis of cellulosic materials using radiant energy," <u>Journal of Applied Polymer</u> <u>Science</u> (1982), <u>27</u>, pp. 4313-4322.

<sup>6</sup>Diebold, J. and Scahill, J., "Ablative fast pyrolysis of biomass in the entrained-flow cyclonic reactor at S.E.R.I.," Presented at the 14th Biomass Thermochemical Conversion Contractors Meeting, Arlington, Virginia June 23-24, 1982 U.S. Department of Energy contract # DE-ACO6-76RL0 1830.

<sup>7</sup>Thurner, F., Mann, U., and Beck, S., "Kinetic investigation of wood pyrolysis," Prepared for Department of Energy, Division of Solar Energy, contract # DE-AS04-79ET20041, June 1980.

<sup>8</sup>Caubet, S., Corte, P., Fahim, C. and Traverse, J.P., "Thermochemical conversion of biomass: Gasification by flash pyrolysis study," <u>Solar Energy</u> (1982), <u>29</u>, No. 6, pp. 565-572.

<sup>9</sup>Hajaligol, M.R., Howard, J.B.,Longwell, J.P. and Peters, W.A., "Product compositions and kinetics for rapid pyrolysis of cellulose," Ind. Eng. Chem. Prod. Res. Dev. (1982), 21, pp. 457-465. <sup>10</sup>Antal Jr., M.J., Friedman, H.L., and Rogers, F.C., "Kinetics of cellulose pyrolysis in nitrogen and stream," <u>Combusion Science</u> <u>and Technology</u> (1980), <u>21</u>, pp. 141-152.

<sup>11</sup>Scott, D.S. and Piskorz, J., "The flash pyrolysis of aspenpoplar wood," <u>The Canadian Journal of Chemical Engineering</u> (1982), <u>60</u>, pp. 666-674.

<sup>12</sup>Brink, D.L. and Massoudi, M.S., "A flow reactor technique for the study of wood pyrolysis 1. Experimental," <u>Journal of Fire and</u> <u>Flammability</u>, <u>9</u>, April 1978, pp. 176-188.

<sup>13</sup>Caubet, S., Corte, P., Fahim, C. and Traverse, J.P., "Gaseous fuel from biomass by flash pyrolysis," <u>"Energy from Biomass</u>" (1981), Applied Science Publishers, pp. 542-547.

<sup>14</sup>Deglise, X., Richard, C., Rolin, A., and Francois, H., "Fast pyrolysis/gasification of lignocellulosic materials at short residence time," 'Energy from Biomass" (1981), Applied Science Publishers, pp. 548-553.

<sup>15</sup>Graef, M., Allen, G.G. and Krieger, B.B., "Product distribution in the rapid pyrolysis of biomass/ligin for production of acetylene," "American Chemical Society Symposium Series," <u>144</u>, 1981, pp. 293-311.

<sup>16</sup>Niksa, S.J., Russel, W.B. and Saville, D.A., "Captive sample reactor for kinetic studies of coal pyrolysis and hydropyrolysis on short time scales," Fuel (1982), <u>61</u>, pp. 1207-1212.

<sup>17</sup>Pyle, D.L. and Zaror, C.A., "The effect of alkali salts on low temperature pyrolysis," Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7 2AZ, England.

<sup>18</sup>Hilado, C.J., and Brandt, D.L., "Char yield and flash-fire propensity of pyrolysis gases from materials," <u>Journal of Fire and Flammability</u>, 9, Oct. 1978, pp. 553-557.

<sup>19</sup>Steinberg, M. and Fallon, P.T., "Flash pyrolysis of biomass with reactive and non-reactive gases," work performed for biomass energy technology division, U.S. Department of Energy, Contract # DE-AC02-76CH00016.

<sup>20</sup>Ross, R.A., and Fong, P., "Catalytic conversion of wood barks to fuel gases," <u>Ind. Eng. Chem. Prod. Res. Dev</u>. (1981), <u>20</u>, pp. 197-203.

<sup>21</sup>Fung, D.P.C., Tsuchiya, Y., and Sumi, K., "Thermal degradation of cellulose and levoglucosan - the effect of inorganic salts," <u>Wood</u> <u>Science</u>, 5, No. 1, July 1972. <sup>22</sup>Tsuchiya, Y., and Sumi, K., "Thermal decomposition products of cellulose," <u>Journal of Applied Polymer Science</u> (1970), <u>14</u>, pp. 2003-2013.

<sup>23</sup>Shafizadeh, F., "Pyrolysis and combusion of cellulosic materials," <u>Carbonydrate Chemistry</u> (1968), <u>23</u>, pg. 419.

<sup>24</sup>Byrne, G.A., Gardiner, D. and Holmes, F.H., "The pyrolysis of cellulose and the action of flame-retardants. II. Further analysis and identification of products," <u>J. Appl. Chem.</u>, (1966), <u>16</u>.

<sup>25</sup>Madorsky, S.L., Hart, V.E., and Straus, S., "Pyrolysis of cellulose in a vacuum," <u>J. Res. Natl. Bur. Std</u>. (1956), 56, p. 343.

<sup>26</sup>Brunner, P.H., and Roberts, P.V., "The significance of heating rate on char yield and char properties in the pyrolysis of cellulose," <u>Carbon</u>, 18, pp. 217-224.

<sup>27</sup>McKee, D.W. and Chatterji, D., "The catalyzed reaction of graphite with water vapor," <u>Carbon</u> (1978), <u>16</u>, pp. 53-57.

<sup>28</sup>Huhn, F., Klein, J. and Juntgen, H., "Investigation on the alkali-catalyzed steam gasification of coal: kinetics and interactions of alkali-catalyst with carbon," Proc. Int. Symp. on Catalyzed Carbon and Coal Gasification, Amsterdam, 1982.

<sup>29</sup>Wen-Yang, Wen, "Mechanisms of alkali metal catalysis in the gasification of coal, char, or graphite," <u>Catal. Rev.-Sci. Eng.</u>, <u>22(1)</u>, 1980, pp. 1-28.

APPENDIX I

PART A - Calculating the resistance in 99.0 percent alumina.

Resistance =  $\rho$  L/A L = Length = 1/4 inch A = area = 1 in. x 1/2 in. = 0.5 in<sup>2</sup>  $\rho$  = resistivity

from <u>Alumina as a Ceramic Material</u> compiled and edited by Walter Gitzen, American Ceramic Society (1970) page 79 for 99.0 percent alumina

$$\rho = 8 \times 10^{\circ} \text{ ohms-cm at } 1,000^{\circ} \text{C}$$

thus

Resistance = 
$$\frac{(8 \times 10^{6} \text{ ohm-cm}) \times (0.25 \text{ in.}) \times 1 \text{ in.}}{(0.5 \text{ in.}^{2})}$$
Resistance = 1,574,804 ohm

PART B - Calculating the power requirements for heating the screens to  $1,000^{\circ}$ C.

An energy balance around the screens gives

Power	required	to	-	Total energy 1	ost
heat	screens		-	to surrounding	S

This is assuming the system is nonadiabatic. The energy lost to the

surroundings is in three forms; conduction, radiation, and free convec-

tion. Therefore,

```
Total energy lost _ Energy lost due _ Energy lost due _ to conduction + to radiation +
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Energy lost due to free convection

A. Calculate the energy lost due to conduction -

For unsteady-state the energy equation is:

 $\rho \hat{C} p = \frac{\partial T}{\partial t} = (\nabla \cdot \kappa \nabla T)$  (See page 352 from <u>Transport Phenomena</u> by Bird, Stewart and Lightfoot)

Assuming the thermal conductivity is independent of temperature



at t = 0 the surface of the screen is raised to  $T_1$  and maintained at that temperature for t > 0. In dimensionless form equation (A) becomes

(B) 
$$\frac{\partial \Theta}{\partial t} = \alpha \frac{\partial^2 \Theta}{\partial y^2}$$
 where  $\Theta = \frac{(T - T_0)}{(T_1 - T_0)}$ 

The boundary conditions are

I.C.		t<0	$T = T_0 = 20^{\circ}C  \Theta = 0 \text{ for all } y$	
B.C.	1	<b>y</b> = 0	$\Theta = 1$ T = T <sub>1</sub> = 1,000 <sup>0</sup> C for all t>0	
B.C.	2	y = ∞	$\Theta = 0$ T = T <sub>0</sub> for all t>0	
B.C.	2	can be T = T <sub>o</sub>	applied to the problem since at $y = 3/8$ in. thus $y = \infty$ , $T = T_0$ .	· ,

The solution to the problem (equation (B)) is

$$\Theta = 1 - \frac{2}{\sqrt{\pi}} \qquad \frac{y/\sqrt{4\alpha t}}{0} e^{-n^2} dn$$

or

(C) 
$$\frac{T - T_0}{T_1 - T_0} = 1 - erf(\frac{y}{\sqrt{4\alpha t}})$$

since (D)  $q| = -\kappa A \frac{\partial T}{\partial y}|$  (fouriers law of heat conduction) y = 0 y = 0

plugging equation (C) into equation (D) gives

$$\begin{array}{l} q \mid = \\ y = 0 \quad \frac{A \kappa}{\sqrt{\pi \alpha t}} \quad (T_1 - T_0) \end{array}$$

integrating this equation with respect to time yields

$$\frac{dq}{dt} \quad \text{or} \quad \int dq = \int A_{\kappa} (T_1 - T_0) dt$$

$$\frac{dq}{dt} \quad \frac{dq}{dt} = \int A_{\kappa} (T_1 - T_0) dt$$

or

(E) 
$$\triangle q = q$$
 conduction  $= \frac{2 \operatorname{Act}^{1/2} (T_1 - T_0)}{\sqrt{\pi \alpha}}$ 

Solving this equation gives the energy lost due to conduction in a helium atmosphere.

In heating the screens from  $20^{\circ}$ C to 1,000°C the properties of density  $\rho$ , viscosity  $\mu$ , thermal heat transfer coefficient  $\kappa$  and Cp will most likely change. Therefore the values used are average values between  $20^{\circ}$ C and 1,000°C or as close to 510°C as possible.

From <u>Heat Transfer</u> by J.P. Holman, fourth edition, McGraw Hill Book Company, for helium at 800<sup>0</sup>F (527<sup>0</sup>C) the following values were found

$$\rho = 0.06023 \frac{\text{Kg}}{\text{m}^3} \qquad \mu = 381.7 \times 10^{-7} \frac{\text{Kg}}{\text{m}} \cdot \text{s}$$

$$Cp = 5.2 \text{ KJ/Kg}^{\text{O}}C \qquad \kappa = 0.275 \text{ w/m}^{\text{O}}C$$

$$\alpha = 8.774 \times 10^{-4} \text{ m}^2/\text{sec}$$

Since t = 1 second, 
$$T_0 = 20^{\circ}C$$
,  $T_1 = 1,000^{\circ}C$ 

Because both sides of the screen will conduct heat the screen area is taken as twice as large, so  $A = 4 \text{ in.}^2$ 

The solution to equation (E) is

$${}^{q} \text{conduction} = \frac{2}{\sqrt{\pi}} + \frac{4 \text{ in.}^{2} + 0.275 \text{ w}}{\text{m}^{0}\text{C}} + \frac{3/\text{sec}}{\text{w}} + \frac{(1 \text{ sec})^{1/2}}{(1 \text{ sec})^{1/2}} + \frac{(1 \text{ s$$

qconduction = 26.49 Joules/sec

B. Calculating the Energy lost due to Radiation -

Radiation between two non-black surfaces is given by

(F) 
$$q_{1,2} = \sigma A_1 \xi_{1,2} (T_1^4 - T_2^4)$$

For one gray surface completely surrounded by another (concentric spheres or cylinders)

$$\xi_{1,2} = (\text{overall interchange} = \frac{1}{\frac{1}{E_1} + \frac{A_1}{A_2} (\frac{1}{E_2} - 1)}$$

$$A_1$$
 = area of enclosed surface (wire mesh) =  
 $A_1$  = 2 in<sup>2</sup> x 2 (for both surfaces) = 4 in.<sup>2</sup>  
 $A_2$  = area of ceramic liner = 2  $\pi$ RL = 2  $\pi$ (0.75 in) (3.0 in)  
 $A_2$  = 7.64159 in<sup>2</sup>

$$E_1$$
 = emissivity of metal = 0.6  
 $E_2$  = emissivity of ceramic = 0.9  
 $T_1$  = temperature of screen = 1,000°C = 1,273°K  
 $T_2$  = temperature of ceramic = 20°C = 293°K

thus

$$\xi_{1,2} = \frac{1}{\frac{1}{0.6} + \frac{4 \text{ in.}^2}{7.64159 \text{ in.}^2} (\frac{1}{0.9} - 1)}$$

$$\xi_{1,2} = 0.579768$$

 $\sigma$  = Stefan - Boltzman Constant = 5.676x10<sup>-8</sup> w/m<sup>2</sup> o<sub>K</sub>4

using equation (F),

<sup>q</sup>radiation = 
$$\frac{5.676 \times 10^{-8} \text{w}}{\text{m}^2 \circ \text{K}^4} + \frac{4 \text{ in}^2}{10.579768} \frac{[(1,273)^4 - (293)^4]}{[(1,273)^4 - (293)^4]} \circ \text{K}$$

$$\frac{J/\text{sec}}{W} + \frac{(2.54 \text{ cm})^2}{1 \text{ m}^2} + \frac{1 \text{ m}^2}{(100 \text{ cm})^2}$$

qradiation = 222.39 Joules/sec

C. Calculate the Energy lost due to Free Convection -

Gr = Grashof Number = 
$$\begin{bmatrix} \frac{\rho^2 \ \beta \ g \ D^3 \ (T_1 - T_0)}{\mu^2} \end{bmatrix}$$
  
 $\rho = 0.06023 \ \text{Kg/m}^3$   $\mu = 381.7 \times 10^{-7} \ \text{Kg/m} \cdot \text{sec}$   
 $g = \text{gravity} = 9.8 \ \text{m/sec}^2$   $\beta = 1/T_{\infty} = 1/293^{0}\text{K}$   
 $D = \text{average distance from screen} \quad \text{Pr} = \text{Prandtl Number} = 0.72$   
to wall of the cylinder = 3/8 in.  
 $T_1 = 1,000^{\circ}\text{C} = 1,273^{\circ}\text{K}$   
 $T_0 = 20^{\circ}\text{C} = 293^{\circ}\text{K}$ 

S0

$$Gr = \left(\frac{0.06023 \text{Kg}}{\text{m}^3}\right)^2 + \frac{9.8 \text{ m}}{293^{9} \text{K sec}^2} + \frac{\left[(1.273^4) - (293^4)^{9} \text{K} + (3/8 \text{ in.})^3\right]}{\left(\frac{2.54 \text{ cm}}{\text{m}^3} + \frac{1 \text{ m}^3}{(100 \text{ cm})^3}\right]}$$
  

$$Gr = 70.58$$

therefore  $Pr \cdot Gr = 50.78$ 

Page 245 in <u>Heat Transfer</u> by J.P. Holman the average free-convection heat transfer coefficients can be found through the following relationship

(g)  $\bar{N}_{\mu}$  (Nusselt Number) = C · (Gr · Pr)<sup>m</sup> =  $\frac{h}{\kappa}$  · x For Gr · Pr in the range  $2 \times 10^4$  - 8 x  $10^6$  for a horizontal plate with upper surface heated

C = 0.54, m = 1/4

Even though I am not in the range mentioned above, to get a rough estimate the C and m values will be used. It is important to recognize that these values are for a isothermal surface, in this case at  $1,000^{\circ}$ C. The screens are assumed to reach  $1,000^{\circ}$ C almost instantly.

The equation for free convection can be written

<sup>q</sup>free convection = h ( $T_1 - T_0$ )A

from equation (g) the heat transfer coefficient h can be calculated to be

$$h = \frac{C\kappa (Gr \cdot Pr)^{m}}{x}$$

$$x = average distance from screen to reactor wall$$

$$x = 3/8 in.$$

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$$\frac{q_{F.C.}}{top} = \frac{C \times (Gr \cdot Pr)^m A (T_1 - T_0)}{x} \qquad A = area of upper side of screen A = 2 in2$$

$${}^{\text{q}\text{F.C.}}_{\text{top}} = \frac{2 \text{ in.}^2 + 0.54 + 0.275 \text{ w} + (1,000 - 20)^{\text{o}\text{C}} + (50.78)^{1/4} + \text{J/sec}}{3/8 \text{ in.}} + \frac{1 \text{ m}}{\text{w}^{\text{o}\text{C}}}$$

qF.C. = 52.6 J/sec top

In the same manner the heat lost due to free convection can be calculated for the bottom of the screen. From the same source for the lower surface of a heated plate with Gr  $\cdot$  Pr in the range  $10^5 - 10^{11}$ 

$$C = 0.58$$
 and  $m = 1/5$ 

therefore

$${}^{q}_{F.C.}_{bottom} = \frac{2 \text{ in}^{2} (0.58) + 0.275_{W} (1,000 - 20)^{\circ}\text{C} (50.78)^{1/5}}{3/8 \text{ in.} \text{m}^{\circ}\text{C}}$$

$$\frac{J/\text{sec}}{3/8 \text{ in.} \text{m}^{\circ}\text{C}}$$

$$\frac{J/\text{sec}}{W} \frac{1 \text{ m} + 2.54 \text{ cm}}{100 \text{ cm}}$$

$$= 46.45 \text{ J/sec}$$
Total Energy
lost due to
$$= {}^{q}\text{F.C.} + {}^{q}\text{F.C.} = (52.6 + 46.45) \text{ J/sec} = 99.05 \text{ J/sec}$$
free convection
$$= \text{top} \text{ bottom}$$

D) Calculate the total energy lost to the surroundings -

E) Calculate the arithmetic average of the resistance over the range 20  $^{\circ}$  C to 1,000  $^{\circ}$  C –

The resistance for an individual wire is given by

$$R_n = \rho_{20} \circ_C \cdot \frac{L}{A}$$

 $^{\circ}_{20}$  = resistivity of stainless steel (304) at  $20^{\circ}$ C

 $^{\circ}20^{\circ}C = 7.2 \times 10^{-5} \text{ ohm} - \text{cm}$ 

L = length of the wire = 2 inches A = area of the individual wire =  $\pi r^2$ r = 0.0007 inches

thus

$$R_{n} = \frac{7.2 \times 10^{-5} \text{ ohm - cm } 2 \text{ in. } 1 \text{ in.}}{\pi (0.0007 \text{ in})^{2}} = 36.828 \text{ ohm}$$

The total resistance  $\mathrm{R}_{20}\mathrm{o}_{\mathrm{C}}$  is given by

$$\frac{1}{R_{20}} = \frac{1}{R_{1}} + \frac{1}{R_{2}} + \dots + \frac{1}{R_{n}} = n \times \frac{1}{R_{n}}$$

where n = 325 because there are 325 wires in a one inch wide screen. Solving for  $R_{20}o_{C}$  you get

$$R_{20}O_{C} = \frac{Rn}{n} = \frac{36.828 \text{ ohm}}{325} = 0.113318 \text{ ohm}$$

Because the resistance in stainless steel is a function of temperature the following relationship was obtained from Principles of Physics by F. Bueche (Section Edition, McGraw-Hill Book Company, p. 374).

$$R(T) = R_{20} \circ_{C} + R_{20} \circ_{C} \cdot \alpha_{20} \circ_{C} \cdot (T - 293^{\circ} K)$$
$$\alpha_{20} \circ_{C} = \frac{3.9 \times 10^{-3}}{\circ_{K}}$$

Since the temperature changes from 20<sup>°</sup>C to 1,000<sup>°</sup>C I desire to calculate a resistance which will give me an average for this temperature range.

Arithmetic Average = 
$$\frac{1}{b-a} = \begin{cases} b \\ f(x) \\ a \end{cases} dx$$

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Arithmetic Average of the resistance = Raa

$$R_{AA} = \frac{1}{1273^{\circ}K - 293^{\circ}K} \frac{1273^{\circ}K}{293^{\circ}K} (R_{20}^{\circ}C + R_{20}^{\circ}C \cdot \alpha_{20}^{\circ}C \cdot \alpha_{20}^{\circ}$$

thus

$$R_{AA} = R_{20}O_{C} [1 - (293O_{K}) \cdot (\alpha_{20}O_{C})] + \frac{(R_{20}O_{C})(\alpha_{20}O_{C})}{980O_{K}}$$

$$\left[\frac{(1273^{\circ}K)^{2}}{2} - \frac{(293^{\circ}K)^{2}}{2}\right]$$

= 0.32920241 ohm F) Calculate the I (current) and V (voltage) required to heat the screens at 1,000°C -

## PART C - Calculate the Gas Plug Dispersion

Because the distance from the liquid nitrogen trap to the G.C. column is so long (107 inches of 1/8 inch copper tubing) it is feared that the plug of gas might disperse before reaching the G.C. column. If this occurred than good separation in the column would not be achieved.

The plug of gas can be modeled as it flows through the tubing as a function of both time and distance. At time equals zero, just before the plug is released from the liquid nitrogen trap, it would look like this.



At some later time which is unknown at this time I determine that the most extreme case which can be tolerated for dispersion of the plug is

$$x = L/2$$
 C = (0.01)C<sub>0</sub>

This plug of gas would graphically look like



I am calculating the half width of the peak. The equation which describes this change is

$$\frac{\partial C}{\partial t} = D_{AB} \frac{\partial^2 C}{\partial x^2}$$

with Boundary Conditions

1.  $t \le 0$ , C = 0, for all x 2. t > 0,  $C = C_0/2$ , x = 03. t > 0, C = 0,  $x \rightarrow \infty$ 

The solution to this equation with the corresponding boundary conditions is given on pages 353-354 of <u>Transport Phenomena</u> by Bird, Stewart and Lightfoot (copyright 1960).

$$\frac{C}{C_{o}} = (1 - erf(\frac{x}{\sqrt{4D_{AB}}}))$$

once again at x = L/2, C = 0.01  $C_0$  the above equation can be written

0.01 = 
$$(1 - erf(\frac{L/2}{\sqrt{4D_{t}}}))$$

for  $C/C_0 = 0.01$  from Figure 4.1-2 page 127 of Bird, Stewart and Lightfoot the (erf) can be solved

(A) 2.0 = 
$$\frac{x}{\sqrt{4 D_{AB} t}}$$

Calculate the diffusion coefficient  $D_{AB}$  for the diffusion of  $CO_2$  (B) through helium (A) at the following conditions

T = 293<sup>°</sup>K P<sub>t</sub> = 101.3 Kw/m<sup>2</sup> = 101.3 x 10<sup>°</sup> w/m<sup>2</sup>  
M<sub>A</sub> = M.W. of helium = 
$$\frac{4 \text{ gm}}{\text{mole}}$$
 M<sub>B</sub> = M.W. of CO<sub>2</sub> =  $\frac{44 \text{ gm}}{\text{mole}}$ 

From Table 2.2 page 33 of <u>Mass Transfer Operations</u> by Robert E. Treybal (third edition) I obtained the following data

$$E_{A}/K = 10.22 \qquad E_{B}/K = 195.2$$

$$r_{A} = 0.2551 \qquad r_{B} = 0.3941$$

$$r_{AB} = \frac{r_{A} + r_{B}}{2} = 0.3246 \qquad \frac{E_{AB}}{K} = \sqrt{\frac{E_{A}}{K} \cdot \frac{E_{B}}{K}} = 44.665$$

$$\frac{KT}{E_{AB}} = \frac{293^{O}K}{44.665} = 6.5599$$

from Figure 2.5 for  $\frac{KT}{E_{AB}}$  = 6.5599  $f(\frac{KT}{E_{AB}})$  = 0.4

$$\sqrt{1/M_{A} + 1/M_{B}} = 0.52223$$

For mixtures of nonpolar gases or of a polar with a nonpolar gas

$$D_{AB} = \frac{10^{-4} \cdot (1.084 - 0.249 \sqrt{1/M_A + 1/M_B}) \cdot T^{3/2} \cdot \sqrt{1/M_A + 1/M_B}}{P_t \cdot (r_{AB})^2 \cdot f(KT/E_{AB})}$$

equation (2.37) Treybal

$$D_{AB} = \frac{10^{-4} + (1.084 - 0.249 + (0.5223) + (293)^{3/2}) + 0.52223 + (100 \text{ cm})^2}{(101.3 \times 10^3)} + (0.3941)^2 + (100 \text{ cm})^2}{(0.3941)^2 + 0.4}$$

$$D_{AB} = 0.397 \text{ cm}^2/\text{sec}$$

Solving equation (A) for time

$$t = \frac{x}{16 D_{AB}}$$
 since x = L/2 = 22 inches/2 = 11 inches  
$$t = \frac{(11 in)^2}{16} \frac{\sec (2.54 cm)^2}{(11 in)^2}$$

t = 122.9 seconds

So this is the time it takes to get to

 $C = 0.01 C_0 \text{ at } x = L/2$ 

Calculate the actual time for the plug of gas to travel from the liquid nitrogen trap to the G.C. column.

area of 1/8 in. copper tubing =  $3.318 \times 10^{-3}$  in.<sup>2</sup> length of tubing is 107 inches

thus volume = (107 in.) x  $(3.318 \times 10^{-3} \text{ in.}^2) = 0.355059 \text{ in.}^3$ 

since the flow rate through the tube is  $30 \text{ cm}^3/\text{minute}$ 

Time required to  
flow through the = 
$$\begin{array}{c} 0.355059 \text{ in.}^3 \text{ min.} 60 \text{ sec } (2.54 \text{ cm})^3 \\ 1 \text{ sube} \\ = 11.64 \text{ seconds} \end{array}$$

Conclusion:

Since there is such a large difference in time between the modeled time of 122.9 seconds and the actual time of 11.64 seconds it is safe to assume that the plug of gas will remain intact up to the time it reaches the column.

