

MINIMUM IGNITION TEMPERATURES OF PYROLYSATE-AIR MIXTURES  
AS A FUNCTION OF PYROLYSATE CONCENTRATION

A THESIS

Presented to

The Faculty of the Division  
of Graduate Studies

By

William Paul Ryszytiwskyj

In Partial Fulfillment

of the Requirements for the Degree  
Master of Science in Mechanical Engineering

Georgia Institute of Technology

March, 1976

Approved:

~~G. T. Colwell~~

Date approved by Chairman: 3/9/1976

## ACKNOWLEDGMENTS

I wish to express my gratitude to Dr. Pandeli Durbetaki, Associate Professor of Mechanical Engineering at the Georgia Institute of Technology, and the chairman of this thesis reading committee, for introducing me to the field of Fire Hazard and Combustion Research, and for his continued interest, concern, patience, and guidance during this investigation.

I also wish to thank Dr. Gene T. Colwell, Associate Professor of Mechanical Engineering, and Dr. Wayne C. Tincher, Associate Professor of Textile Engineering, both at the Georgia Institute of Technology, members of this thesis reading committee, for their advice and helpful criticisms during the completion of this work.

I am particularly grateful to Mr. T. E. Clopton, electronic technician in the School of Mechanical Engineering, and Mr. Donald Lillie, glassblower in the School of Chemistry, for their efforts, assistance, and advice on several aspects of this research.

My gratitude is extended to my father and mother, Semko and Eva, for their constant encouragement and support.

I would like to thank the National Science Foundation for sponsoring this research under Grant No. GI-31882 of the RANN Program; Mr. Paul T. Williams, for designing and constructing the test equipment; and all of the people who

have contributed either directly or indirectly to this work, but have not been mentioned here by name.

Finally, I would like to express my warmest and most sincere appreciation to my wife, Patricia, for her patience and understanding throughout.



## TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS. . . . .	ii
LIST OF TABLES . . . . .	vi
LIST OF ILLUSTRATIONS. . . . .	vii
NOMENCLATURE . . . . .	ix
SUMMARY. . . . .	xi
Chapter	
I. INTRODUCTION. . . . .	1
Relevance of Flammability Research	
Previous Efforts and Accomplishments	
Research Objectives	
Literature Survey	
II. EQUIPMENT AND INSTRUMENTATION . . . . .	12
The Pyrolysate Generating Furnace	
The Sample Holder Tube	
The Accumulator Barrel and Volatile Reservoir	
The Dry Air Supply	
The Nitrogen Supply	
The Pyrolysate and Air Metering System	
The Reaction Cell	
Temperature Recording and Ignition Detection	
Instrumentation	
Temperature Measuring and Recording	
Instrumentation	
Ignition Detection Instrumentation	
Molecular Weight Determination Instrumentation	
Auxiliary Systems and Components	
Guard Heaters	
Gas Lines and Valves	
Pyrolysate Cold Trap Condenser	
System Vacuum Pump	
System Pressure Gauge	
Modifications Made to Original Design	

Chapter	Page
III. EXPERIMENTAL PROCEDURE. . . . .	46
Ignition Temperature Measurements on Propane-Air Mixtures	
Ignition Temperature Measurements on Pyrolysate-Air Mixtures	
Preparation of Sample and Initial Tasks	
Nitrogen Flushing Procedure	
Pyrolysis of Thermally Degradable Materials	
Setting of Ignition Heater	
Attainment and Recording of Minimum Ignition Temperatures	
Molecular Weight Determination	
Cleaning Procedure	
Difficulties Encountered	
IV. DATA REDUCTION. . . . .	68
Molecular Weight Determination of Pyrolysate Gases	
Calculation of Pyrolysate Concentration	
Computation of Minimum Ignition Temperatures	
V. EXPERIMENTAL RESULTS AND DISCUSSION . . . . .	78
Propane-Air Mixtures	
Pyrolysate-Air Mixtures	
Interesting Observations Sighted	
VI. CONCLUSIONS AND RECOMMENDATIONS . . . . .	96
Appendix	
A. EXPERIMENTAL ERROR ESTIMATION WITH SAMPLE CALCULATIONS. . . . .	100
B. DATA REDUCTION SAMPLE CALCULATIONS. . . . .	107
Molecular Weight Determination	
Pyrolysate Mass Fraction Determination	
Minimum Ignition Temperature Determination	
C. SUMMARY OF MINIMUM IGNITION TEMPERATURE AND MASS FRACTION DATA FOR PROPANE-AIR AND PYROLYSATE-AIR MIXTURES. . . . .	111
D. CALIBRATION OF BROOKS R-2-15-AAA FLOW TUBE. . . . .	121
BIBLIOGRAPHY . . . . .	123

## LIST OF TABLES

Table		Page
1.	Sample Summary of Minimum Ignition Temperature and Mass Fraction Data for GIRCFF Fabric No. 17, 65/35% Polyester/Cotton. . . . .	76
2.	Summary of Molecular Weights and Ignition Temperature Ranges of Pyrolysate Gases . . . . .	91
3.	Experimentally Determined Molecular Weights of Known Gases. . . . .	93
B.1.	Sample Data Sheet. . . . .	108
C.1.	Summary of Minimum Ignition Temperatures and Mass Fraction Data for Commercial Propane. . . .	112
C.2.	Summary of Minimum Ignition Temperatures and Pyrolysate Mass Fraction Data for GIRCFF Fabric No. 4 . . . . .	115
C.3.	Summary of Minimum Ignition Temperatures and Pyrolysate Mass Fraction Data for GIRCFF Fabric No. 15. . . . .	117
C.4.	Summary of Minimum Ignition Temperatures and Pyrolysate Mass Fraction Data for GIRCFF Fabric No. 17. . . . .	118
C.5.	Summary of Minimum Ignition Temperatures and Pyrolysate Mass Fraction Data for Wood Chips (Fir). . . . .	120



## LIST OF ILLUSTRATIONS

Figure	Page
1. A Simplified Model for the Mechanism of Thermal Decomposition of Cellulose in a Vacuum. . . . .	11
2. Flow Diagram for Lower Ignition Temperature and Concentration Apparatus (LITACA). . . . .	14
3. The Lower Ignition Temperature and Concentration Apparatus (LITACA). . . . .	15
4. Cross Section of Furnace and Accumulator for LITACA. . . . .	16
5. Quartz Sample Holder Tube and Accumulator Barrel Assembly. . . . .	19
6. Accumulator Barrel Showing High Temperature Vacuum and Pressure Seal, Guard Heater, and Piston Head . . . . .	21
7. Cross Section of Reaction Cell for LITACA . . . . .	25
8. Reaction Cell for LITACA. . . . .	28
9. Schematic for the Temperature Recording and Ignition Detection Instrumentation Used with LITACA. . . . .	34
10. Temperature Recording and Ignition Detection Instrumentation Used with LITACA. . . . .	35
11. Molecular Weight Determination Apparatus. . . . .	40
12. Typical Thermocouple EMF History at Time of Ignition. . . . .	56
13. Typical Thermocouple EMF History for an Accelerating Reaction with a Quenching Point. . . . .	57
14. Typical Thermocouple EMF History for a Step Increase in Heating Rate Due to Exothermicity of Chemical Reactions. . . . .	58

Figure	Page
15. Temperature Profile Along Axis of the Ignition Tube, Steady Air Flow of $3.3 \text{ cm}^3/\text{s}$ . . . . .	79
16. Time Dependent Transverse Temperature Profile of Gases in the Ignition Tube, Steady Air Flow of $3.3 \text{ cm}^3/\text{s}$ . . . . .	80
17. Minimum Ignition Temperature of Propane-Air Mixtures. . . . .	82
18. Minimum Ignition Temperatures of Pyrolysate-Air Mixtures, GIRCF Fabric Number 4, 100% Cotton . .	86
19. Minimum Ignition Temperatures of Pyrolysate-Air Mixtures, GIRCF Fabric Number 15, 65/35% Polyester/Rayon . . . . .	87
20. Minimum Ignition Temperatures of Pyrolysate-Air Mixtures, GIRCF Fabric Number 17, 65/35% Polyester/Cotton. . . . .	88
21. Minimum Ignition Temperatures of Pyrolysate-Air Mixtures, Wood Chips (Fir). . . . .	89

## NOMENCLATURE

A	area
M	molecular weight
m	mass
$\dot{m}$	mass flow rate
P	pressure
R	universal gas constant
T	temperature
V	volume
$\dot{V}$	volumetric flow rate
v	gas velocity
w	weight
$\rho$	gas density
$\bar{\rho}$	mean gas density
$\tau$	time
$\langle \tau \rangle$	mean time

Subscripts

a	air
av	average
B,1	balloon number 1
B,2	balloon number 2
c	calibration
e	exit

exp	exposure
f	fuel
fl	float
i	inlet
ig	ignition
p	pyrolysate
t	test conditions
1	referenced to balloon number one
2	referenced to balloon number two



## SUMMARY

Experimental and analytical research is being carried out in the Fire Hazard and Combustion Research Laboratories of the School of Mechanical Engineering at the Georgia Institute of Technology to measure and predict thermally thin and thermally thick material ignition times as a function of material properties and heating intensities. The ignition analysis initiated for thermally thin media, and currently being developed for thermally thick materials, utilizes an ignition criterion imposed on the reacting boundary layer at the heated surface. This ignition criterion considers ignition to occur in the boundary layer of the pyrolyzing solid, when the pyrolysate-air mixture locally reaches its concentration-dependent minimum ignition temperature.

The objective of this thesis is to use the Lower Ignition Temperature and Concentration Apparatus (LITACA) to measure ignition temperatures of pyrolysis gases generated from thermally thin (fabrics) and thermally thick (furniture, interior decorations) media.

LITACA consists of eight major components, which are:

- (i) the pyrolysate generating furnace;
- (ii) the sample holder;
- (iii) the accumulator barrel and volatile reservoir;
- (iv) the dry air system;

- (v) the nitrogen supply;
- (vi) the pyrolysate and air metering system;
- (vii) the reaction cell; and
- (viii) the temperature recording and ignition detecting instrumentation.

LITACA was used initially with propane to establish testing procedures and the results were compared with published values. Later, minimum ignition temperature tests were run with pyrolysate gases that were generated by heating three different GIRCFF fabrics and fir wood chips in the generating furnace. At the same time, molecular weights were determined from measurements on the same pyrolysate gases.

This research is an outgrowth of the Flammable Fabrics Act of 1953 as amended in 1967, and is supported by the National Science Foundation under Grant No. GI-31882A#3 of the RANN Program.

## CHAPTER I

### INTRODUCTION

#### Relevance of Flammability Research

The climbing death rate and increasing loss of health, property and resources from accidental fires in the United States, the leader in fire losses of all the industrial nations, calls for a concerted effort by government, industry and the consumer to develop improved attitudes toward the use of potential ignition sources and new means for fire loss reduction. The direct damage caused by apparel fires is either death or a burn injury, which can be measured in severity either by the depth of tissue destruction and the total area burned, or by the impairment of the respiratory system [1].\* At least one child is burned to death daily due to fabric ignition. Each year 12,000 Americans die and 300,000 are injured as a result of accidental fires. The accompanying financial losses have been estimated to be 11.4 billion dollars. A substantial portion of these accidents result from garment and fabric fires [2].

On August 18, 1975, the Atlanta Constitution reported that an Atlanta woman dropped a match into the lap of her synthetic nightgown. Police reported that the woman died

---

\*Numbers in brackets refer to the Bibliography.

within seconds when the gown "went up like gasoline."

Lt. H. J. Jones, of the Atlanta Bureau of Fire Services, reported that "most night clothes that adults wear will catch fire just that way."

These awesome statistics have moved the United States Government to legislation enabling independent groups to conduct research in an attempt to reduce injuries and their associated economic cost resulting from apparel fires. One of the first federal efforts in this area was the Flammable Fabrics Act (FFA) of 1953, which was amended in 1967. Research began in 1969 and was monitored through December, 1972, by the Government-Industry Research Committee on Fabric Flammability (GIRCFF), the membership representing the National Science Foundation, the National Bureau of Standards, the American Textile Manufacturers Association, the Cotton Council of America, and the Man-Made Fiber Producers Association [3].

The GIRCFF formulated a statement which is regarded to be the central problem of fabric flammability studies [4]. It states:

The determination of the relationship between fabrics in a test method, on the one hand, and hazard it presents in actual use, on the other hand, is necessary to develop meaningful standards.

In order to fight problems which result in fabric fires, ignorance must be combated with education--through campaigns to enable the public to recognize potential fire



hazards--and sympathy with regulation--by setting universal standards for materials which have the potential of being involved in destructive fires. The National Commission on Fire Prevention and Control found [2] that the majority of fire accidents are due to the carelessness of people, largely through lack of concern and ignorance of hazards. The modification of combustible materials to reduce ignition probability and the modification of frequently involved ignition sources is desperately needed.

The ultimate goal of this research is to provide information which may be used to establish sound and politically admissible flammability standards for fire hazard assessment of fabrics and building materials. It must be emphasized that the purpose is to present the principles of fire hazard assessment rather than gathering a vast amount of statistical data and obtaining numerical results for actual probabilities. The findings would influence federal, state, and local policies regarding the setting of fire safety standards for buildings, interior decorating and construction materials, as well as for furniture. Hopefully, these standards will result in a reduction in the number of deaths and injuries caused by garment fires.

The School of Mechanical Engineering at the Georgia Institute of Technology received sponsorship for research from the National Science Foundation (NSF) on November 1, 1970, under Grant No. GK-27189. Additional work was supported

by Grant No. GI-31882 of the RANN program. The goal of the research is to give information about the conditions necessary for the ignition of various materials. Studies are currently being made on twenty commonly worn fabrics which are supplied by the GIRCFF, the majority of which are 100% cotton and 65/35% polyester/cotton.

#### Previous Efforts and Accomplishments

The present work being carried out in the Fire Hazard and Combustion Research Laboratories of the School of Mechanical Engineering at the Georgia Institute of Technology, concerns itself with the burn injury hazard associated with garments, furniture, interior decorations and building materials. It is a combined experimental and analytical program with objectives to measure and predict the ignition times of thermally thin and thermally thick materials. The main interest of the research is to reduce fire related losses in terms of property damage, natural resource destruction, and human loss and suffering.

A set of twenty different widely used fabrics in apparel were supplied by the U. S. Government Industry Research Committee on Fabric Flammability for this research. It included fabric samples of cotton, nylon, polyester, acetate, wool, and blends.

Other participants in this program have been the Massachusetts Institute of Technology, the Factory Mutual

Research Corporation, and the Gillette Research Institute.

Fuels come in a variety of shapes, sizes and forms. They can either be man-made fuels, such as plastics, or they can be natural (cellulosic) fuels, such as cotton or wood. These materials are fuels by definition because if they are sufficiently exposed to an ignition source they will ignite, and will continue burning until extinguished or until they self-extinguish. Consequently, a fuel, as defined above, has a certain hazard associated with its use; it can result in a burn injury or in a loss of property or life.

First generation standards have been established for children's sleepwear, mattresses, carpets, and rugs [5,6]. General information on any of these standards can be obtained from References [7] and [8].

Since the behavior of a fabric in a laboratory testing facility and in actual use obviously varies, the prediction of the associated fire hazard under actual circumstances requires a fabric ignition model which provides an accurate description of the flame-fabric interaction if relevant and reasonable standards are to be established for fabric flammability. A sound relationship between the hazard measure (a quantitative description) and the characteristic material response time, after exposure to an ignition source, is required.

Questions such as the following must be answered for a true fire hazard assessment of a given material:



1. What is the likely cost of the material or the finished product?

2. Who is likely to use it?

3. What is the likelihood that it will be exposed to certain ignition sources? (These can be open flames, burning cigarettes, radiant heat sources, such as electric stoves or electric heaters, etc.).

4. What is the likelihood that a given material will ignite when exposed to an ignition source?

5. Once ignited, what is the likelihood that the flame will propagate?

6. Will it extinguish easily or not?

7. What is the likelihood of tissue destruction if the fire cannot be extinguished?

Questions similar to numbers 1, 2 and 3 are ~~stochastic~~ <sup>stochastic</sup> in nature due to the human element involved. Surveys will have to be made to statistically determine these answers, which in turn will help determine the type of environment various materials are exposed to.

Myron Tribus [9] was the first to propose that a fire hazard can be quantitatively measured and related to a prescribed loss in terms of probabilities associated with all the events starting with the manufacturer of the material and ending with the consumer and the conditions he (or she) exposes it to. The probability of burn injury given usage is one way in which the fire hazard of a system can be quantified.

It can be expressed as a product of three subsequent probabilities: the probability of burn injury given ignition, the probability of ignition given exposure, and the probability of exposure given use. Since the first of the major events which leads to a loss from fire is ignition, the probability of ignition given exposure plays an important role in the hazard ranking of garment fabrics. It is a highly system-related quantity for the assessment of a system's fire hazard [10]. The determination of this probability "would be an enormous step forward in our understanding of the relationships between material performance and hazard" [11].

The physiochemical processes involved in the ignition process are all transient in nature, as it was recognized first by Evans, Wulff and Zuber [12], that they depend primarily on the ratio of two characteristic times, namely the exposure time  $\tau_{\text{exp}}$  over the mean ignition time  $\langle \tau_{\text{ig}} \rangle$ . The exposure time is the independent variable, ~~stochastic~~ <sup>Stochastic</sup> in nature, which characterizes human response to an ignition source, while the ignition time characterizes material properties, exposure conditions, and fabric response.

In the pursuit of developing an analytical model which will predict the mean ignition time under given exposure conditions, Wulff has proposed [13] a new ignition criterion for pyrolyzing solids. If a thermally degradable material is suddenly exposed to an ignition source, generation of

pyrolysis gases will commence. If the material is porous, the pyrolysis gases will enter the boundary layer through the solid surface. If, however, the material is not porous, it becomes porous (like wood) or melts (like nylon) and evaporates and also permits volatile gases to enter into the boundary layer. According to Wulff, ignition occurs at some point in the gaseous boundary layer adjacent to the heated solid surface where the local pyrolysate-air concentration attains, for the first time, its corresponding minimum ignition temperature [14,15]. This criterion requires the measurement of the lowest ignition temperature of pyrolysate-air mixtures as a function of pyrolysate concentration. The Lower Ignition Temperature and Concentration Apparatus, LITACA, has been designed and constructed to accomplish this task.

### Research Objectives

The objectives of the conducted research are:

1. to use the Lower Ignition Temperature and Concentration Apparatus (LITACA) to measure minimum ignition temperatures of pyrolysate gases generated from thermally thin and thermally thick media; and
2. to determine the molecular weights from measurements on the same pyrolysate gases.

### Literature Survey

This literature survey is concerned with the pyrolysis



or thermal degradation of cellulosic materials as well as with the mechanism involved. Pyrolysis is a preignition phenomenon. For a pyrolyzing material ignition will occur when a suitable combination of fuel (pyrolysate gases), oxygen, and thermal energy is available.

During the pyrolysis of a cellulosic material, many complex volatile products, both combustible and noncombustible, emerge from the solid. The solid material undergoes thermal decomposition without the presence of a melting stage. Holmer and Shaw [16] observed that these products are independent of temperatures above 275 C and that the dominant mechanism of degradation is depolymerization with the production of levoglucosan; below 275 C, the rates of dehydration predominate.

Tang and Bacon [17] proposed that the predominant mechanism for the thermal decomposition of cellulose is composed of four successive stages:

1. from 25 to 150 C: the desorption of physically absorbed water;
2. from 150 to 240 C: the dehydration of the cellulose unit, i.e. the splitting off of structural water;
3. from 240 to 400 C: thermal cleavages, or depolymerization, and the breaking of C-O and C-C bonds within ring units accompanied by the evolution of more water, CO, and CO<sub>2</sub>; and
4. above 400 C: aromatization, or formation of

graphite-like layers.

Madorsky [18] and Major [19] concluded that cellulosic materials which were pyrolyzed above 250 C yielded volatile products consisting mainly of aqueous distillates, tars and fixed gases ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ , etc.). However, in the 70-250 C temperature range, water was observed to be the major product.

A simplified model for the mechanism of thermal decomposition of cellulose in a vacuum has been proposed by Parker and Lipska [20] and is shown in Figure 1. Cellulose,  $\text{C}_6\text{H}_{10}\text{O}_5$ , is normally composed of long molecules with a high degree of polymerization. As the molecules gain thermal energy from, say, an ignition source, the thermal vibrations are so pronounced that they break the molecular C-O and C-C bonds resulting in a number of smaller organic molecules. The C-O bonds are weaker than the C-C bonds and hence these weaker links in the cellulosic structure break first. Approximately 60% (by weight) of the severed units go into levoglucosan which eventually decomposes to form most of the observed volatile pyrolysis products. Typical examples are  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , acetol, furfural, and a variety of unsaturated aldehydes and ketones. Secondary pyrolysis products decompose and interact with each other causing third generation pyrolysis products. The remaining 40% of the above mentioned severed cellulosic units go into char formation which produces  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2$ . The final char is about 9% by weight of the original cellulose.

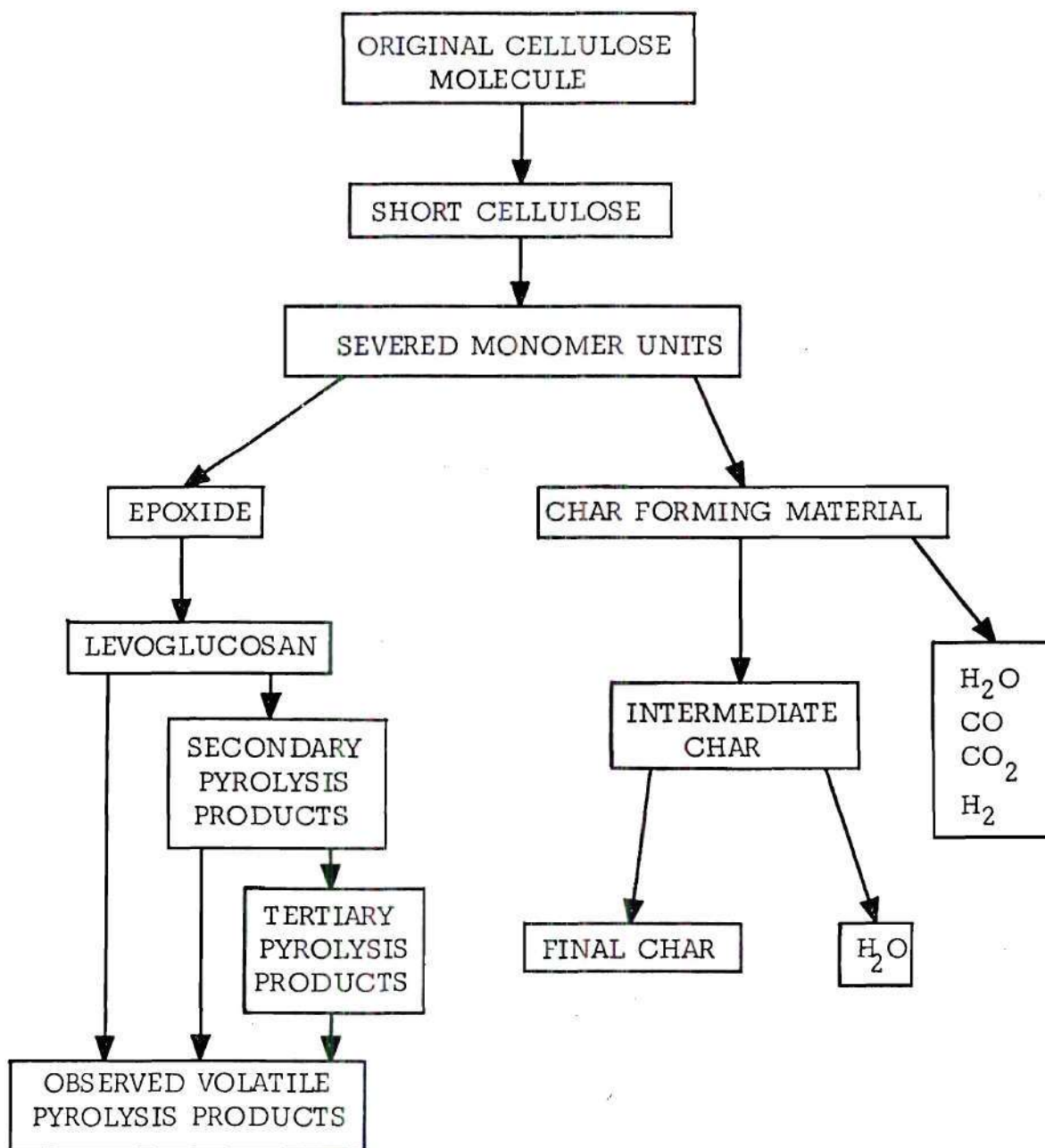


Figure 1. A Simplified Model for the Mechanism of Thermal Decomposition of Cellulose in a Vacuum [20]

## CHAPTER II

### EQUIPMENT AND INSTRUMENTATION

In this chapter, the equipment and instrumentation required for the determination of minimum ignition temperatures of pyrolysate-air and propane-air mixtures is presented first. Later, the equipment and instrumentation which was used to determine molecular weights of the same pyrolysate gases is described. Several modifications were made to the original design which will also be mentioned.

An apparatus called the Lower Ignition Temperature and Concentration Apparatus (LITACA) was designed and constructed by P. T. Williams [21]. The functions of the apparatus are to:

- (1) thermally decompose pyrolyzing materials,
- (2) store the pyrolysates,
- (3) mix the pyrolysates with dry air at controlled mass fractions,
- (4) heat the mixture until ignition takes place,
- (5) measure the minimum ignition temperature at which self-ignition occurs to within  $\pm 5$  C,
- (6) afford pyrolysate sampling for molecular weight determination, and
- (7) transport the pyrolysates without permitting



condensation of the water vapor in the apparatus.

Figure 2 is a flow diagram for LITACA and Figure 3 shows a physical view of the apparatus. The major components of LITACA are:

- (1) the pyrolysate generating furnace,
- (2) the sample holder tube,
- (3) the accumulator barrel and volatile reservoir,
- (4) the dry air supply,
- (5) the nitrogen supply,
- (6) the pyrolysate and air metering system,
- (7) the reaction cell, and
- (8) the temperature recording and ignition detection instrumentation.

The following sections present a description of the components in detail.

#### The Pyrolysate Generating Furnace

The furnace, shown in Figure 4 (key to the figure on page 17), is made up of two cylindrical half-shell, 1720 watt, 230 volt, Model RH256 heaters (part 22) from Thermal Corporation, Huntsville, Alabama. The two half shells were wired in parallel and were connected to two 20 ampere-115 volt variable auto-transformers wired in series. The heater consists of helically wound chrome-aluminum-iron resistance wires placed in ceramic backings which are embedded in a ceramic core. The maximum operating temperature is 1200 C.

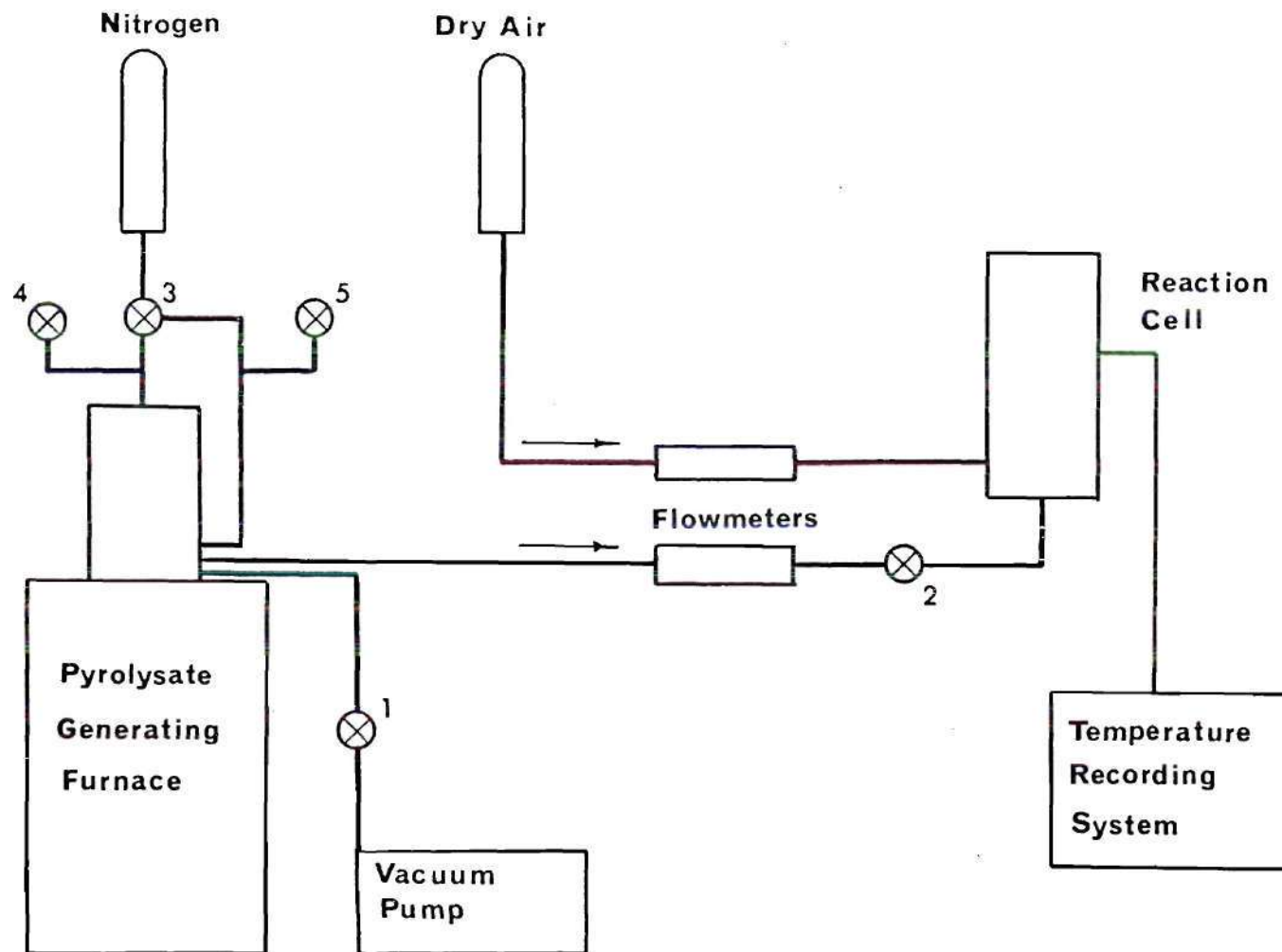


Figure 2. Flow Diagram for Lower Ignition Temperature and Concentration Apparatus (LITACA)

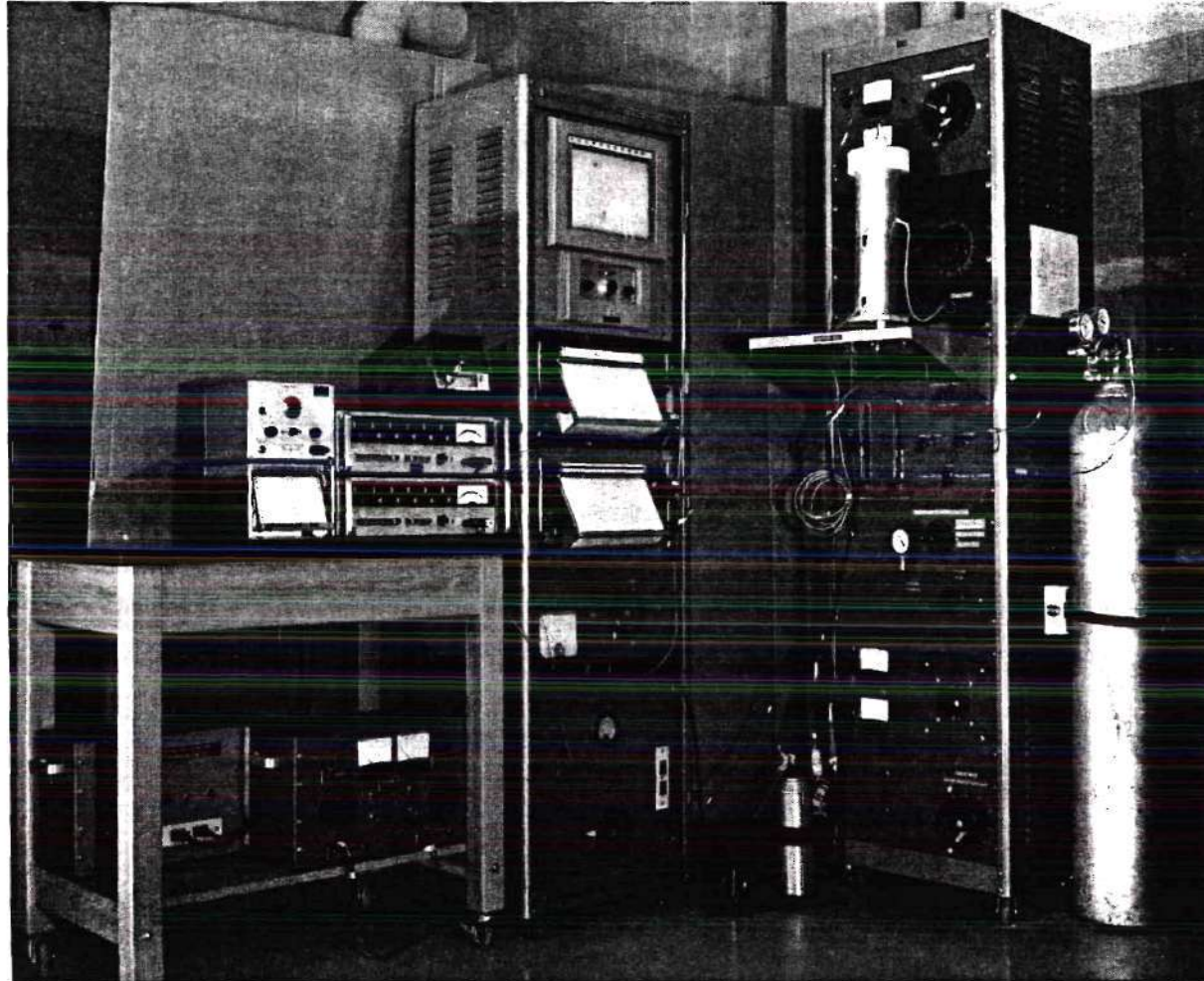


Figure 3. The Lower Ignition Temperature and Concentration Apparatus (LITACA)

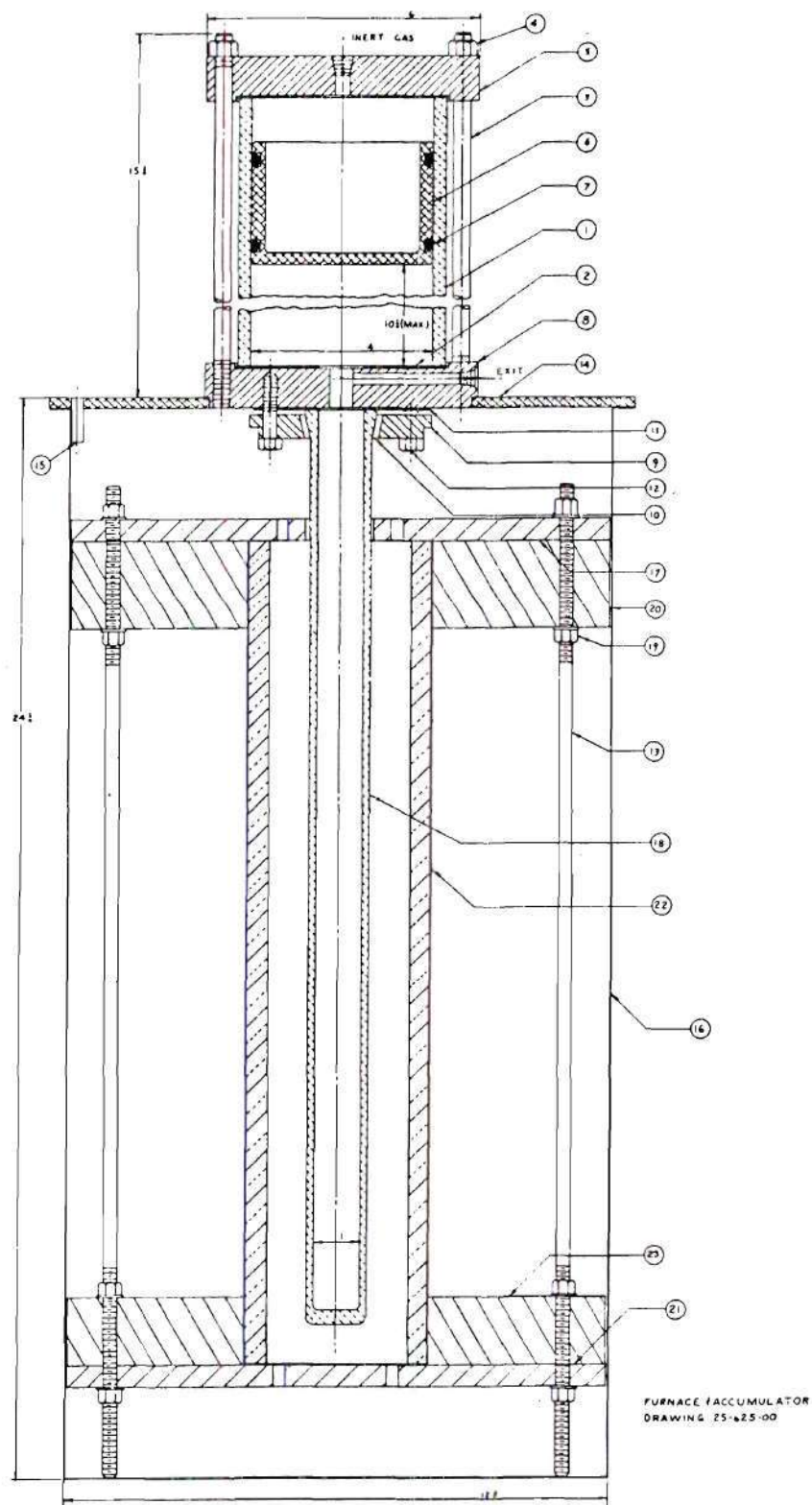


Figure 4. Cross Section of Furnace and Accumulator for LITACA [21]



## Key to Figure 4

Part No.	Description	Material	Req'd
1	Accumulator Barrel	Drawn 6061-T6 Aluminum	1
2	Gasket	Teflon	1
3	Threaded Rod	Cold Worked Steel	6
4	3/8-24 UNF Hex Nut	SAE Grade 5	6
5	Accumulator End Cap	304 Stainless Steel	1
6	Accumulator Piston	6061-T6 Aluminum	1
7	"O" Ring	Neoprene	2
8	Accumulator Manifold	304 Stainless Steel	1
9	Flange	Cast Iron	1
10	Insert	Molded Asbestos	1
11	Gasket	Teflon	1
12	5/16-18UNC Hx Hd Bolt	SAE Grade 5	4
13	5/16-18UNC Threaded Rod	SAE Grade 5	4
14	Furnace Mounting Plate	6061-T6 Aluminum	1
15	ESNA "Rollpin"	Steel	3
16	Furnace Housing	3003-H14 Aluminum	1
17	Furnace Heater Support	Transite	1
18	Sample Holder Tube	Fused Quartz	1
19	5/16-18UNC Hx Hd Nut	SAE Grade 5	16
20	Upper Support Ring	Asbestos	1
21	Furnace Heater Support	Transite	1
22	Heating Element Casing	Ceramic	1
23	Lower Support Ring	Asbestos	1

The following empirical expression was used to approximate the heating rate for a given auto-transformer setting between the 40% and the 85% positions:

$$\text{Furnace Heating Rate} \approx 0.005(\% \text{ Setting})^{1.9} \text{ C/min} \quad (1)$$

The heaters are supported by an asbestos supporting ring (parts 20 and 23) and a transite support plate arrangement (parts 17 and 21) on both ends which are fastened together by four 22 inch x 5/16 inch cold worked steel threaded rods (part 13). A 2-1/2 inch clearance exists between the top aluminum furnace mounting plate and the transite heater support, and a similar 2 inch clearance exists at the other end of the furnace. The heater assembly sits in a 24-1/4 inch long, 12-1/8 inch diameter cylindrical aluminum housing (part 16). A chromel-alumel thermocouple was positioned near the center of the furnace core, outside the sample holder tube (part 18), to monitor the furnace temperature.

#### The Sample Holder Tube

The sample holder tube is a custom made 20-1/2 inch x 1 inch I.D. (see Figures 4 and 5) test tube (part 18) made of "Vitreosil" fused quartz, fabricated by the Thermal American Fused Quartz Company, Montville, New Jersey. The opening of the tube has a groove for the proper positioning of a molded

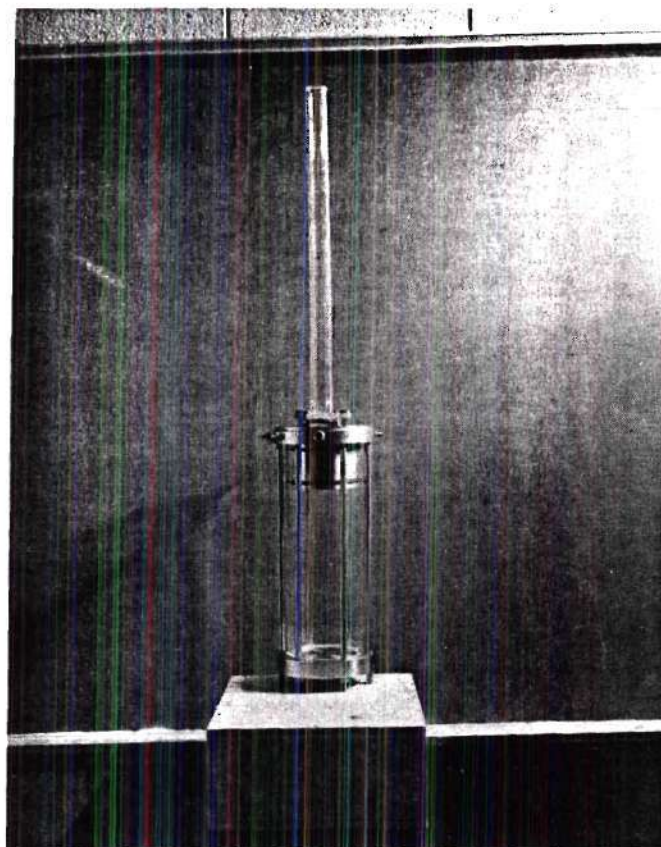


Figure 5. Quartz Sample Holder Tube and Accumulator Barrel Assembly (Overall Height is 90 cm)



gasket. The O.D. at the upper end is 1-9/16 inches (with a wall thickness of 9/32 inches) and is tapered to an O.D. of 1-15/16 inches (with a wall thickness of 5/32 inches). The sample holder tube is fastened to the bottom of the accumulator manifold (part 8) by a cast iron flange (part 9) and four bolts (part 12). A molded asbestos insert (part 10) is used between the neck of the tube and the flange, and a 1/16 inch molded teflon gasket (part 11) is used between the accumulator manifold and the grooved surface of the tube.

#### The Accumulator Barrel and Volatile Reservoir

The accumulator barrel as shown in Figures 4, 5 and 6 serves as a pyrolysate gas accumulator as well as a reservoir for these gases after the pyrolysis process has come to completion. Its maximum capacity is approximately 1.9 liters. Initially, a 13-1/4 inch length of 4-1/2 inch x 0.250 inch pyrex glass pipe was used for the accumulator barrel. However the mechanical stresses associated with the proper sealing of the barrel along with the thermal stresses associated with the accumulator guard heater (shown in Figure 6 and to be discussed later) and the hot accumulator manifold (Figure 4, part 8) led to the failure of the pyrex glass barrel. A 1/4 inch neoprene gasket was used in place of the original 1/16 inch teflon gasket (part 2), but the extreme heat from the accumulator manifold deteriorated it. Finally, the pyrex pipe was replaced with a drawn 6061-T-6 aluminum tube of the

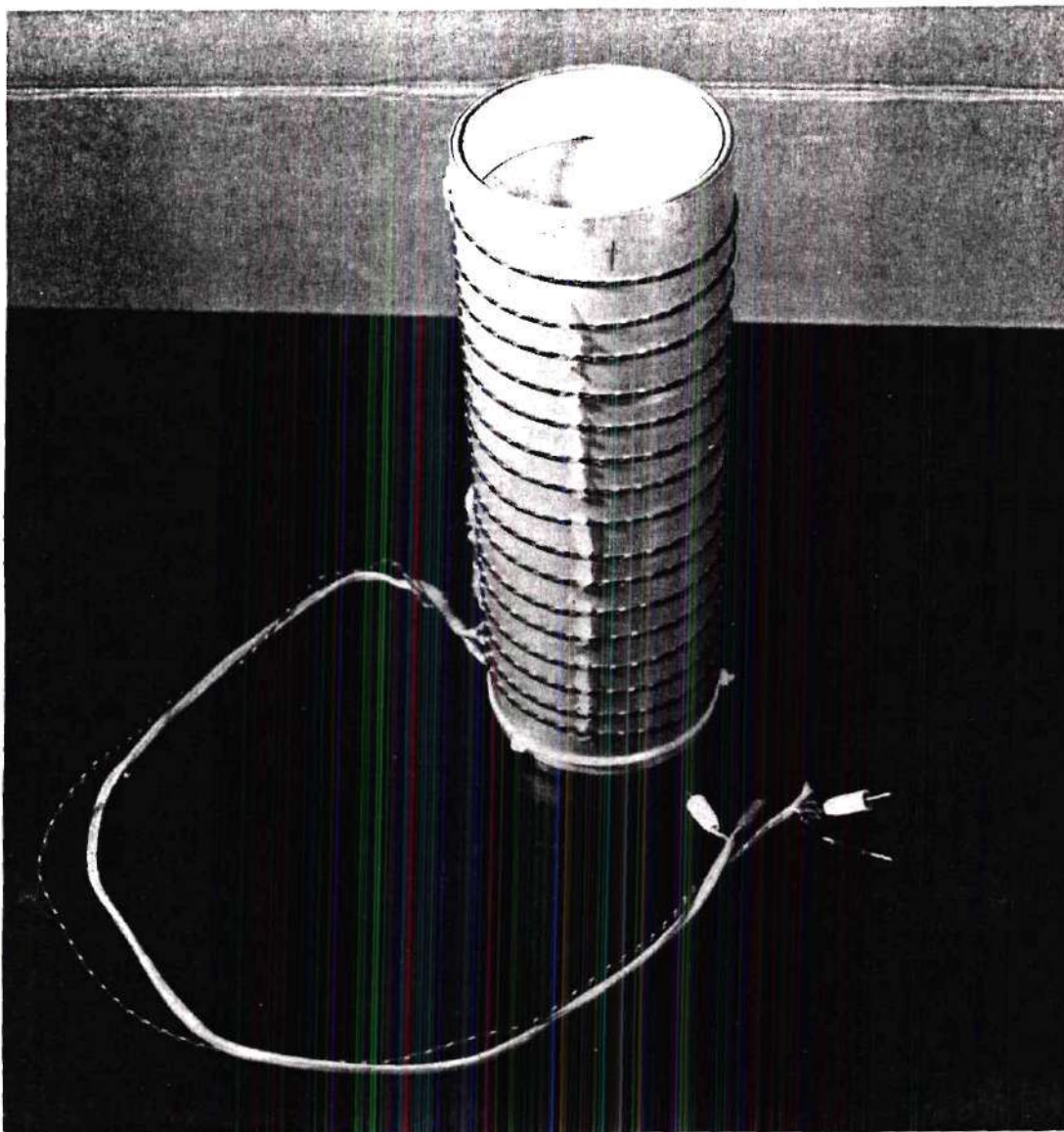


Figure 6. Accumulator Barrel Showing High Temperature Vacuum Pressure Seal, Guard Heater, and Piston Head

same size (part 11). An arc (0.0943 inch radius) was machined into the bottom surface of the accumulator barrel to act as a housing for a high temperature silicone "O" ring as shown in Figure 6 which acts as a sealing gasket between the accumulator barrel and the #304 stainless steel accumulator manifold. The groove was machined to 0.17125 inches by 0.10875 inches. The top end of the accumulator barrel was closed off by a #304 stainless steel end cap and a 1/16 inch teflon gasket. The above arrangement formed a reliable high temperature-high pressure seal. Seventeen windings of 20 gauge chromel-alumel thermocouple wire as shown in Figure 6 were wrapped around the accumulator barrel. They were used as guard heaters to prevent any condensation of the pyrolysates on the inner wall of the barrel. A chromel-alumel thermocouple was positioned on the outer surface of the accumulator barrel to monitor its temperature.

A floating piston (Figure 4, part 6) is positioned inside the accumulator barrel and is sealed by two 4 inch x 3/16 inch neoprene "O" rings (part 7). The upper end of the piston has the capability of being either vented to the atmosphere when it accumulates the gases, or being pressurized by nitrogen when it serves as the reservoir and pushes the gases into the flow metering system through the accumulator manifold.

The accumulator manifold (part 8) is positioned on the aluminum furnace mounting plate (part 14) and provides five



ports for access to other parts of the system. These ports are connected to (a) the vacuum pump, (b) the gas sampling tap, (c) the pyrolysate flow meter, (d) the system pressure gauge, and (e) the nitrogen supply.

#### The Dry Air Supply

High pressure air (70-80 psig) is available in the Fire Hazard and Combustion Research Laboratories. The air is dried by a Wilkerson Model 4001-2 drier which used silica gel as the drying agent, and the pressure is regulated by an Air-Products pressure regulator adjustable from 0 to 60 psig. Flexible 1/4 inch pressure tubing connects the filtered air supply to the test apparatus as shown in Figure 2. The air passes through a flow meter and into the reaction cell where it is mixed at a controlled rate with the pyrolysate gases.

An alternative supply of dry air is a pressurized tank which can be directly connected to LITACA through a two-stage pressure regulator, without the need of a filter or drier.

#### The Nitrogen Supply

A pressurized tank of nitrogen gas along with a 2-stage pressure regulator is used to pressurize the top side of the accumulator piston via the accumulator end cap (Figure 4, part 5) to 15 psig. This causes the ejection of pyrolysate gases from the accumulator barrel (part 1) and the generating furnace into the pyrolysate flow meter at a controlled rate.



The nitrogen is also used to flush the system through the accumulator manifold (part 8) to permit the pyrolysis gases to be generated in the absence of an oxidizing atmosphere.

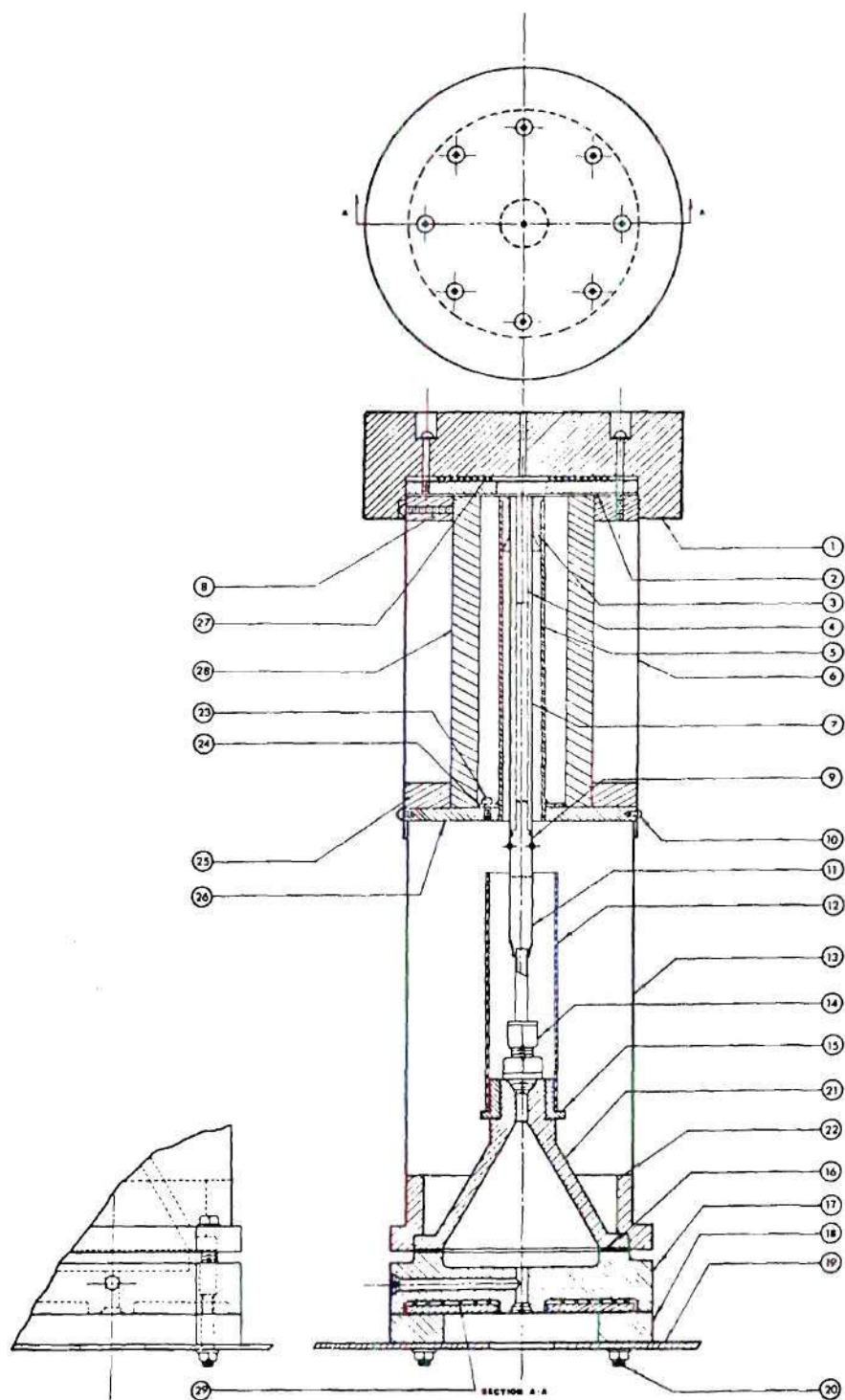
#### The Pyrolysis and Air Metering System

Two Brooks instrument flow meters as shown in Figure 2 are used to measure the volumetric flow rates of the pyrolysis gases (or propane) and the air, respectively. The flow metering system is located just upstream of the mixing chamber of the reaction cell (Figure 7, part 17). Two valves are also provided adjacent to the flow meter entrances which permit a variable mass fraction of the pyrolysis-air mixture which enters the mixing chamber. For the pyrolysis gases, an R-2-15-AAA flow tube with glass and stainless steel floats (maximum capacity of 49 std. cm<sup>3</sup>/s and 147 std. cm<sup>3</sup>/s, respectively) is used. For the dry air, an R-2-15-D flow tube with glass and stainless steel floats (maximum capacity of 375 std. cm<sup>3</sup>/s and 830 std. cm<sup>3</sup>/s, respectively) is used.

A u-tube manometer was used [21] to determine the pressure in the flow meter tube. Measurements indicated that the pressure was near atmospheric and consequently only the barometric pressure is used to carry out the necessary corrections on the flow meter readings.

#### The Reaction Cell

The reaction cell is positioned on an aluminum supporting shelf located about midway up the test apparatus



GEORGIA INSTITUTE OF TECHNOLOGY	REACTION CELL ASSEMBLY	DR BY <i>P. T. L.</i>	SCALE FULL
		DRAWING NO. 221-221-RCF	DATE 10-17-72

Figure 7. Cross Section of Reaction Cell for LITACA  
[21]

## Key to Figure 7

Part No.	Description	Material	Req'd
1	Insulation Cap	Asbestos	1
2	Reaction Cell Lid	Transite	1
3	Bushing	Transite	1
4	Tube Bundle	Quartz	1
5	Ignition Tube Shield	Stainless Steel	1
6	Upper Cell Housing	6061-T6 Aluminum	1
7	Ignition Tube	Fused Quartz	1
8	Bushing	Transite	1
9	Graded Seal	Quartz-Pyrex Glass	1
10	6-32UNC Rd Hd Mach Scr	SAE Grade 5	4
11	Seal	Pyrex Glass-Kovar	1
12	Preheater Support	Stainless Steel	1
13	Lower Cell Housing	6061-T6 Aluminum	1
14	1/8NPT-1/4 Male Conn.	316 Stainless Steel	1
15	Bushing	Transite	1
16	Gasket	Teflon	1
17	Mixing Chamber	Chrome Plated Brass	1
18	Spacer	Transite	2
19	Support Shelf	Aluminum	1
20	1/4-20UNC Nut & Bolt	SAE Grade 5	4
21	Flame Arresting Chamber	Chrome Plated Brass	1
22	Bushing	Transite	1
23	6-32UNC Hx Hd Mach Scr	SAE Grade 5	3
24	Flange	Stainless Steel	1
25	Bushing	Transite	1
26	Upper Cell Base	Transite	1
27	Upper Guard Heater	Nichrome Wire	1
28	Ignition Heater	Chrome-Al-Fe Wire	1
29	Lower Guard Heater	Nichrome Wire	1



as shown in Figure 3. A cross section of the reaction cell is shown in Figure 7 (key to figure on page 26) and a close-up view of the reaction cell is shown in Figure 8.

The purpose of the reaction cell is threefold:

- (1) to mix the pyrolysate gases with dry air,
- (2) to act as a flame arrester to prevent any upstream flame propagation, and
- (3) to heat the fuel-air mixture at a controlled heating rate to the temperature at which self-ignition occurs.

The chamber at the lower section of the reaction cell is formed by parts 17 and 21 as shown in Figure 7. This chamber serves both as a mixing chamber for the fuel and air which enter at its base and side, respectively, and a flame arresting chamber. It was made of chrome plated brass with a nickel undercoating, and was filled with 3 mm diameter pyrex glass beads. A nichrome wire guard heater (part 29) was built into the lower section of the mixing chamber to prevent any pyrolysate condensation. Two transite spacers (part 18) insulate this section from the supporting plate to minimize conduction losses from the guard heater.

The ignition tube (part 7) is fastened to the top of the flame arresting chamber with a stainless steel fitting. It consists of the following four sections fused together:

- (1) a 10 mm I.D. quartz tube, 128 mm long,
- (2) a quartz-to-glass graded seal, 15 mm long,



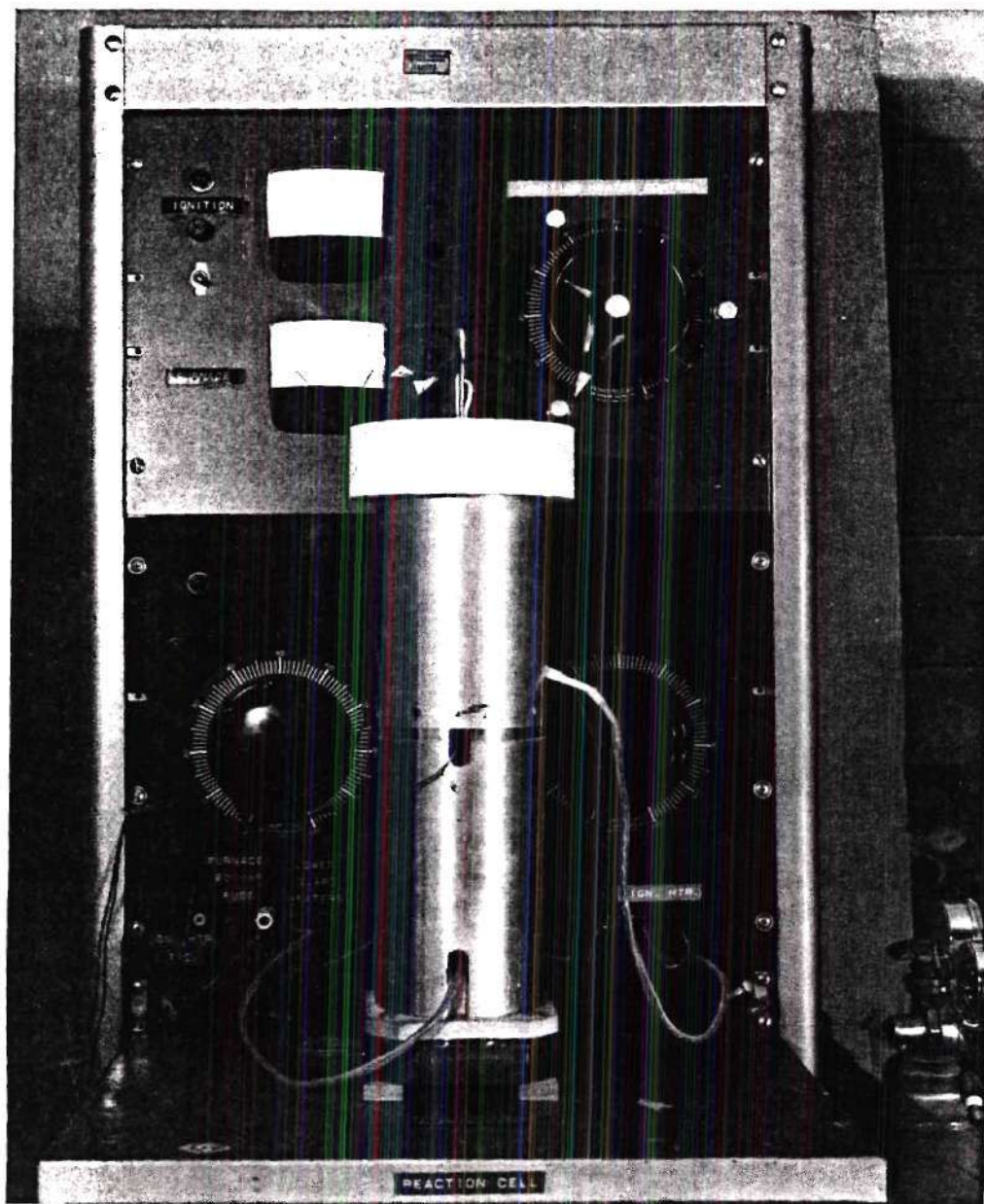


Figure 8. Reaction Cell for LITACA

- (3) a 6 mm I.D. pyrex glass tube, 75 mm long, and
- (4) a 1/4 inch O.D. pyrex glass-kovar graded seal, 35 mm long.

A quartz tube bundle (part 4) made up of seven 3 mm O.D. and 2 mm I.D. tubes, 30 mm long, is positioned 3 mm below the top opening of the ignition tube. The tubes are held together by two 0.005 inch diameter stainless steel wire rings and are kept in position by two stainless steel wire hooks which are hung from the top of the ignition tube opening. The purpose of these tubes is to guide and hold the ignition sensing thermocouples which are discussed in the instrumentation section later in this chapter.

Two tungsten pins, sealed into the pyrex section of the tube, were previously used as part of a nickel resistance wire ignition detection system [21]. These pins were not used in the present system.

A transite bushing (part 15) which fits over the top end of the flame arresting chamber acts as a base for the mixture preheater support (part 12). The preheater was wrapped onto the stainless steel preheater support and encloses most of that part of the ignition tube which is in the lower section of the reaction cell. It preheats the air-fuel mixture as it enters the ignition tube from the mixing chamber and also prevents any condensation in that part of the tube. A second transite bushing (part 22) overlapping the skirt of the flame arresting chamber serves as the seat

for the cylindrical aluminum lower cell housing (part 13).

The upper cell housing (part 6), also aluminum, contains the ignition heater (part 28) and the ignition tube shield (part 5). The stainless steel shield has a flange welded to its base which is secured to the transite upper cell base (part 26) by three machine screws. Two transite bushings (parts 8 and 25), one on either end of the ignition heater, assure that the heater is properly centered in the housing. Asbestos is used as the insulator between the heater and the cell housing.

The ignition heater (part 28) consists of two 515 watt, 115 volt cylindrical half shell heaters, Model RH221, which were wired in series and were supplied by the Thermal Corporation, Huntsville, Alabama. The heating elements are chrome-aluminum-iron wires, helically wound, placed in ceramic backings and embedded in a ceramic core, whose maximum temperature is 1200 C. The ceramic core was wrapped with an asbestos insulation and was placed into the upper cell housing. The asbestos minimizes heat losses from the ignition heater to the surrounding atmosphere. The annular region between the ignition heater and the ignition tube shield (part 5) was filled with aluminum oxide to permit maximum heat transfer from the ignition heater to the ignition tube shield. The ignition heater is energized by a 15 amp-115 volt variable auto-transformer. The following empirical expression was used to relate the ignition heating



rate to the auto-transformer setting between the 40% and 95% positions:

$$\text{Ignition Heating Rate} \approx 6.24 \times 10^{-7} (\% \text{ Setting})^{4.0} \text{ C/min} \quad (2)$$

An insulating cap (part 1), a transite reaction cell lid (part 2), and an upper guard heater (part 27) are the major components of a bonnet which sits on top of the upper cell housing. The guard heater is a 10 ohm coil of nichrome wire embedded in the asbestos insulating cap with Sauereisen Insa-Lute adhesive cement. Its main function is to suppress heat losses from the top of the ignition heater.

Three 6 inch long ceramic thermocouple insulator tubes are used as guides and holders for the ignition sensing chromel-alumel thermocouples. These 1/16 inch O.D. tubes are inserted through their respective holes located at, and just off, the center line of the insulating cap, and through the quartz tube bundle into the ignition tube. The center ceramic tube has 4 holes and handles 2 thermocouples which are positioned 5-1/2 and 7-1/2 cm below the top edge of the ignition tube. The two remaining tubes have only one pair of holes each and position thermocouples at 3-1/2 and 12 cm below the top edge of the ignition tube. Thirty gauge chromel-alumel thermocouple wires with a small thermocouple bead are used which allow a very small response time. The thermocouple positions were chosen from a transverse ignition



tube temperature profile which yielded that region where ignition would initiate.

The transite bushing, shown as part 3 in Figure 7, was not used during the present studies. The ignition tube could be centered without the aid of this bushing and at the same time the absence of this bushing reduced the chances of breakage of the ignition tube.

#### Temperature Recording and Ignition Detection Instrumentation

The temperature recording and ignition detection instrumentation initially used for minimum ignition temperature tests on propane-air mixtures consisted only of one chromel-alumel thermocouple along with:

- (1) one Hewlett-Packard Model 34703-A DCV/DCA/ohm meter,
- (2) one Hewlett-Packard Model 34750 Five Digit Display Unit,
- (3) one Hewlett-Packard Model 34721-B BCD Module,
- (4) one Hewlett-Packard Model 581-A Digital to Analog Converter,
- (5) one Hewlett-Packard Model 680 Strip Chart Recorder, and
- (6) one chromel-alumel ice point reference junction.

This thermocouple was located 3-1/2 cm below the top edge of the ignition tube, since this portion of the tube was assumed to be isothermal [21]. However, temperature profiles of the

ignition tube were again measured, and an isothermal region was not observed. Instead, a maximum temperature point was repeatedly observed 5-1/2 cm below the top edge of the ignition tube for both steady state and transient tube temperature conditions. These temperature profiles and the conditions under which they were obtained are given later in Chapter V. Since a problem was encountered with the ignition detection of pyrolysate-air mixtures due to the flame's low exothermicity, the sensitivity of the temperature recording and ignition detection instrumentation was increased from a 0 to 50 mV full scale reading to a 0 to 2 mV full scale reading (on a 25 cm scale). Three more chromel-alumel thermocouples were also installed at 4, 7, and 9-1/2 cm below the top edge of the ignition tube. The latter part of Chapter III discusses the history of how this problem was discovered and resolved. The modified temperature recording and ignition detection instrumentation arrangement is shown schematically in Figure 9 and physically in Figure 10. The major components of the instrumentation are:

- (1) eleven chromel-alumel thermocouples,
- (2) three iron-constantan thermocouples,
- (3) one Hewlett-Packard Model 34703-A DCV/DCA/OHM Meter,
- (4) one Hewlett-Packard Model 34750 Five Digit Display Unit,
- (5) one Hewlett-Packard Model 34721-B BCD Module,

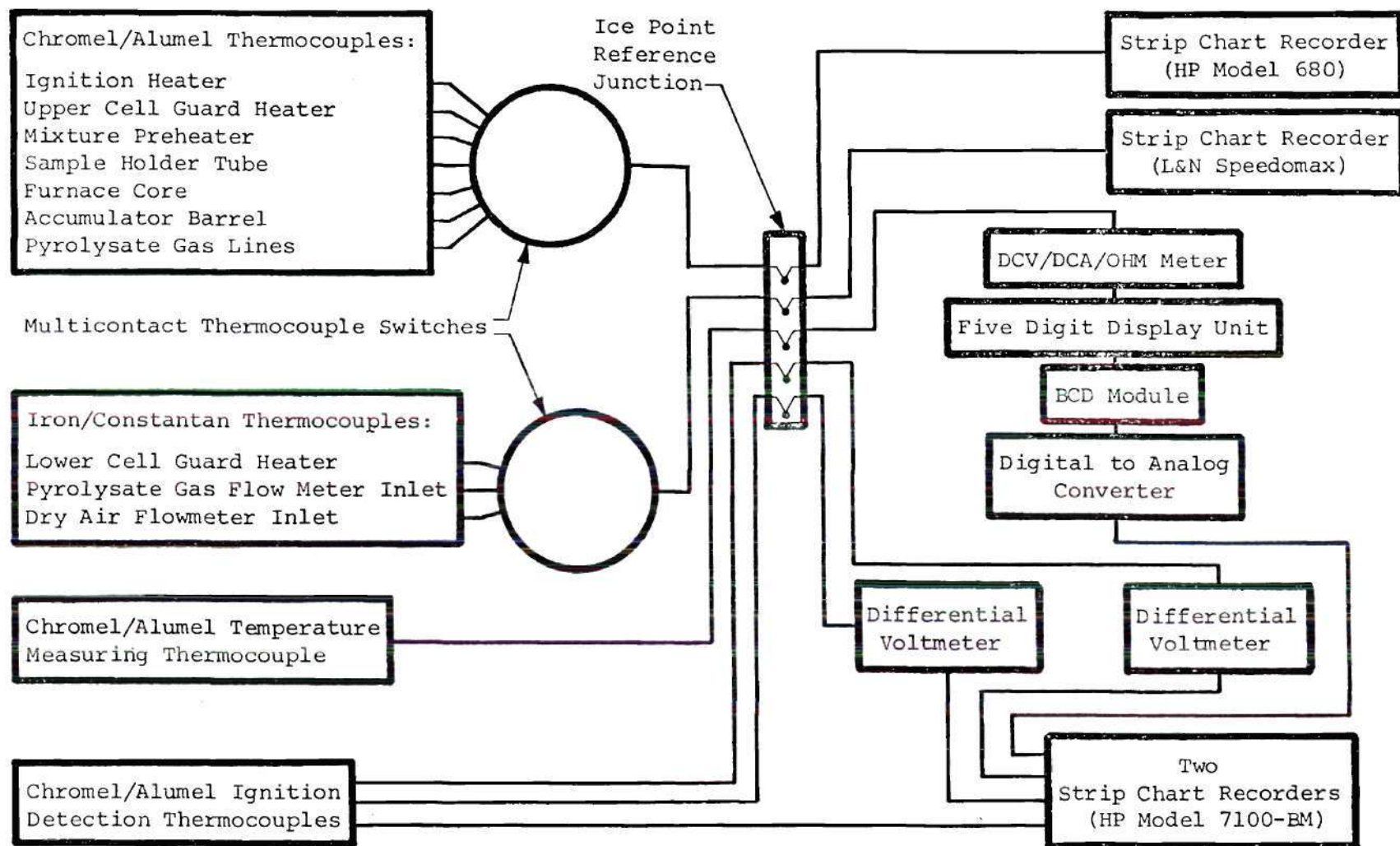


Figure 9. Schematic for the Temperature Recording and Ignition Detection Instrumentation Used with LITACA



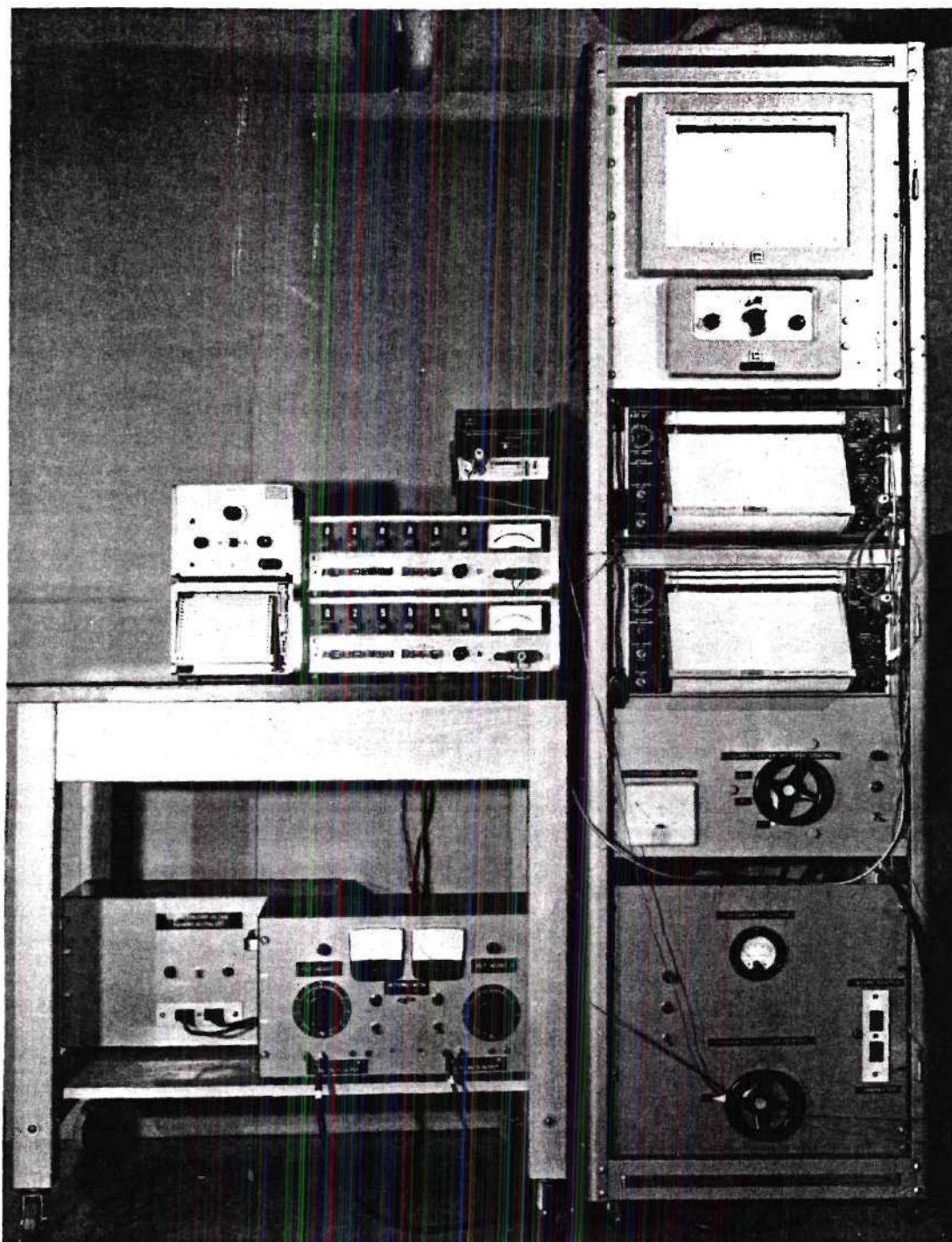


Figure 10. Temperature Recording and Ignition Detection Instrumentation Used with LITACA



- (6) one Hewlett-Packard Model 581-A Digital to Analog Converter,
- (7) two Hewlett-Packard Model 3420-B DC Differential Voltmeters,
- (8) one Hewlett-Packard Model 680 Strip Chart Recorder,
- (9) one L&N Speedomax Strip Chart Recorder,
- (10) two dual-channel Hewlett-Packard Model 7100-BM Strip Chart Recorders,
- (11) two multicontact thermocouple switches,
- (12) four chromel-alumel ice point reference junctions,
- and (13) one iron-constantan ice point reference junction.

#### Temperature Measuring and Recording Instrumentation

The temperature measurements were made with three different sets of thermocouples. The first set, as shown in Figure 9, consisted of seven chromel-alumel thermocouples which monitored the temperature of:

- (1) the ignition heater (Figure 7, part 28),
- (2) the upper cell guard heater (part 27),
- (3) the mixture preheater,
- (4) the sample holder tube (Figure 4, part 18),
- (5) the furnace core,
- (6) the pyrolysate accumulator barrel (part 1), and
- (7) the pyrolysate gas lines.

A multicontact chromel-alumel thermocouple switch connected these seven thermocouples to a common ice point reference junction which in turn is connected to the Hewlett-Packard

Model 680 strip chart recorder. This arrangement permitted any one of the seven thermocouple signals to be manually selected and to have its temperature-time history recorded.

The second set of temperature measuring thermocouples consisted of three iron-constantan thermocouples which monitor the temperatures of:

- (1) the lower cell guard heater (Figure 7, part 29),
- (2) the pyrolysate gas (or propane) at the inlet of the pyrolysate flow meter, and
- (3) the dry air at the inlet of the dry air flow meter.

The last two temperatures were necessary to determine the actual gas flow rates from standard calibration condition data. A multicontact iron-constantan thermocouple switch connected the three thermocouples to a common ice point reference junction which in turn is connected to an L&N Speedomax strip chart recorder. As above, this arrangement permitted the manual selection of any of the three thermocouple signals to be monitored and recorded.

The third set of the temperature measuring thermocouples consisted of one chromel-alumel thermocouple which monitored the maximum temperature of the gases flowing through the ignition tube. The maximum temperature occurred at 5-1/2 cm below the top edge of the ignition tube. This thermocouple also acted as an ignition detector if a reaction occurred in its vicinity. It was connected to an ice point

reference junction which in turn was connected to the Hewlett-Packard DCV/DCA/OHM Meter. This meter, used as a voltmeter, measures the thermocouple emf to 1/100 mV in the range used. The voltmeter reading was then displayed on the Hewlett-Packard Five Digit Display Unit. The Hewlett-Packard BCD Module then changed this thermocouple signal into a noninsulated BCD output for operation with the Hewlett-Packard Digital to Analog Converter whose DC output was connected to the input module of one Hewlett-Packard Model 7100-BM strip chart recorder. The Digital to Analog Converter permits any three adjacent digits as seen on the Five Digit Display Unit to be monitored. When the value of the pre-selected three digit combination exceeds the maximum scale reading of the strip chart recorder, the Digital to Analog Converter automatically resets the recorder to a zero reading. This feature permitted for a high thermocouple sensitivity and automatic switching of the recorder pen from full scale to zero.

#### Ignition Detection Instrumentation

The ignition detection instrumentation consisted of three chromel-alumel thermocouples which monitored the temperature of the gases flowing through the ignition tube. They were positioned at 3-1/2, 7-1/2, and 12 cm, respectively, below the top edge of the ignition tube. The thermocouple which was positioned at 3-1/2 cm below the top edge of the ignition tube was connected directly to the input of one



Hewlett-Packard Model 7100-BM strip chart recorder. The remaining two thermocouples were each connected to their respective ice point reference junctions which were in turn each connected to the two differential voltmeters as shown in Figure 9. The differential voltmeters served as amplifiers for the incoming thermocouple signals and provided a sensitivity of 1 mV full scale deflection for the Hewlett-Packard Model 7100-BM strip chart recorders to which they were connected. Manual switching of the differential voltmeters was required to suppress the amplified output once it exceeded 1 mV.

#### Molecular Weight Determination Instrumentation

The instrumentation used in determining molecular weights of the pyrolysate gases is shown in Figure 11. The major components of the instrumentation are:

- (1) two three inch single-valve glass balloons,
- (2) one Vac-Torr Model D-25 Vacuum Pump,
- (3) one Kinney Model KTPG-1 Thermistor Gage Control,
- (4) one Model H51 Mettler Balance, and
- (5) one Fisher Isotemp Oven (not shown in the figure).

In order to measure the molecular weights of the generated pyrolysate gases, it was necessary to collect a known sample volume of gas from the accumulator barrel. Two three-inch single-valve glass balloons which were supplied by the Fisher Scientific Company were used for this purpose.



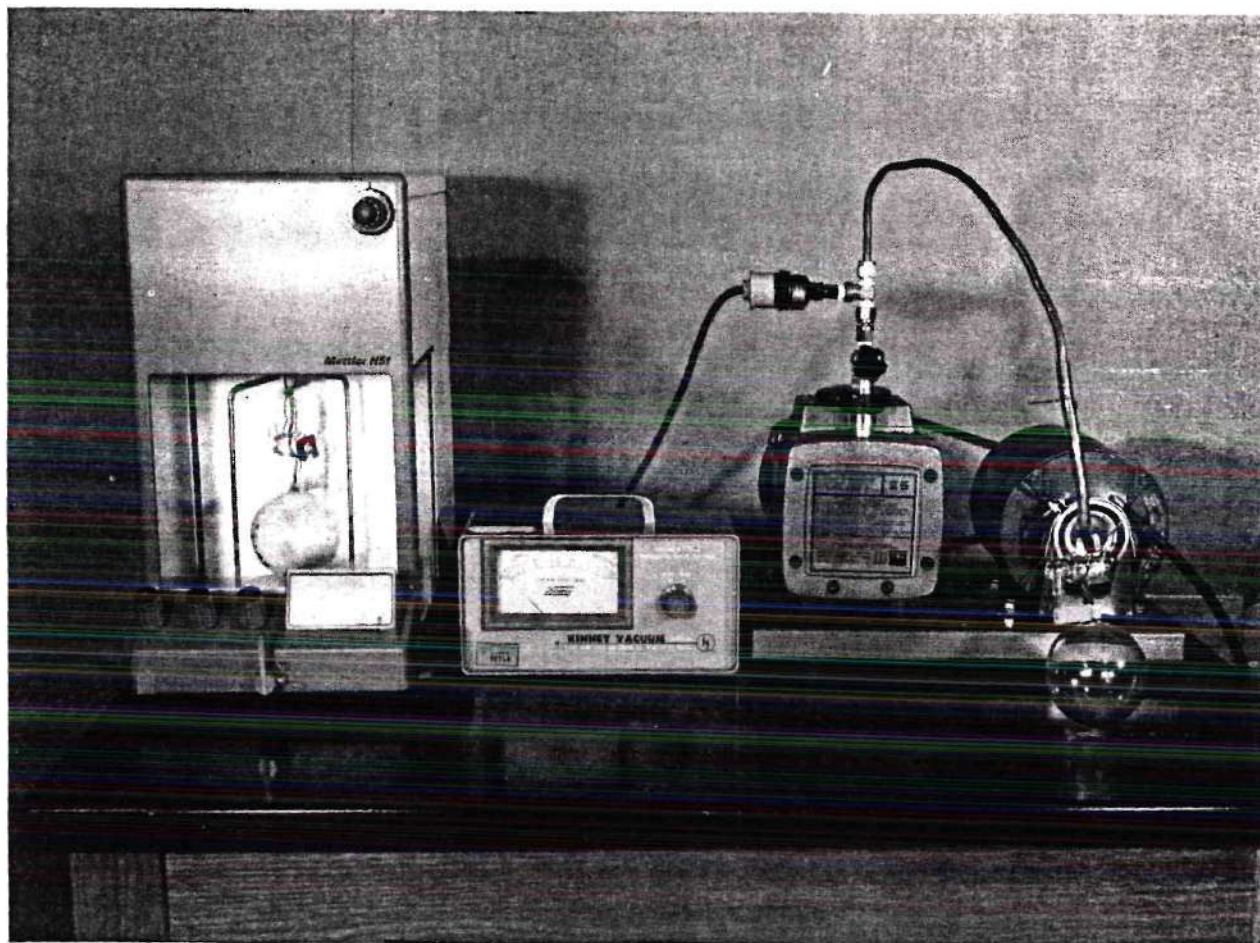


Figure 11. Molecular Weight Determination Apparatus

Their volumes were determined by internal mercury displacement. Initially dual-valve glass balloons were used, but their valves had a vacuum leakage problem at the higher temperatures (110-120 C) which was not tolerable. This will be discussed later in Chapter III.

One Vac-Torr Model D-25 vacuum pump was used to evacuate each balloon to 200 microns vacuum to remove any residual gases before any tare weight measurements were taken. A Kinney Model KTPG-1 Thermistor Gage Control along with a pressure transducer were used to monitor the vacuum in the balloon.

Gross (balloon plus sampled pyrolysate gases) and tare weights of the balloons were made with the aid of a Model H51 Mettler Balance which has a resolution of  $10^{-5}$  grams. A Fisher Isotemp oven was used to provide a known reference temperature for the sampled pyrolysate gases to come to thermal equilibrium.

### Auxiliary Systems and Components

#### Guard Heaters

The accumulator was wrapped with 20 gauge chromel-alumel thermocouple wire, as shown in Figure 6, which was connected to a 115 volt-5 ampere variable autotransformer. The wire served as a guard heater to minimize any pyrolysate condensation on the inner wall of the accumulator barrel. The thermocouple wire was kept in place on the accumulator

barrel with three beads of G.E. Silicone Rubber running vertically down the barrel wall as shown in Figure 6.

The pyrolysate fuel lines and pyrolysate flow meter were also wrapped with chromel-alumel thermocouple wires and connected to a 115 volt-5 ampere variable autotransformer. This arrangement served as a guard heater to prevent any condensation of the pyrolysate gases from the time they leave the accumulator barrel until the time they enter the reaction cell.

The guard heaters were set to maintain a temperature of 110-120 C. A Honeywell Model 333-R Digital Multimeter was used to set all heater voltages to allow for the repeatability of guard heater temperatures.

#### Gas Lines and Valves

All gas lines were made of 1/8 inch O.D. SS316 stainless steel tubing. The gas line which carried the pyrolysate gases from the accumulator barrel to the cold trap condenser was replaced with 1/4 inch O.D. SS316 stainless steel tubing. This was done because the excessive accumulation of tars on the inner tube wall constantly plugged up that portion of the pyrolysate gas line.

The valves controlling the flow of the pyrolysate gases are SS316 stainless steel with teflon packings. The remaining valves controlling the flow of oxygen and nitrogen gases are brass.



### Pyrolysate Cold Trap Condenser

A cold trap condenser was used to remove condensibles down to 0 C from the pyrolysate gases as generated by LITACA. It was located on the pyrolysate gas line between the accumulator manifold and the flow meter inlet. The cold trap condenser is made of a 200 ml glass balloon which was placed in an 800 ml pyrex beaker filled with water and crushed ice. A rubber stopper was used to close off the glass balloon as well as to provide an inlet for the incoming pyrolysate gases and an exit for the pyrolysate gases whose condensibles were removed.

### System Vacuum Pump

A Vac-Torr Model D-25 vacuum pump was used to evacuate the system prior to pyrolysate generation. It is a two stage pump with a 1/3 hp motor, a vented exhaust and a 25 liter per minute free air displacement.

### System Pressure Gauge

A pressure gauge was connected to one of the access points on the accumulator manifold (Figure 4, part 8). It monitored the pressure in the quartz sample holder tube and the accumulator barrel assembly which is shown in Figure 5. The pressure gauge reads both positive and negative gauge pressures with a range from 30 psig down to 30 inches Hg.

### Modifications to Original Design

The following modifications were made to the original



design of LITACA either out of necessity or convenience:

1. Pilot lights and voltage meters were installed in series with all fused power lines so that a quick observation of the control panels would reveal which portions of the system were energized.

2. Thermocouples were added to monitor the temperature of the gas lines, the accumulator barrel, and the wall of the furnace test tube. (A stainless steel band was used along with a spring to act as a clamp for the thermocouple on the furnace tube.)

3. The main power lines for LITACA were rewired to set all the grounds at the same potential.

4. The accumulator barrel, originally made of pyrex glass pipe, was replaced by an aluminum tube because the combination of the mechanical and thermal stresses it was exposed to resulted in the glass pipe's failure. A groove was machined into the bottom of the accumulator barrel to act as a housing for a high temperature silicone "O" ring which would seal the junction of the accumulator barrel to the manifold against any vacuum or pressure leaks.

5. A 1/4 inch copper tube was added to the pyrolysate gas line between the cold trap condenser and the flow meter to see whether the gases that have thin condensibles removed burn more readily than the gases that have their condensibles present.

6. The upper insulating cap, located on top of the

reaction cell, had two 2-1/2 mm holes drilled just to the right and just to the left of the cap's centerline to serve as entrances for the additional ignition sensing and temperature measuring thermocouples mentioned earlier.

7. The pyrolysate flow meter was wrapped with several turns of chromel-alumel thermocouple wire and was connected to the circuit controlling the gas line temperature. This prevented any condensation in the flow tube and minimized the sticking of the floats to the inner tube walls.

## CHAPTER III

### EXPERIMENTAL PROCEDURE

The previous chapter dealt with the instrumentation and equipment. This chapter describes in detail the experimental procedures used in measuring the ignition temperatures of both propane-air and pyrolysate-air mixtures as well as in determining molecular weights. Before any tests were made, all recorders, voltmeters, differential voltmeters, power supplies and the digital to analog converter were turned on to let the equipment stabilize for later use.

#### Ignition Temperature Measurements on Propane-Air Mixtures

The ignition temperature measurements on propane-air mixtures were conducted without the use of the pyrolysate generating furnace, the sample holder tube, the accumulator barrel, and the system vacuum pump. The gas line heaters were also not used since propane has no condensibles at room temperature. A pressurized tank of commercial grade propane was directly connected to the gas line of LITACA between the condenser and the inlet of the fuel flow meter through a two stage pressure regulator. The delivery pressure was adjusted to remain at approximately 5 psig. The dry air supply is described in detail in Chapter II. Initially, the propane

was allowed to flow through the gas lines, flow meter, and into the ignition tube of the reaction cell for several minutes to clear the system of any gases remaining from previous tests. The upper and lower guard heaters of the reaction cell and the ignition heaters were next energized to 17 volts each. From this point on, the procedure for minimum ignition temperature measurements on propane-air mixtures followed that described later in this chapter for pyrolysate-air mixtures.

#### Ignition Temperature Measurements on Pyrolysate-Air Mixtures

The minimum ignition temperature measurements on pyrolysate-air mixtures requires that the material being tested must first be pyrolyzed and then the gaseous products must be stored until they are ready to be used.

#### Preparation of the Sample and Initial Tasks

Approximately a 20 gram sample of the material to be tested was placed into a desiccator for a period of at least 24 hours to remove any physically absorbed moisture. It was then loosely packed into the quartz sample holder tube and a 4 inch clearance was left at the top and bottom because material placed in the end regions of the tube will undergo only partial pyrolysis due to the heat losses associated with the ends of the furnace heaters.

In the case of pyrolyzing wood, the 20 gram sample



was chipped into thin slivers approximately three inches long and then dried in the oven for two hours at 150 C. To prevent the chips from falling to the bottom end of the tube, a stainless steel screen cup was inserted into the tube. A stainless steel wire was spot welded to the screen to allow for easy removal.

After the sample material to be pyrolyzed had been placed into the sample holder tube, a thin coat of Apiezon Type H High Temperature-High Vacuum Grease was applied to both sides of the teflon gasket shown as part 11 in Figure 4 of Chapter II. The gasket was placed in the groove provided on the flange of the sample holder tube. The molded asbestos insert (part 10) was then placed on the tube flange and this assembly bolted to the accumulator manifold (part 8) with the cast iron flange (part 9). Each bolt (part 12) was first hand tightened and then given one turn to properly seat the teflon gasket. The sample holder tube and accumulator barrel assembly, shown in Figure 5, were tested for vacuum leaks. Four of the five access ports on the accumulator manifold were closed off by using the appropriate brass fittings and the final access point was attached to a supply of nitrogen gas. The assembly was pressurized to 25 psig and checked for leaks by using the soap-bubble method.

After verifying that no leaks were present, the assembly was positioned above the furnace mounting plate and slowly lowered to let the sample holder tube enter the furnace core

through the orifice provided in the transite top heater support (Figure 4, part 17). The five access ports on the accumulator manifold were connected to their respective lines: the vacuum pump, the gas sampling tap, the system pressure gauge, the pyrolysate flow meter, and the nitrogen supply. The nitrogen supply was also connected to the end cap at the top of the accumulator barrel.

The cold trap was placed in the crushed ice bath and connected to the pyrolysate flow lines if the condensibles were to be removed from the pyrolysate gases in the upcoming tests. After the cold trap had been readied, all of the valves which come in contact with the pyrolysate gases were checked to make sure they were closed. The system was again checked for vacuum leaks. Valves 2, 3, 4, and 5 as labeled in Figure 2 were closed; valve 1 was opened. The vacuum pump was turned on and a vacuum of approximately  $10^{-4}$  torr Hg was drawn on the system. The system pressure gauge was then observed. If any leakages were detected, the system was pressurized by nitrogen to 15 psig and the soap-bubble method was used to locate the problem. If, however, after a period of 10 minutes no loss in vacuum was observed, the system was considered ready for the next step. In the interim, the upper and lower guard heaters and the ignition preheater in the reaction cell were energized to 17 volts each. The ignition heater was also energized to about a 35% auto-transformer setting.

### Nitrogen Flushing Procedure

It is necessary to carry out the pyrolysis of the solid material in the absence of any oxidizing gases. Consequently, an inert gas flushing procedure was instituted as the next step in the preparation for pyrolysate gas generation. Valve 1 which connects the system to the vacuum pump, as shown in Figure 2, was opened and the system once again evacuated for approximately 10 minutes. Valve 1 was then closed. Valve 3 is a three-way valve which permits the nitrogen supply to be accessible either to the top side of the accumulator piston through the accumulator end cap or to the sample holder and the pyrolysate gas lines through the accumulator manifold. Valve 3 was opened and nitrogen allowed to fill the sample holder tube to a slightly positive gauge pressure. Valve 3 was then closed. The nitrogen was allowed to mix for approximately 5 minutes and dilute the residual gases that could still be present in the sample holder tube. Valve 1 was opened to reevacuate the system. The flushing and evacuation procedure was repeated five times and a final vacuum was pulled on the system. By now, any moisture that may have been absorbed by the sample between the time it was removed from the desiccator and the time it was placed in the sample holder tube should have been removed. Valve 1 was finally closed and the system vacuum pump turned off. The pyrolyzing process was ready to begin at this time.



### Pyrolysis of Thermally Degradable Materials

After completion of the inert gas flushing sequence and after having the system evacuated for the final time, all of the valves controlling the flow of pyrolysate gases were closed. The accumulator guard heater was turned on and set to provide a temperature of about 120 C at the wall of the accumulator barrel. This minimized the condensation of vapors and tars on the inner wall of the accumulator barrel and the bottom of the piston. It also helped prevent the piston rings from sticking to the wall. The pyrolyzing furnace was then energized by simultaneously rotating the two variable auto-transformers, which were wired in series, and control the power applied to the heater. Depending on the heating rate desired, the auto-transformers were set between 40% and 85% of the maximum allowable voltage which corresponds to approximately 5 C/min and 20 C/min, respectively. The Hewlett-Packard Mosley Model 680 Strip Chart Recorder was wired to monitor and record this heating rate, as is shown in Figure 9.

As the temperature of the furnace began to rise past approximately 250 C, the pressure of the system started to increase. Valve number 4 as shown in Figure 2 was opened to permit the top side of the floating piston in the accumulator barrel to remain at atmospheric pressure. As the pressure in the furnace rose above atmospheric pressure, the piston gradually rose until it reached its maximum displacement.



The furnace was controlled to keep the maximum system temperature below 400 C. At the lower heating rates (40% settings), it took about 60 minutes for the pressure in the system to start rising and about another 30 minutes for the pyrolysis process to reach completion. At the higher heating rates (90% settings) these times were about 15 minutes and 10 minutes, respectively.

The top side of the piston in the accumulator barrel was vented to the atmosphere to allow the pyrolysis gases to occupy the full displacement volume and at the same time to prevent the pressure to build up over 15 psig for 20 grams of material being pyrolyzed. Otherwise, leakage became a problem. When the pyrolysis process was completed, valve 4 was closed and the top of the piston was pressurized with nitrogen to 15 psig, using valve number 3 as shown in Figure 2. The guard heaters which control the temperature of the fuel lines and the pyrolysate flow meter were then energized and the temperature set to remain at about 120 C. These guard heaters were used to prevent the condensation of water and to minimize the accumulation of tars on the inner walls of the gas lines and flow meter. Valve 5 was opened to let some pyrolysate gases in the system discharge into the atmosphere; a match was used to ignite these pyrolysate gases to see if they will burn and a visual study of the nature of the flame was made. A tap was also provided in the gas lines just after the cold trap condenser to visually

observe if the flame was different when the condensibles were removed from the pyrolysate gases. It should be noted that the second observation of the flame could be made only when the condenser was connected in the system.

#### Setting of Ignition Heater

The auto-transformer energizing the ignition heater was set at about 35% during the procedure described above. It was then adjusted to achieve the desired heating rate. The range of available heating rates was from 1.4 to 43.2 C/min. An empirical expression relating the ignition heating rate to the variac setting is given as equation (2) in Chapter II. The Hewlett-Packard Mosley Model 680 Strip Chart Recorder which was used to record the furnace heating rate was next switched over to record the ignition heating rate by rotating the appropriate multicontact thermocouple switch, as is shown in Figure 9.

#### Attainment and Recording of Minimum Ignition Temperatures

When performing minimum ignition temperature tests on propane-air mixtures, a recorder sensitivity of 50 mV full scale reading provided excellent temperature-time plots for the determination of ignition points. At most, a 500 C temperature increase of the gaseous mixture was observed when propane ignited. However, when investigating pyrolysate-air mixtures, a 1 mV full scale reading of 25 cm on the recorder was used. Pyrolysate-air mixture ignition was clearly identifiable when using this sensitivity. The

necessity for increasing the sensitivity of the ignition detection and temperature measuring instrumentation arose from the fact that the flame temperature for pyrolysate-air mixtures was found to be at most 20 C higher than the surrounding gas temperature and at worst 0.2 C higher. The 50 mV full scale deflection sensitivity could not detect these magnitudes of temperature change.

After initiating the heating cycle in the ignition tube, the local barometric pressure was recorded and the L&N Speedomax strip chart recorder monitoring the emf from the two flow meter thermocouples was put into the recording mode. The pyrolysate was adjusted to a preselected flow rate when the temperature of the gases in the ignition tube just passes about 350-400 C. The dry air flow rate was also adjusted to a preselected value. At this time, the two dual-pen Hewlett-Packard strip chart recorders together with the associated instrumentation start monitoring the output of the four ignition tube thermocouples. These instruments were discussed in Chapter II and, as noted there, one of these thermocouples was positioned at the maximum temperature point in the ignition tube. The associated instrumentation for this temperature measuring thermocouple was set for a 1 mV full scale recorder reading. Automatic suppression voltage switching was provided to give a continuous 0 to 1 mV strip chart recorder input. The next two thermocouples which act as ignition detectors also have their associated



instrumentation, as noted in Chapter II, set for a 1 mV full scale recorder reading. Manual adjustment of the suppression voltages was required on the differential voltmeters (see Figure 9 in Chapter II) to provide for a 0 to 1 mV strip chart recorder input at all times. The final ignition detection thermocouple was coupled directly into the input of a strip chart recorder which was adjusted to a 50 mV full scale deflection.

By monitoring the temperature-time history of a particular fuel flowing through the ignition tube, the minimum ignition temperature of the fuel-air mixture could be determined. Three different categories of ignition signals were observed. These are shown in Figures 12, 13 and 14. The criterion for ignition used in this research was a sudden excursion of the thermocouple emf from its steady state rise as shown in Figure 12. An accelerating exothermic reaction as shown in Figure 13 which eventually quenches out was not considered an ignition point. A step increase in heating rate due to the exothermicity of the chemical reaction as shown in Figure 14 was also not considered an ignition point.

Depending on the fuel being tested, popping sounds can sometimes be heard from the reaction cell when ignition occurs. This phenomenon was especially noticeable when the air-fuel mixture flowing through the ignition tube was in the fuel-lean region.

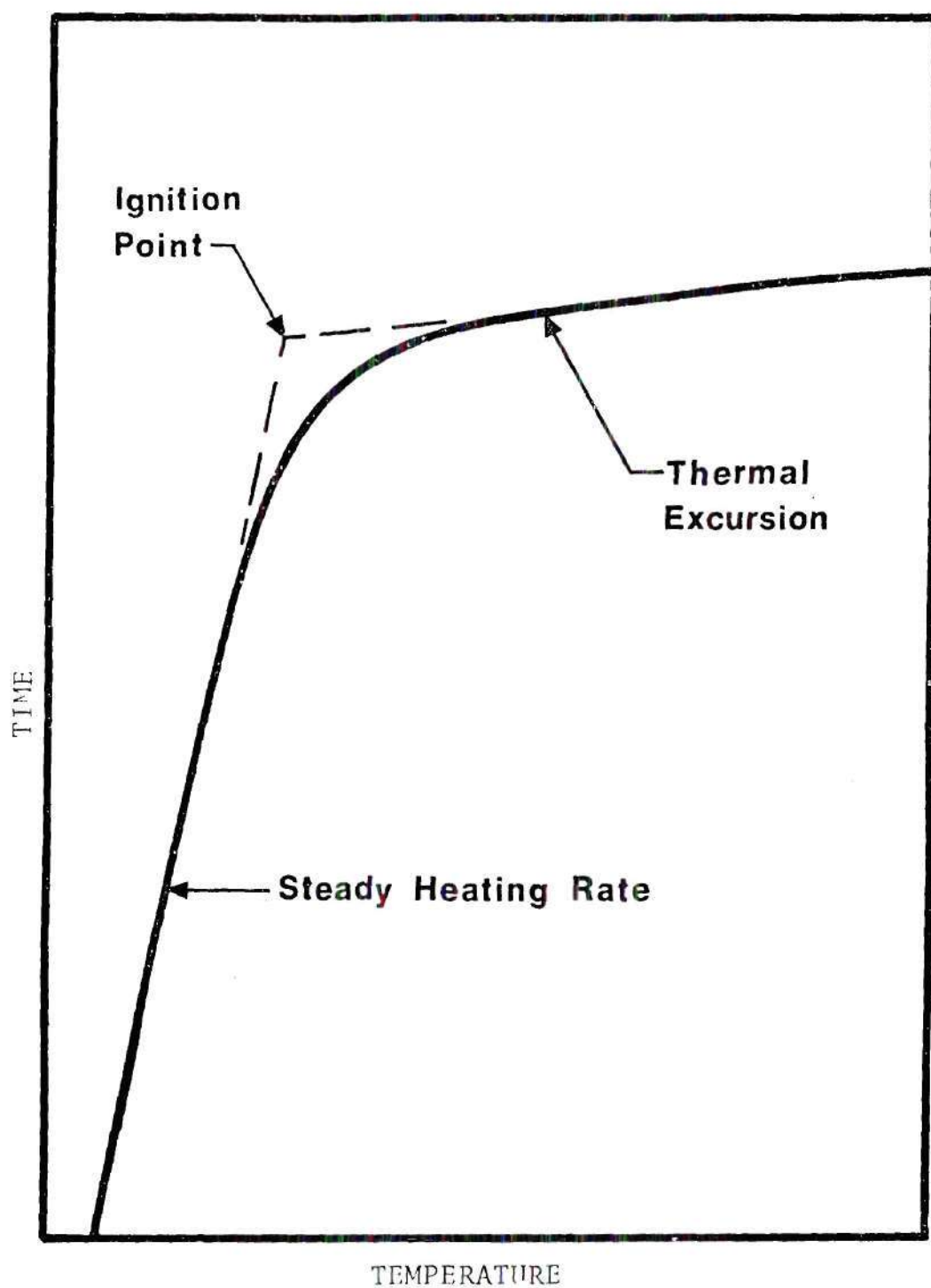


Figure 12. Typical Thermocouple emf History at Time of Ignition

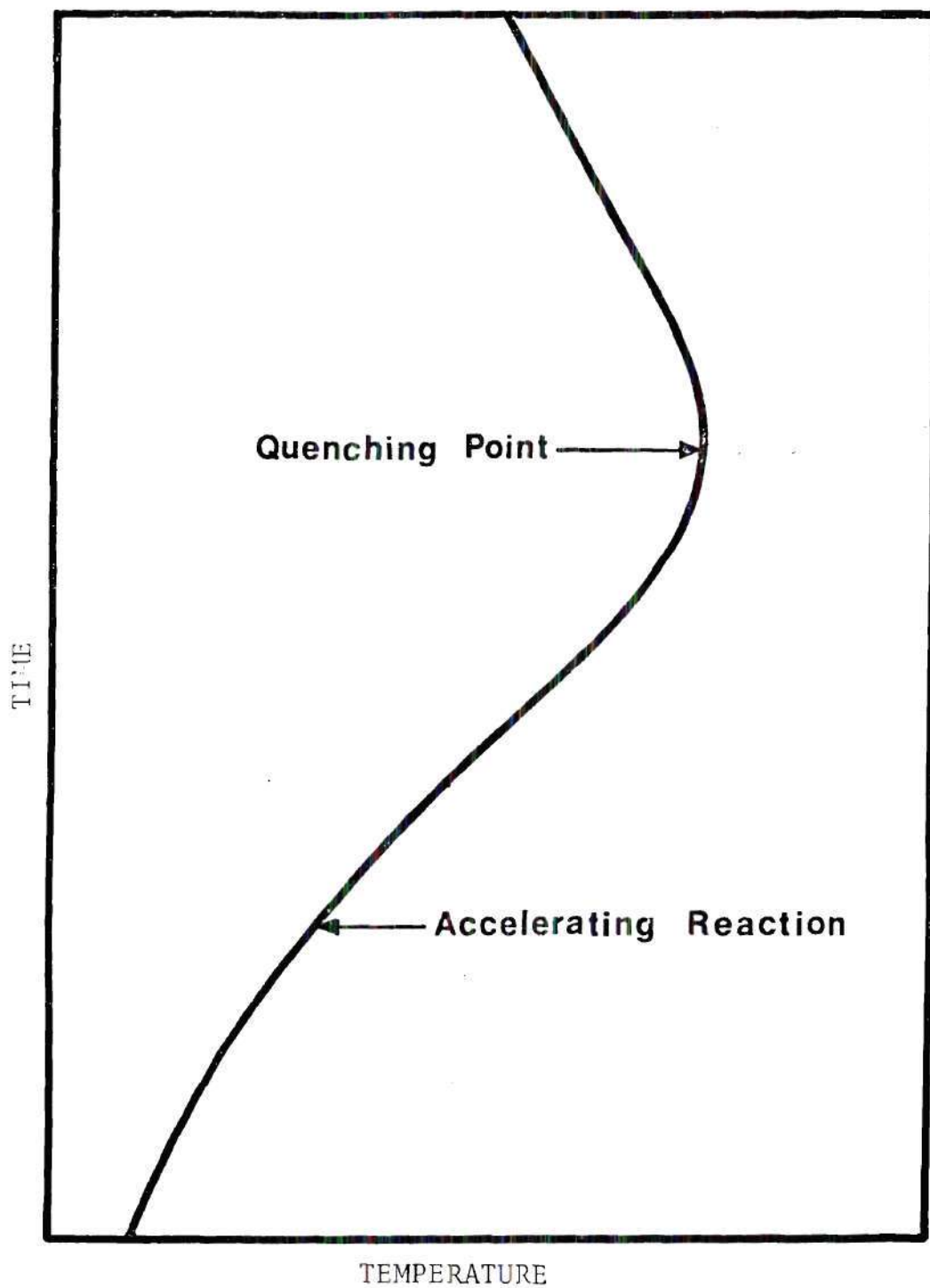


Figure 13. Typical Thermocouple emf History for an Accelerating Reaction with a Quenching Point



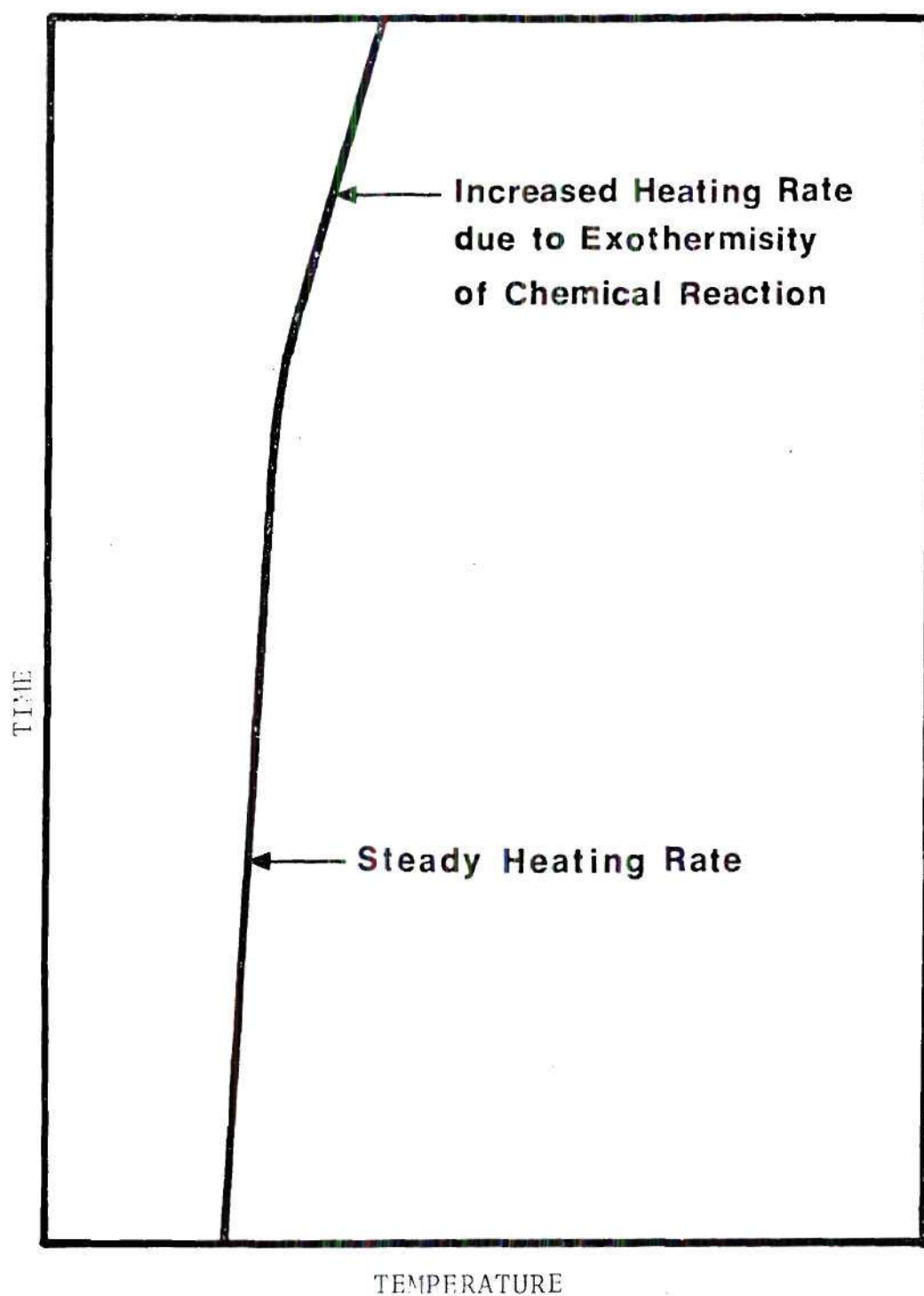


Figure 14. Typical Thermocouple emf History for a Step Increase in Heating Rate Due to Exothermicity of Chemical Reactions

When ignition was detected, the following steps were immediately taken:

1. The fuel scale readings were recorded for both the glass and stainless steel floats in the flow meter.
2. The scale reading of the air flow meter was recorded.
3. The thermocouple switch controlling the selection of the temperatures of the fuel and air at the inlet of the flow meters (refer to Figure 9 in Chapter II) was rotated to let the strip chart recorder read both emf's.
4. The fuel supply was shut off by closing valve number 2 as shown in Figure 2.
5. The ignition heater was turned off.
6. All strip chart recorders were returned to a stand-by mode.

The air flow was left on to flush out the residual gases from the mixing chamber and ignition tube as well as to help cool the ignition heater.

The minimum ignition temperature was obtained from the thermocouple emf-time plots such as the one shown in Figure 12. The temperature at the inlets of both flow tubes was also evaluated from the corresponding emf plots. This procedure hence yields an experimentally determined minimum ignition temperature for a pyrolysate-air mixture.

If ignition did not occur by the time the maximum temperature thermocouple reading reached 900 C, the test was terminated. The ignition heater was turned off immediately. The fuel supply was shut off and all strip chart recorders were returned to a stand-by mode.

When conducting tests on pyrolysate-air mixtures, the accumulator barrel usually contained enough fuel to carry out several minimum ignition temperature measurement tests. However when using propane-air mixtures, any number of tests can be conducted because the propane was supplied from a pressurized tank. If another test was to be made, then the ignition heater was again energized when the temperature in the ignition tube reached about 350-400 C. The procedures presented above were followed again.

#### Molecular Weight Determination

Molecular weight measurements on pyrolysate gases were carried out using the apparatus discussed in Chapter II and shown in Figure 11. The two glass sampling balloons were first prepared by greasing the stopcocks before every test with a coat of Apiezon Type H High Temperature-High Vacuum Grease. The outer surface of the balloons were then cleaned with acetone to remove any grease films which may have been present. These may vaporize when placed in the oven and introduce unnecessary error into the molecular weight calculations. From here on, the balloons were handled only



by a pair of forceps and a pair of pliers which were both cleaned of any dirt or grease. The two balloons were then placed in a Fisher Isotemp oven set at 110-120 C for a period of 10 minutes to evaporate any remaining acetone, and were evacuated to 200 microns of vacuum with the system shown in Figure 11. The evacuation process took approximately 30 minutes for each balloon.

Subsequent to the evacuation process the tare weights of the balloons were measured using the Mettler balance shown in Figure 11. A sample of the pyrolysates was taken by allowing the gas to expand into the evacuated balloon from the gas sampling tap connected to the accumulator manifold. Care was taken to prevent all physical contact with the balloon at any time during this procedure. At this point the balloons were placed back into the oven and remained there for at least two hours to allow the sampled pyrolysate gases to reach approximately 110-120 C, the equilibrium temperature for which the oven was set. The balloons were then vented to the atmosphere by temporarily opening the stopcock and permitting the balloon pressure to equalize with the known ambient pressure. The weight of the balloon filled with the pyrolysates was measured using the Mettler balance. The mass of the sample could be found by taking the difference between the gross weight of the balloon (balloon with pyrolysates) and the tare weight of the balloon.

The molecular weights of the pyrolysate gases could be experimentally determined through the procedure outlined above and by assuming an ideal gas behavior. In addition to the measurements of differential weight discussed above, it was necessary to know the pressure, temperature and volume of the sample. The sample pressure was determined by recording the local atmospheric pressure at the time of the balloon venting procedure. The sample temperature was determined by recording the thermometer reading of the Fisher Isotemp oven. The volume of the sample was measured by internal mercury displacement of the sampling balloons. The calibration conditions of the graduated cylinders used in the volume measurements were duplicated in an environmental chamber to insure accurate readings.

#### Cleaning Procedures

After completing the pyrolysate gas generation process, measurements of minimum ignition temperatures and measurements of molecular weights for a given material, the equipment was disassembled and cleaned. The gas lines were flushed with pressurized nitrogen while the heaters remained at 120 C. This procedure eliminated the problem of residual gas condensation on the inner gas line walls as they cooled down to room temperature. If a line was badly clogged, an attempt was made to unplug it by using heavy gauge wire. If the results were not satisfactory, the clogged portion of

the line was replaced.

The pyrolysate flow meter and the accumulator manifold openings and passages were cleaned with acetone and standard pipe cleaners. The floats from the flow meter were soaked in acetone, dried, and then placed back into the flow meter tube. The piston and the neoprene "O" rings were removed from the accumulator barrel and were scrubbed of all adhering tars with both acetone and Sparkleen. The inside wall of the accumulator barrel was similarly cleaned and regreased with Dow Corning High Temperature Grease before the piston and ring assembly was reinserted.

The quartz sample holder tube was removed and the pyrolysis products were discarded. The tube was then bolted back to the accumulator manifold and this assembly was placed in the furnace. A 1/8 inch diameter copper tube supplying oxygen at very low flow rates (approximately  $5 \text{ cm}^3/\text{min}$ ) was inserted all the way down to the base of the sample holder tube. The furnace was then energized to a 45% setting for a period of three to five hours, depending on the material pyrolyzed, until all of the carbon deposits had been vaporized. This cleaning process was completed when no more smoke can be seen leaving the opening of the accumulator manifold. Care was taken not to disturb the copper tube supplying the oxygen because the oxygen is unstable at these high temperatures and tends to ignite.

The balloons were cleaned by flushing them internally



and externally with acetone and water. They were dried with the petcock opened in the Fisher Isotemp oven for at least one half hour at 110-120 C. Consequently any water or acetone which may have accumulated on the surface and in the crevices of the valve of the sampling balloon(s) would evaporate. This helped minimize errors associated with molecular weight determination.

The cold trap condenser was removed and cleaned of any tars which may have accumulated. Acetone provided excellent cleaning results when used with a brush.

Finally, the valves controlling the flow of pyrolysate gases were also cleaned. This was especially necessary if the gases did not have their condensibles removed. The accumulation of tars condensing around the valve seats causes the flow of pyrolysates into the ignition tube to taper off with time thereby upsetting the desired steady flow of gases. The valves were cleaned with acetone and pipe cleaners each time the other equipment was disassembled and cleaned.

#### Difficulties Encountered

In order to pass on some of the experience gained in running minimum ignition temperature and molecular weight tests with the apparatus used, some of the difficulties encountered will now be discussed.

While making initial molecular weight measurements,

two dual-petcock sampling balloons were used. The valves were sealed with Dow Corning High Vacuum grease. When the balloons were exposed to the higher temperatures of the Fisher Isotemp oven (110-120 C), the grease failed to seal the petcocks. Only a 0.25 atmosphere vacuum existed in the balloons. It was believed that the seats and the valves were improperly fitted and consequently could not seal the balloon properly. After consulting with a representative of the Fisher Scientific Company, the author switched to using single oblique petcock sampling balloons. The leakage rate was somewhat reduced but was still too substantial. The Dow Corning High Vacuum grease was replaced with Apiezon Type H High Temperature-High Vacuum grease. The leakage rate dropped considerably, but was still present. A relationship between the amount of air leakage into the balloon was necessary. The procedure used was very straightforward. A stopwatch was triggered just after the balloon pressure equalized with the local atmospheric pressure and the petcock on the balloon was closed. By using the Mettler balance, several readings of the balloon weight are recorded at known time periods. An expression was then written for the gross weight of the balloon as a function of time. The true sample weight was obtained by evaluating the expression at time equals zero. Typical corrections ranged from  $5 \times 10^{-4}$  to  $7 \times 10^{-4}$  grams for a one minute interval after the pressure of the balloon was equalized. These corrections were not

necessary if the balloons were only used at room temperatures.

One of the major problems encountered during ignition tests was with the sensitivity of the ignition detection system. For tests conducted on propane-air mixtures, ignition points were clearly identifiable by using a single thermocouple whose output was recorded on a temperature-time plot having a 0 to 50 mV full scale sensitivity. This was not the case with pyrolysate-air mixtures. Initial pyrolysate-air tests were conducted using the same 0 to 50 mV full scale sensitivity as was used for the above mentioned propane-air ignition tests. However, ignition was not being detected. During one such test, a popping sound was heard coming from the reaction cell similar to the one heard when propane was being ignited. When the lights were turned off in the room with the experimental setup, a flame was repeatedly observed traversing the ignition tube and quenching out. This observation led to the conclusion that the magnitude of the thermal excursion at the time of ignition for pyrolysate gases was much smaller than it was for propane. Consequently, the sensitivity of the ignition detection system had to be increased for pyrolysate-air minimum ignition temperature tests. This was accomplished by increasing the sensitivity of the strip chart recorder input signal amplifier to a 2 mV full scale sensitivity. Three additional thermocouples, spaced approximately 1-1/2 cm apart, were added to the ignition detection and temperature measuring system. This



increased the sensitivity range in the ignition tube. All of the associated instrumentation for these thermocouples was discussed in Chapter II.

## CHAPTER IV

### DATA REDUCTION

A program was written for the Wang 720C calculator coupled with a 702 printer-plotter to carry out the computations for

1. calculating the molecular weights of the sampled pyrolysate gases,
2. calculating the mass fraction of the pyrolysate gases, and
3. converting mV data from the temperature measuring and ignition sensing thermocouples into temperature data.

The methods used in carrying out the above mentioned calculations will now be presented. The assumption was made that the pyrolysate gases behave ideally in the surroundings to which they are exposed during the tests.

#### Molecular Weight Determination of Pyrolysate Gases

As described in Chapter III, the molecular weight determination procedure involves knowing the weight of the evacuated balloon (tare weight) and the weight of the balloon filled with a fuel sample (gross weight) after the sample's temperature reaches equilibrium with a known temperature and its pressure equalized with the local barometric pressure.

At temperatures above 100 C and atmospheric pressure, the entire sample was assumed to be in a gaseous phase. By knowing the volume of the balloon, the ideal gas equation of state could be used to determine molecular weights:

$$M = \frac{m R T}{P V} \quad (3)$$

where  $m$  is the mass of the sample,  $R$  is the universal-gas constant,  $T$  and  $P$  are the absolute temperature and pressure of the gas, and  $V$  is the volume of the balloon.

Since two samples of molecular weights were taken, the program calculated both values and computed an average molecular weight which was used in subsequent computations.

#### Calculation of Pyrolysate Concentration

The minimum ignition temperature measurements were carried out with a steady flow of the air-fuel mixture, and the mass fraction of pyrolysate in the mixture is defined as

$$Y_p = \frac{\dot{m}_p}{\dot{m}_p + \dot{m}_a} \quad (4)$$

where  $\dot{m}_p$  and  $\dot{m}_a$  are the mass flow rates of the pyrolysates and air, respectively.

A relationship giving the volumetric flow rates under standard conditions for various flow meter readings was determined from tabular calibration data using the



least-squares method of fit. To determine the actual flow rates, corrections were made to account for the test conditions not being the same as the calibration conditions of the flow meter. The procedure for making these corrections follows.

The flow of the gas enters the bottom of the tapered vertical flow meter and positions the float at a point where the drag forces on the float are just balanced by the weight of the float. The buoyancy forces are assumed to be negligible. The annular area which exists between the float and the tapered glass tube will be considered to be the exit area for the gases in this analysis. The inlet area is that of the opening at the base of the tube. A momentum balance is made on a control volume of the gases which include the above mentioned inlet and exit areas as the boundaries. For two different gases flowing through two identical flow meters, the momentum balances can be written as

$$\dot{m}_c(v_e - v_i)_c = w_{f\ell} \quad (5a)$$

and

$$\dot{m}_t(v_e - v_i)_t = w_{f\ell} \quad (6a)$$

where  $\dot{m}_c$  and  $\dot{m}_t$  are the mass flow rates at the calibrated and test conditions, respectively;  $v_e$  is the exit velocity around

the annular opening;  $v_i$  is the velocity at the entrance of the flow meter; and  $w_{fl}$  is the weight of the float.

For steady flow conditions the continuity equation can be used to relate velocity to area, gas density, and mass flow rate. Applying this relationship to the inlet and exit velocities yields

$$v_e = \frac{\dot{m}}{\rho_e A_e} \quad (7)$$

and

$$v_i = \frac{\dot{m}}{\rho_i A_i} \quad (8)$$

The assumption is made that the pressure drop across the length of the flow tube is negligible and therefore

$$\rho_i \approx \rho_e = \rho \quad (9)$$

Substitution of equations (7), (8), and (9) into equations (5a) and (6a) yields

$$w_{fl} = \dot{m}_c \left( \frac{\dot{m}}{\rho} A_e - \frac{\dot{m}}{\rho} A_i \right)_c \quad (5b)$$

and

$$w_{fl} = \dot{m}_t \left( \frac{\dot{m}}{\rho} A_e - \frac{\dot{m}}{\rho} A_i \right)_t \quad (6b)$$

Considering that the floats are the same for both cases, their weights are equal. Hence the previous two equations can be equated to yield

$$\frac{\dot{m}_c^2}{\rho_c} \left( \frac{1}{A_e} - \frac{1}{A_i} \right)_c = \frac{\dot{m}_t^2}{\rho_t} \left( \frac{1}{A_e} - \frac{1}{A_i} \right)_t \quad (10)$$

If the scale reading is the same for both flow meters, then the exit areas are equal. (Note that the inlet areas are also equal since the analysis considers two identical flow tubes but with a different gas flowing through each.) This further simplifies equation (10) to

$$\frac{\dot{m}_c^2}{\rho_c} = \frac{\dot{m}_t^2}{\rho_t} \quad (11)$$

and permits the mass flow rate at the test conditions to be expressed in terms of the calibrated flow rate at standard conditions by

$$\dot{m}_t = \dot{m}_c \left( \frac{\rho_t}{\rho_c} \right)^{0.5} \quad (12)$$

The data is measured in volumetric flow rates rather than mass flow rates, so equation (12) is written as

$$\dot{V}_t \rho_t = \dot{V}_c \rho_c \left( \frac{\rho_t}{\rho_c} \right)^{0.5} \quad (13a)$$



or

$$\dot{V}_t = \dot{V}_c \left( \frac{\rho_c}{\rho_t} \right)^{0.5} \quad (13b)$$

By introducing the ideal-gas equation of state, this can be further simplified to

$$\dot{V}_t = \dot{V}_c \left( \frac{P_c T_t M_c}{P_t T_c M_t} \right)^{0.5} \quad (13c)$$

When the flow meter is used for metering air, the ratio of  $M_c/M_t$  equals unity if the calibration fluid was air. Therefore, the volumetric flow rate for air at test conditions is given by

$$\dot{V}_{t,a} = \dot{V}_{c,a} \left( \frac{P_c T_{t,a}}{P_t T_c} \right)^{0.5} \quad (14a)$$

Recalling again the ideal-gas equation of state, the mass flow rate for air is given by

$$\dot{m}_{t,a} = \rho_{t,a} \dot{V}_{t,a} = \frac{P_t M_a \dot{V}_{t,a}}{R T_{t,a}} \quad (14b)$$

Further simplification yields

$$\dot{m}_{t,a} = \frac{\dot{V}_{c,a} M_a}{R} \left( \frac{P_c P_t}{T_c T_{t,a}} \right)^{0.5} \quad (14c)$$

For the pyrolysate gases, the volumetric flow rate at test conditions is given by

$$\dot{V}_{t,p} = \dot{V}_{c,p} \left( \frac{P_c T_{t,p} M_a}{P_t T_c M_{p,av}} \right)^{0.5} \quad (15a)$$

Recalling the value for the average molecular weight of the pyrolysate gases as determined using the procedures presented in the previous section, the mass flow rate of pyrolysate gases is given by

$$\dot{m}_{t,p} = \bar{\rho}_{t,p} \dot{V}_{t,p} \quad (15b)$$

or

$$\dot{m}_{t,p} = \frac{\dot{V}_{c,p}}{2} \left( \frac{m_1}{V_{B,1}} + \frac{m_2}{V_{B,2}} \right) \left( \frac{P_c T_{t,p} M_a}{P_t T_c M_{p,av}} \right)^{0.5} \quad (15c)$$

where  $m_1$  and  $V_{B,1}$  are the mass of sample number one and the volume of balloon number one, and  $m_2$  and  $V_{B,2}$  are the mass of sample number two and the volume of balloon number two.

Finally, the expression for the mass fraction of pyrolysate gases present in a given mixture is arrived at by substituting equations (14c) and (15c) into equation (4). This yields, after simplification

$$Y_p = \left\{ 1 + \frac{2}{R} \left( \frac{\dot{V}_{c,a}}{\dot{V}_{c,p}} \right) \left[ \frac{P_t}{\left( \frac{m_1}{V_{B,1}} \right) + \left( \frac{m_2}{V_{B,2}} \right)} \right] \left( \frac{M_a}{T_{t,a}} \frac{M_{p,av}}{T_{t,p}} \right)^{0.5} \right\}^{-1} \quad (16)$$

### Computation of Minimum Ignition Temperatures

The minimum ignition temperature is obtained from the appropriate strip chart recorder in mV. A relationship giving the temperature in C for the chromel-alumel thermocouple emf in mV was determined using the least squares method of fit. It is incorporated into the calculator program in such a way that only the mV thermocouple reading needs to be entered.

This completes all of the calculations necessary for determining the mean molecular weights, the mass fraction of pyrolysate gases in the mixture, and the minimum ignition temperature. A sample data sheet is given in Table B1 of the Appendix. A sample summary of the evaluated parameters is presented in Table 1. The complete set of results for all the material tested is in Appendix C.

Test number 118 was chosen and the experimental accuracies were calculated as follows:

1.  $\pm 0.005$  g/g mole for molecular weight determination,
2.  $\pm 0.005$  g/g for pyrolysate and propane mass fraction determination, and
3.  $\pm 1$  C for minimum ignition temperature determination.



Table 1. Sample Summary of Minimum Ignition Temperature and Mass Fraction  
Data for GIRCFF Fabric No. 17, 65/35% Polyester/Cotton

PYROLYSATE MINIMUM IGNITION TEMPERATURES--LITACA

Date: 11/9/1975

Fuel: Pyrolystate Fabric No. 17

Exp. No.	M,1 g/mole	M,2 g/mole	M,av g/mole	V,f cc/s	$\dot{m}_f$ g/h	V,a cc/s	$\dot{m}_a$ g/h	Y,f g/g	T,ig °C
117	37.30	37.31	37.30	.312	1.372	2.28	9.18	.129	831.5
	37.30	37.31	37.30	.250	1.099	2.28	9.18	.106	831.5
118	37.30	37.31	37.30	.337	1.482	1.52	6.15	.193	796.9
	37.30	37.31	37.30	.269	1.181	1.52	6.15	.160	796.9
119	37.30	37.31	37.30	.353	1.551	.92	3.72	.294	814.8
	37.30	37.31	37.30	.284	1.246	.92	3.72	.250	814.8
120	37.30	37.31	37.30	.364	1.598	.48	1.94	.450	807.8
	37.30	37.31	37.30	.284	1.246	.48	1.94	.390	807.8
121	37.30	37.31	37.30	.332	1.459	.19	.78	.651	770.2
	37.30	37.31	37.30	.269	1.181	.19	.78	.602	770.2

The method used for arriving at these values and sample calculations are given in Appendix A and Appendix B, respectively.

## CHAPTER V

### EXPERIMENTAL RESULTS AND DISCUSSION

This chapter first presents the experimentally determined minimum ignition temperatures for propane-air and pyrolysate-air mixtures. Later some interesting observations made by the author are presented.

#### Propane-Air Mixtures

Two series of ignition test measurements were conducted using propane-air mixtures. The first series had one thermocouple positioned 35 mm below the upper guard heater and just below the quartz tube bundle. When a transverse temperature profile of the ignition tube was taken, it was discovered that the portion of the tube which was assumed to be isothermal [21] was indeed not. Temperature profiles in the ignition tube were obtained. Figure 15 shows two steady state centerline ignition tube temperature profiles for 41% and 45% ignition heater settings. The temperatures were obtained by axially traversing a chromel-alumel thermocouple through the ignition tube after allowing several hours for the tube temperature to stabilize. Figure 16 shows two transient centerline ignition tube temperature profiles for 75% and 80% ignition heater settings. These temperatures were obtained by four stationary chromel-alumel



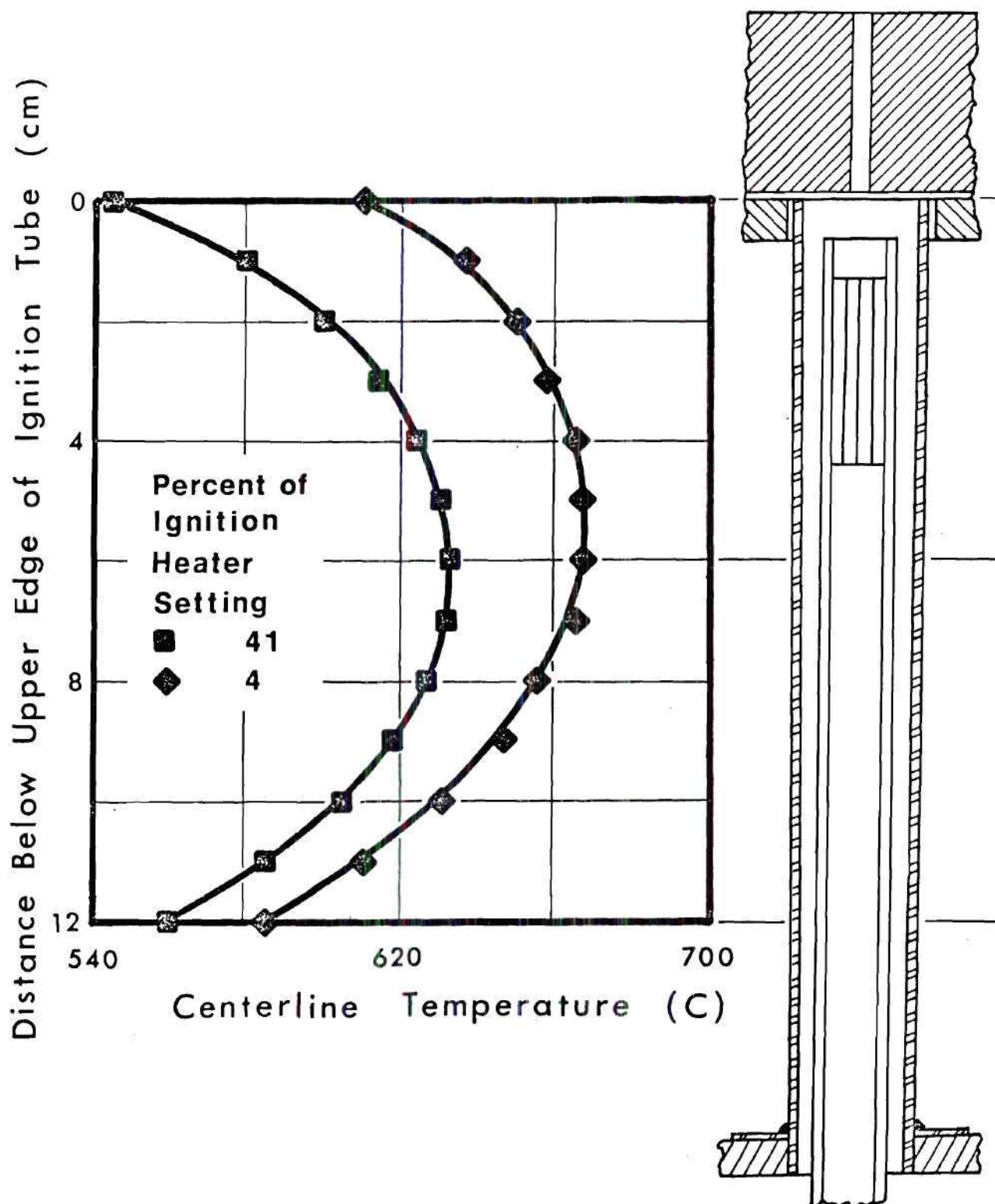


Figure 15. Temperature Profile Along Axis of the Ignition Tube, Steady Air Flow of  $3.3 \text{ cm}^3/\text{s}$

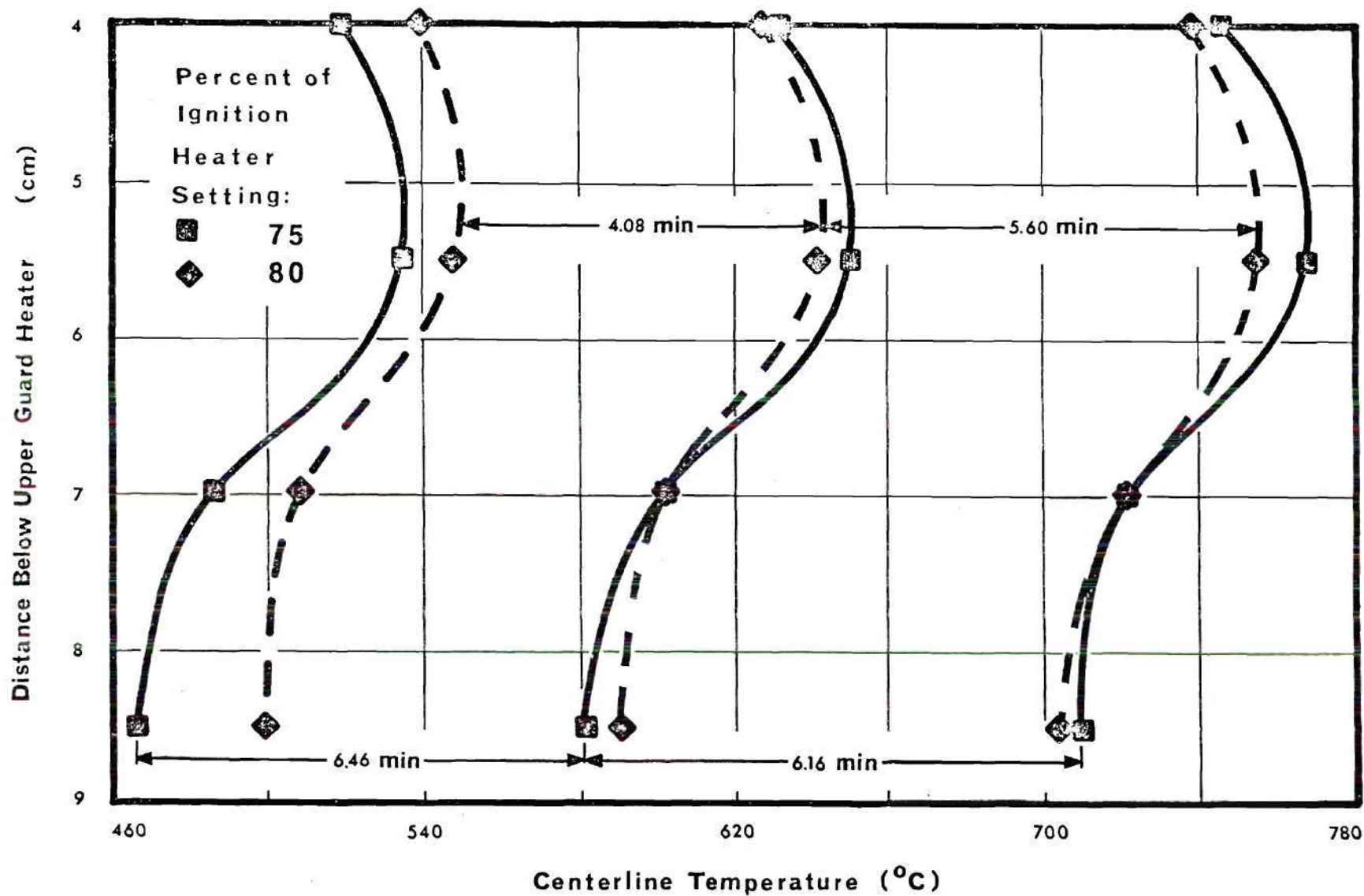


Figure 16. Time Dependent Transverse Temperature Profile of Gases in the Ignition Tube, Steady Air Flow of  $3.3 \text{ cm}^3/\text{s}$

thermocouples positioned at 4, 5-1/2, 7 and 9-1/2 cm below the upper edge of the ignition tube. For both figures, the air flow rate through the ignition tube was steady at 3.3 cm<sup>3</sup>/s. The maximum temperature was found to be consistently at 5-1/2 cm below the top edge of the ignition tube.

The second series of tests was made with the thermocouple repositioned to the maximum temperature point. Only a 10 C temperature difference existed between the 3-1/2 and 5-1/2 cm positions below the top edge of the ignition tube. Consequently the first series of test results for propane were corrected by adding 10 C to them and were tabulated together with the second series of test results in Table C1 of the Appendix. The rest of all the propane tests are plotted in Figure 17. No distinction is made between the two series of tests in the figure. The mixture velocity in the ignition tube for these tests ranged from 0.7 to 5.6 cm/s.

The lowest ignition temperature obtained for propane in air was 478 C for a mixture of 0.086 grams of propane per gram of mixture. The comparison of these results to other experimentally determined published information shows that there is some agreement. Scott, et al. [22] measured the minimum ignition temperature for propane in air to be 493 C by using the modified drop method. This method first liquifies the propane using either dry ice or liquid nitrogen and then introduces it into a heated crucible in air. At the time of

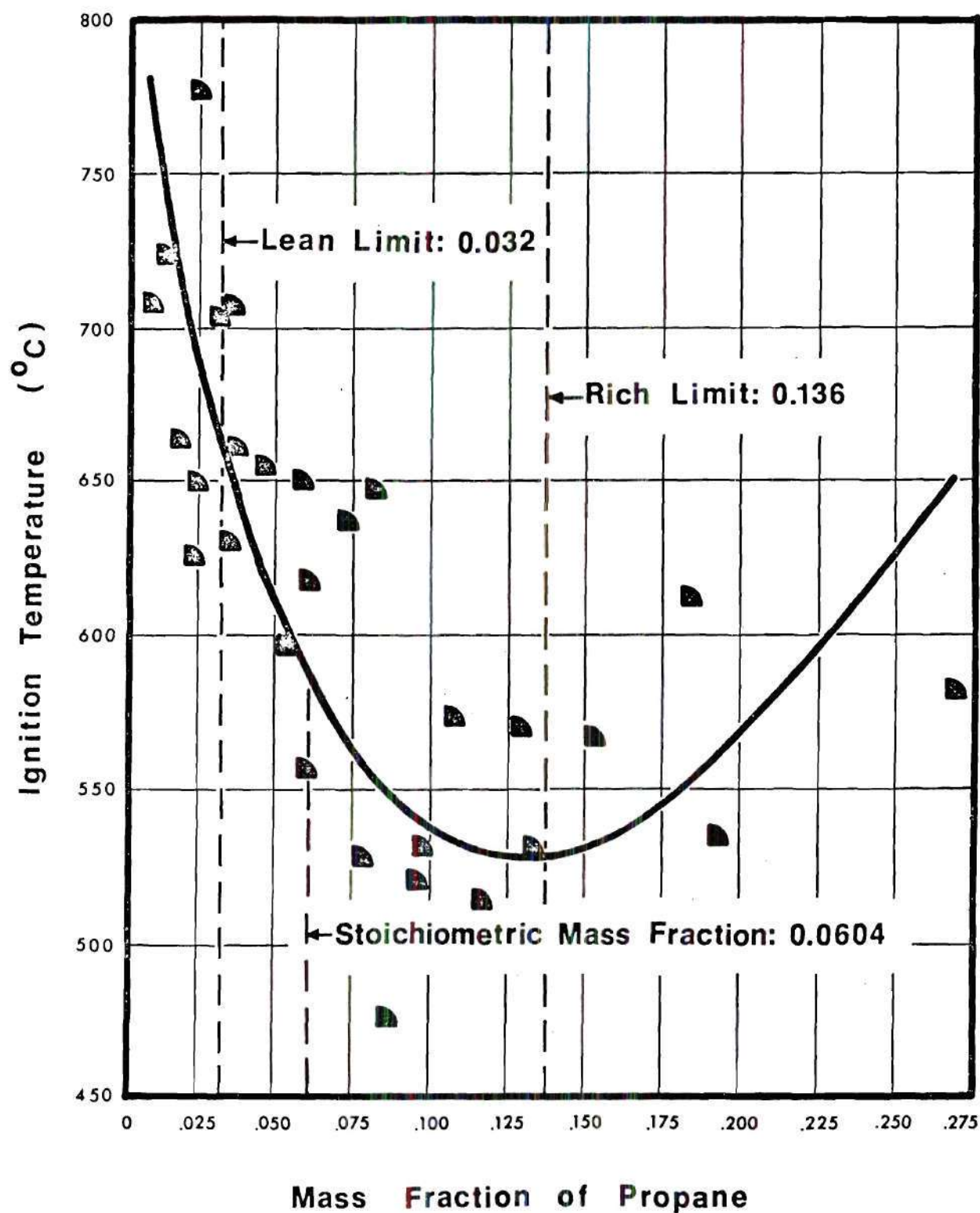


Figure 17. Minimum Ignition Temperatures of Propane-Air Mixtures. Lean and Rich Limits were Taken from Reference [23]



ignition, the minimum ignition temperature is recorded as the crucible temperature. The mass fraction of fuel is assumed to be stoichiometric (0.0604 grams of propane per gram of propane-air mixture).

Jones and Scott [23] reported that the flammability limits of propane in air are 0.0323 and 0.136 grams of propane per gram of mixture for the lean and rich limits, respectively. These asymptotes are shown in Figure 17. As Coward and Jones [24] defined them, the flammability limits are those borderline mixtures which with a slight change in one direction produce a flammable mixture and in the other direction produce an inflammable one.

According to Dr. Felix Weinberg, however, at a seminar given at the School of Aerospace Engineering at the Georgia Institute of Technology in the fall of 1975, he has "gone 82% of the way from burning the limit of flammability to pure air." In his words, "Effectively there are no limits of flammability if you recycle heat without simultaneous dilution." That is to say, if a fuel is preheated before it is ignited, ignition can occur outside the so-called limits of flammability. Dr. Weinberg also stated that the leaner the mixture, the higher is the activation energy necessary to initiate ignition. However, if there is a high enough heating rate leading to ignition, the required activation energy is reduced.

Belles and Swett [25] have stated that ignition data

obtained by different methods cannot be compared because of the difference in experimental apparatus and technique. However, if one method is used, the effects of different variables can be shown.

The criterion for ignition used by LITACA is a thermal excursion of the gaseous air-fuel mixture. Such a thermal excursion can be observed on the temperature history plots of the mixture in the ignition tube. This may be resulting from a flame or from a highly accelerating exothermic reaction as is shown in Figure 12 of Chapter III. The design of the equipment prohibits the visual detection of a flame as the criterion for ignition. Only if a flame should propagate down the ignition tube past the opening in the reaction cell can a flame be seen.

During the ignition temperature measurements two other distinct temperature history curves were observed and these are shown in Figures 13 and 14 of Chapter III. The first of these, presented in Figure 13, indicates the onset of an accelerating reaction which quenches out after a brief time elapse. While in the second case, shown in Figure 14, there occurs only a minor change in the slope of the temperature-time curve. These two cases are taken not to constitute ignition points.

#### Pyrolysate-Air Mixtures

Minimum ignition temperature tests were carried out on

pyrolysate gases generated from wood and three different fabrics, the latter selected by the Government-Industry Research Committee on Fabric Flammability and consisting of pure cotton and blends. They are

- (1) GIRCFF Fabric No. 4: navy blue denim, 100% cotton;
- (2) GIRCFF Fabric No. 15: brown durable press fabric, 65/35% polyester/rayon; and
- (3) GIRCFF Fabric No. 17: white batiste, 65/35% polyester/cotton.

Properties of these fabrics can be obtained from Reference [3]. The wood chips were a type of fir.

All of these materials were pyrolyzed at a maximum furnace temperature of 400 C. The results from these tests are shown in Figures 18-21 and Tables C.2-C.5 of the Appendix.

Due to some scatter and inadequate repeatability of data points, a strong relationship between the fuel mass fraction and the minimum ignition temperatures is not available. It can be seen, however, that a relationship is more prevalent for the fuel lean mixtures, except in the case of GIRCFF fabric number 17. For the fuel rich mixtures, only a region of ignition is observed which appears to be independent of fuel mass fraction. The reason for this is probably that the amount of noncombustible gases present dilute the amount of oxygen to such a great extent that the heating of the mixture is carried out in a virtually non-oxidizing atmosphere, and hence a process similar to the



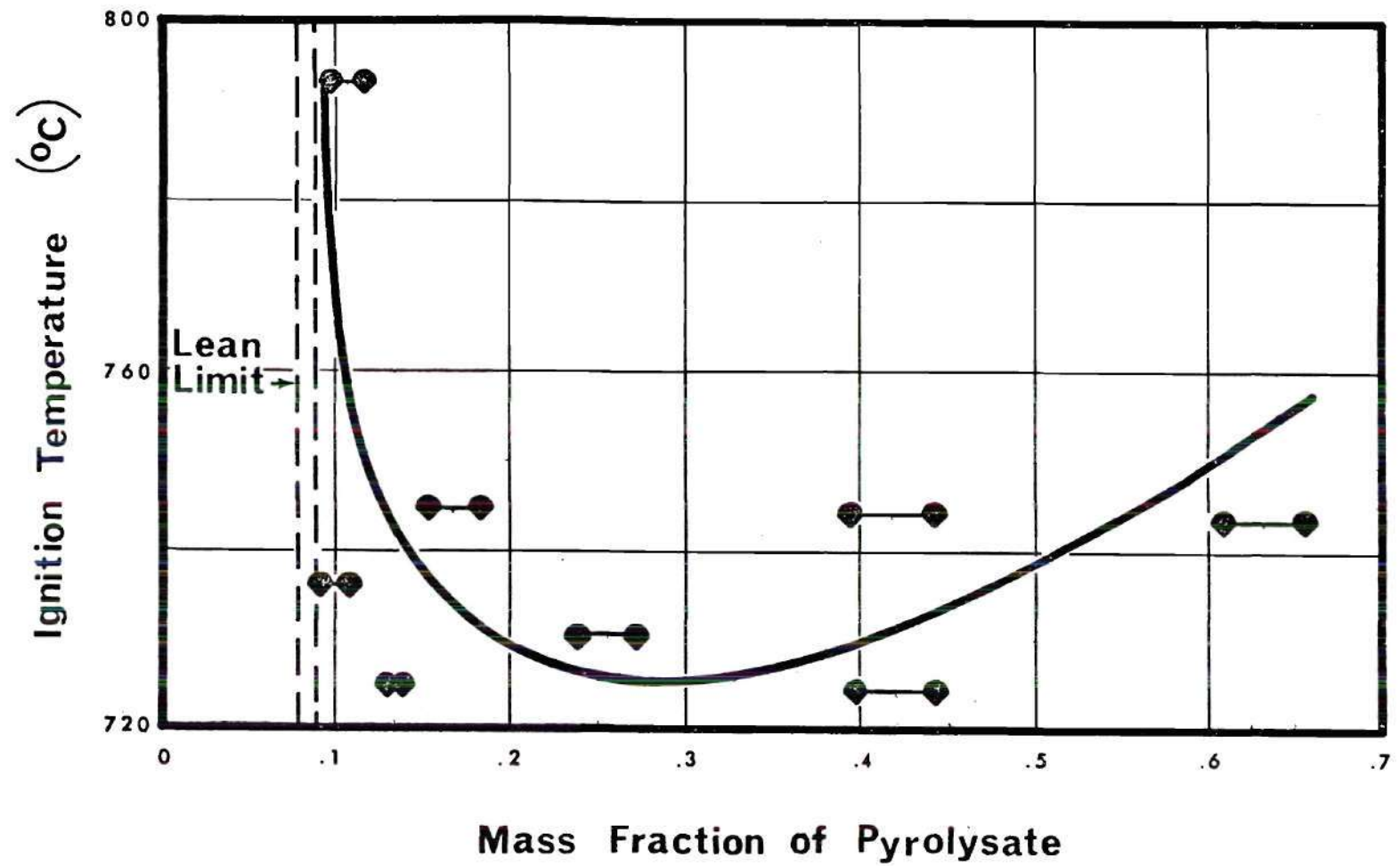


Figure 18. Minimum Ignition Temperatures of Pyrolysate-Air Mixtures, GIRCFF Fabric Number 4, 100% Cotton



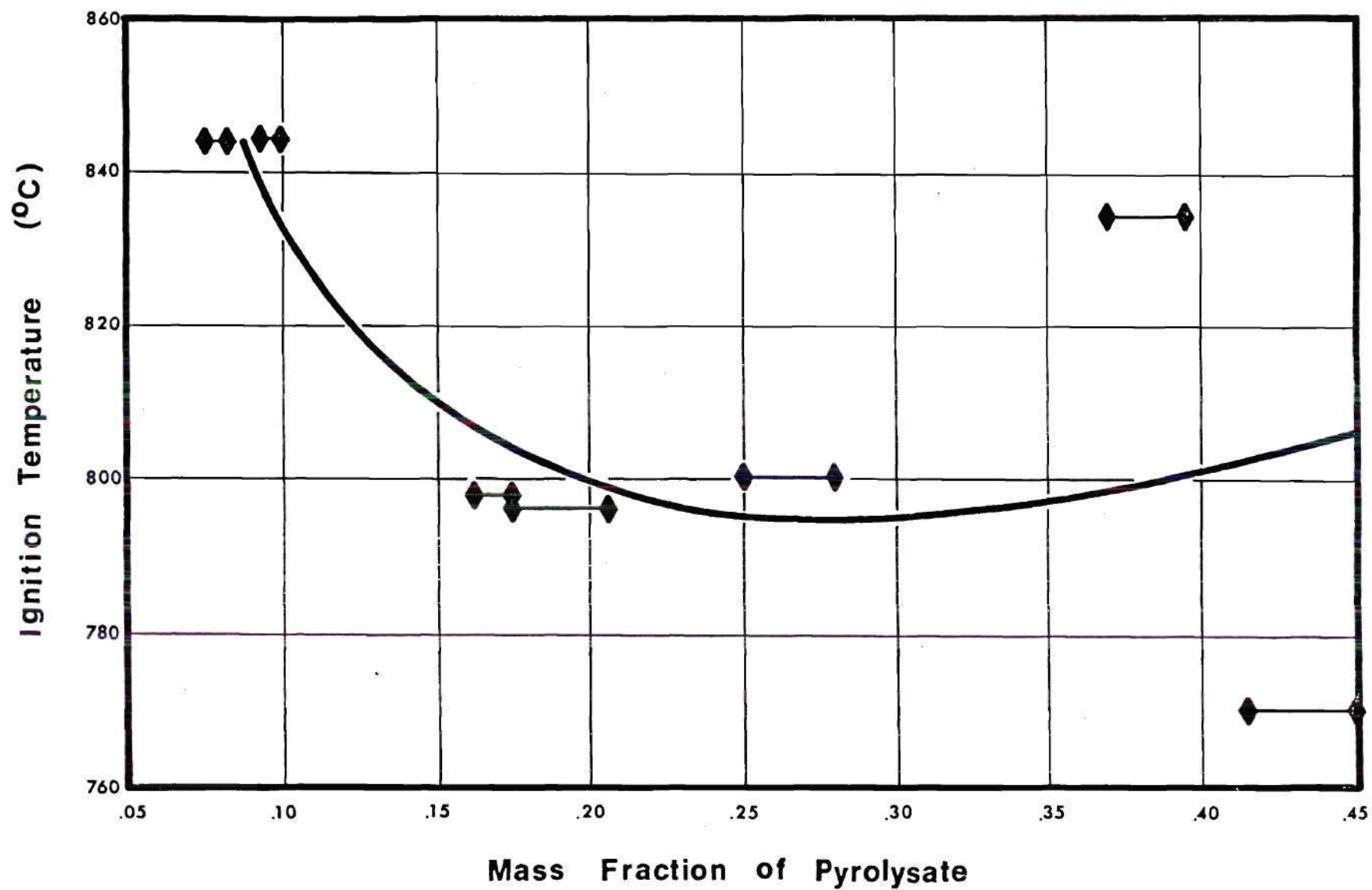


Figure 19. Minimum Ignition Temperatures of Pyrolysate-Air Mixtures, GIRCFF Fabric Number 15, 65/35% Polyester/Rayon

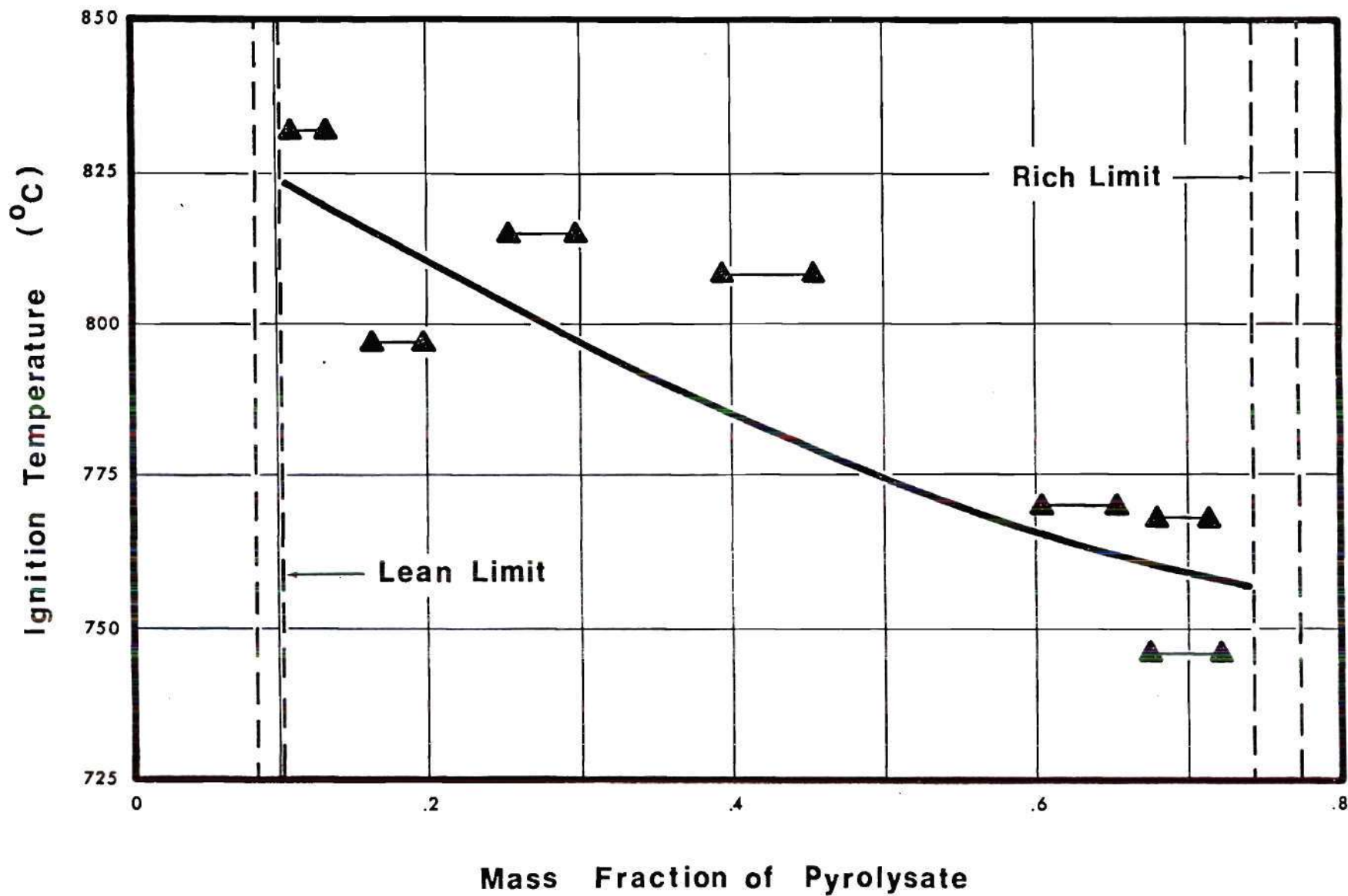


Figure 20. Minimum Ignition Temperatures of Pyrolysate-Air Mixtures, GIRCEFF Fabric Number 17, 65/35% Polyester/Cotton

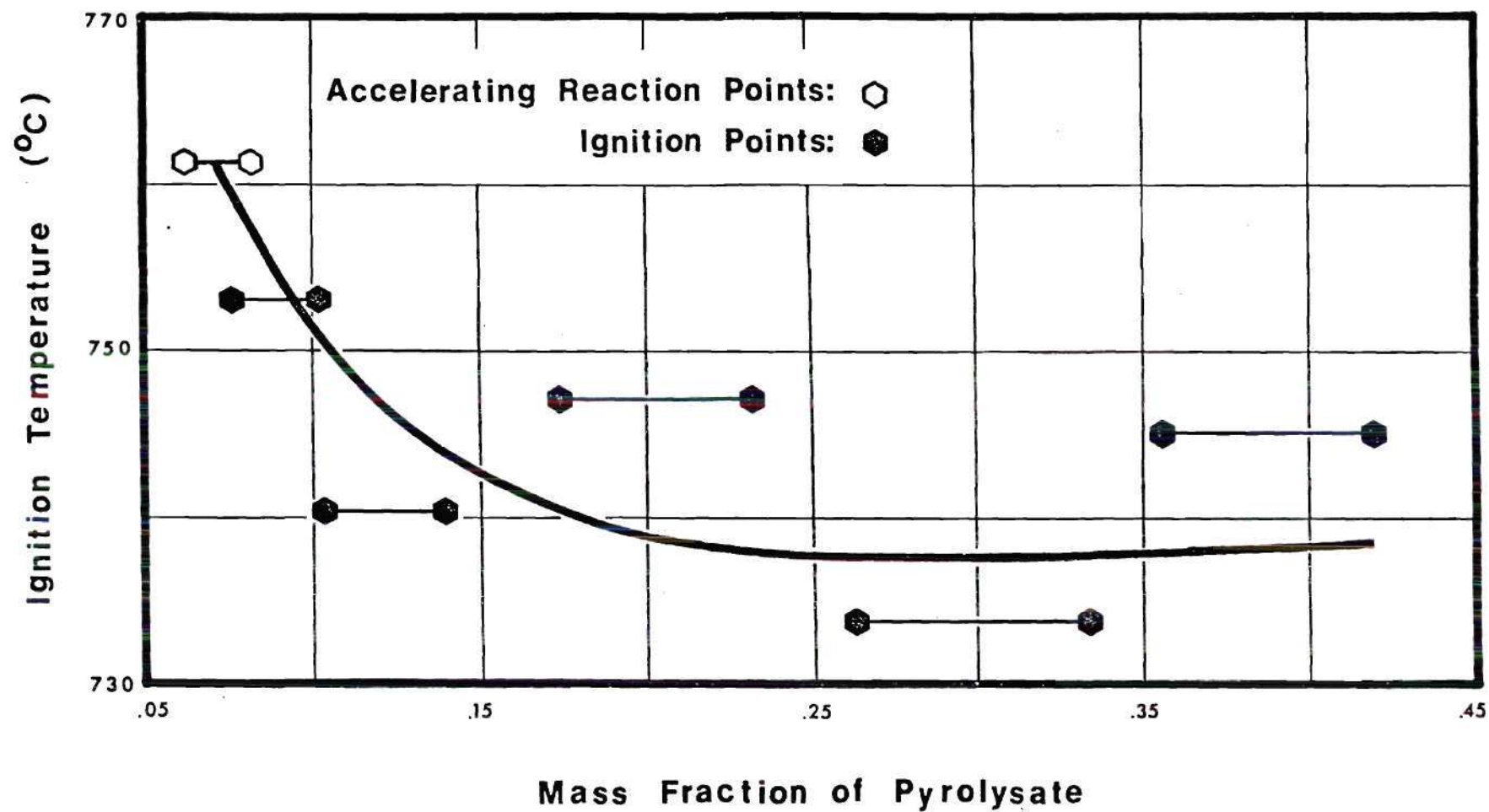


Figure 21. Minimum Ignition Temperatures of Pyrolysate-Air Mixtures, Wood Chips (Fir)

cracking process is being observed.

The mixture velocity in the ignition tube for these tests ranged from 0.6 to 6.5 cm/s.

The molecular weights of the pyrolysates, for the four materials tested, are presented in Table 2 together with the ranges of ignition temperatures. At first glance, a trend may appear to exist between the molecular weights of the sample pyrolysate gases and their regions of ignition. However, the group of molecular weights are within the range of experimental accuracy and consequently the stated trend is not conclusive.

When condensibles were removed from the pyrolysate gases at 0 C by using a cold-trap condenser and ice bath, the range of ignition temperatures was observed to be lower. In the case of the wood chips, no tests were made with condensibles removed. A possible explanation for the lower ignition temperature ranges is that a purer fuel enters the ignition tube and hence ignition can occur at the lower temperature. These points were not plotted since no molecular weight measurements were made with condensibles removed at 0 C and hence the proper mass fraction of fuel present at the time of ignition is unknown for them. These temperature ranges are nonetheless tabulated in Table 2 for comparison with the temperature ranges having condensibles present.

Sample molecular weights were initially made using three known gases to gain some experience with the procedures



Table 2. Summary of Molecular Weights and Ignition Temperature Ranges of Pyrolysate Gases

Pyrolyzed Material	Average Molecular Weight*	Standard Deviation	Ignition Temperature Range (C)	
			Condensibles Present	Condensibles Removed at 0 C
GIRCFF Fabric No. 4	36.0	3.2	724-793	667-766
Wood Chips (fir)	36.1	0.8	734-762	---
GIRCFF Fabric No. 17	37.3	1.8	746-832	752-772
GIRCFF Fabric No. 15	40.4	2.7	768-842	710-735

\* This is the average molecular weight of the gases which have condensibles removed down to a temperature of 120 C. The heavier tars which condense out down to 120 C do not enter into these measurements.

and calculations involved. The experimental error was also calculated. These results are tabulated in Table 3.

#### Interesting Observations Sighted

The following are some interesting observations made during the experimentation.

1. At the beginning of the ignition tests for GIRCFF fabric number 4 (100% cotton) a visual observation of the nature of the flame was made. It was approximately 3 mm in length and quenched out rapidly. Towards the end of the minimum ignition temperature tests, the pyrolysis generating furnace had been turned off and had cooled to slightly above room temperature. A second visual observation was made. The flame was approximately 3 cm long and it was self sustaining. The reason for this phenomenon is probably that the majority of the heavier gases were either used up in the minimum ignition temperature tests (since the pyrolysates are supplied from the base of the accumulator barrel) or that they had condensed in the cooler sample holder tube. This could in turn have permitted more of the lighter gases to be sampled which would have consisted of a mixture having fewer tars and noncombustibles present.

2. At very low furnace heating rates (furnace setting at 18%--about 1 C/min) the products leaving GIRCFF fabric number 4 (100% cotton) were observed to be clear in nature. This is because, at very low heating rates, the principal

Table 3. Experimentally Determined Molecular Weights of Known Gases

Gas Sample	Average Experimental Molecular Weight	Actual Molecular Weight	% Error
N <sub>2</sub>	29.58	28.02	5.6
Ar	39.86	39.94	0.2
He	4.19	4.003	4.6

thermal decomposition product is water. Hence, the clear gas observed was primarily water vapor. At higher heating rates (furnace setting at 85%--about 20 C/min) the pyrolysis products were opaque and yellow in color. This change in color and transparency can be explained by the degree and nature of the pyrolysis reaction.

3. During the pyrolysis of the fabrics and wood chips, the materials went through some very obvious physical changes:

- (i) their color changed to black,
  - (ii) a large percentage of the original fabric turned into a charred residue,
  - (iii) the size and weight of the sample was reduced,
  - and (iv) flexibility and mechanical strength were lost.
- Also GIRCFF fabric number 15, a 65/35% polyester/rayon, turned into a black crust that easily crumbled into a powder.

4. Whenever a flame was visually observed to be traversing the ignition tube, it either quenched out when it reached the tungsten pins (discussed in section on the Reaction Cell in Chapter II) or it positioned itself just above the pins where the ignition tube diameter suddenly decreases. In the former case, the flame quenched out because the pins acted as heat sinks for the energy of the flame. In the latter case, the flame did not quench out because the mixture velocity vector was larger in the small diameter portion of the tube than was the flame velocity



vector. This velocity vector cancelling effect prevented the flame from coming into contact with the tungsten pins.

5. Previous self-ignition tests were made on pyrolysate gases from cellulosic materials by P. T. Williams [21]. However, self-ignition of the resulting pyrolysate-air mixtures was unsuccessful. In view of this previous inability to achieve self ignition, a cold trap condensor was installed between the accumulator manifold and the inlet of the pyrolysate flow meter.

It was discovered during the present investigation that ignition was occurring whether condensibles were removed or not and that the sensitivity of the ignition detection system needed improvement.

## CHAPTER VI

### CONCLUSIONS AND RECOMMENDATIONS

Minimum ignition temperatures of propane-air and pyrolysate-air mixtures were obtained and plotted as a function of fuel mass fraction. These have been shown in Figures 17 through 21, and the data is tabulated in Tables C.1 through C.5 of the Appendix.

Two regimes of ignition behavior were observed, the fuel-lean and the fuel-rich region. In the fuel lean region, a relationship between the ignition temperatures and the fuel mass fraction was observed which yields a lean limit asymptote. For the fuel rich region, the variation of the fuel mass fractions had no effect on the ignition temperatures; they all remained within a certain upper and lower bound.

The flame temperature in pyrolysate-air mixtures is at most only a few degrees higher than the surrounding gaseous mixture. High sensitivity ignition detection instrumentation is necessary for proper ignition point determination.

The experimentally determined molecular weights for the wood chips (fir) and blue denim (100% cotton) fabric were approximately equal. The molecular weights were slightly higher for the polyester/cotton and polyester/rayon blends. However, the molecular weights of the four pyrolysate gases

are grouped within the range of experimental accuracy and this trend is not conclusive.

At the time LITACA was originally designed, the effects of heating rates on pyrolysis products were unknown. However, the gas composition is a strong function of the decomposing heating rate. The heating rate obtainable from LITACA is about 20 C/minute, a rate much too small compared to the several 100 C/minute in actual fires. Redesign of the pyrolysate generating furnace using tungsten lamp radiant heaters focused on the sample is urged to simulate actual fire environments.

More thermocouples should be installed in the ignition tube to allow for definite ignition detection at all flow-rates, i.e., to allow for flame detection along the whole ignition tube. Flame speeds can also be determined with this setup if the time between two adjacent thermocouple flame detections of the same flame is known. This can yield some information about the stoichiometry of the gases since the flame speed is highest at the stoichiometric mixture and tapers off for either richer or leaner mixtures. An oscilloscope would provide an adequate time sweep for these measurements.

Larger pyrolysate gas lines are recommended over the 1/8 inch tubing used to minimize the problem of gas line clogging and to allow for easier cleaning of these lines.

The machined groove at the base of the accumulator

barrel along with the silicone "O" ring provided such superior performance over any other arrangement or material used that the author feels justified in recommending this type of high temperature vacuum and pressure sealing geometry wherever it could be used when redesigning LITACA.

Finally the vacuum and pressure seal between the sample holder tube and the accumulator manifold requires some redesigning due to its poor capability of keeping the seal at the high furnace temperatures.



## APPENDICES

## APPENDIX A

EXPERIMENTAL ERROR ESTIMATION  
WITH SAMPLE CALCULATIONS

The accuracy to which the results presented in this work will now be estimated. The analysis takes into consideration all of the uncertainties in the experimental measurements.

The mass fractions of pyrolysis gases,  $Y_p$  of a given pyrolysis-air mixture is expressed (see equation 16) in terms of several parameters:

$$Y_p = Y_p (\dot{V}_{c,a}, \dot{V}_{c,p}, P_t, m_1, m_2, \\ V_{B,1}, V_{B,2}, M_{p,av}, T_{t,a}, \\ T_{t,p}, R, M_a) \quad (17)$$

The uncertainties of all these variables must be approximated if the uncertainty of  $Y_p$  is to be calculated. This is done by partially differentiating an expression for  $Y_p$  and then substituting numerical values for the resulting terms. Due to the complexity of partially differentiating equation (16) explicitly, another equation is used.

By starting with equation (4) and manipulating the

terms of the equation, the mass fraction of pyrolysates can be expressed as

$$Y_p = \left[ 1 + \frac{\frac{\dot{m}_{t,a}}{(\frac{\dot{m}_{t,a}}{\rho_{t,a}}) \rho_{t,a}}}{\frac{\dot{m}_{t,p}}{(\frac{\dot{m}_{t,p}}{\bar{\rho}_{t,p}}) \bar{\rho}_{t,p}}} \right]^{-1} \quad (18a)$$

$$Y_p = \left[ 1 + \frac{\dot{V}_{t,a} \rho_{t,a}}{\dot{V}_{t,p} \bar{\rho}_{t,p}} \right]^{-1} \quad (18b)$$

By substituting for the ideal gas equation of state for the densities, and by substituting in equations (14a) and (15a) for the volumetric flow rates, the equation simplifies to

$$Y_p = \left[ 1 + \frac{\dot{V}_{c,a}}{\dot{V}_{c,p}} \left( \frac{M_a}{M_{p,av}} \cdot \frac{T_{t,p}}{T_{t,a}} \right)^{1/2} \right]^{-1} \quad (18c)$$

For simplifications of calculations, let

$$\alpha = \frac{\dot{V}_{c,a}}{\dot{V}_{c,p}} \quad (19a)$$

and

Page missing from thesis



However,  $\delta(M_{p,av})$  must also be expanded. Since

$$M_{p,av} = \frac{\bar{\rho}_{t,p} R T_o}{P_t} \quad (23)$$

and

$$\bar{\rho}_p = \frac{m_1}{V_{B,1}} + \frac{m_2}{V_{B,2}} \quad (24)$$

then

$$\begin{aligned} \delta(M_{p,av}) &= \delta(T_o) \left[ \frac{R}{2P_t} \left( \frac{m_1}{V_{B,1}} + \frac{m_2}{V_{B,2}} \right) \right] - \delta(P_t) \\ &\quad \left[ \frac{R T_o}{2P_t^2} \left( \frac{m_1}{V_{B,1}} + \frac{m_2}{V_{B,2}} \right) \right] + \frac{R T_o}{2P_t} \left[ \delta(m_1) \left( \frac{1}{V_{B,1}} \right) \right. \\ &\quad \left. - \delta(V_{B,1}) \left( \frac{m_1}{V_{B,1}^2} \right) + \delta(m_2) \left( \frac{1}{V_{B,2}} \right) - \delta(V_{B,2}) \left( \frac{m_2}{V_{B,2}^2} \right) \right] \end{aligned} \quad (25)$$

Now the numerical values for the uncertainties are considered. The flow meters can be read within an accuracy of  $\pm 2.5$  std.  $\text{cm}^3/\text{min}$  for air flow and  $\pm 0.5$  std.  $\text{cm}^3/\text{min}$  for the pyrolysates. The flow meter inlet gas temperatures are known within  $\pm 1$  C. The oven temperature used in molecular weight determination is known to within  $\pm 1$  C. The local barometric pressure can be read to  $\pm 0.01$  inches Hg. The

Mettler balance is accurate to  $\pm 2 \times 10^{-5}$  grams. The volume of the balloons are known to  $\pm 5 \times 10^{-4}$  liters. This information on the uncertainties can be summarized as

1.  $\delta(\dot{V}_{c,a}) \approx 5 \text{ std. cm}^3/\text{min},$
2.  $\delta(\dot{V}_{c,p}) \approx 1 \text{ std. cm}^3/\text{min},$
3.  $\delta(T_{t,p}) = \delta(T_{t,a}) \approx 2 \text{ C},$
4.  $\delta(T_o) \approx 2 \text{ C},$
5.  $\delta(P_t) \approx 0.02 \text{ inches Hg},$
6.  $\delta(m_1) = \delta(m_2) \approx 4 \times 10^{-5} \text{ grams, and}$
7.  $\delta(V_{B,1}) = \delta(V_{B,2}) \approx 10^{-3} \text{ liters.}$

Due to the problem of the floats sometimes sticking to the wall of the pyrolysate flow meter, two values of  $\dot{V}_{c,p}$  can be obtained. For test number 118 (GIRCFB Fabric No. 17) these two flow rates are 16.2 and 20.4 std.  $\text{cm}^3/\text{min}$  for the glass and stainless steel floats, respectively. The 20.4 std.  $\text{cm}^3/\text{min}$  reading will be used in the following calculations because the stainless steel float is the least likely to stick. For test number 118, the data is

$$m_1 = 0.23513 \text{ grams}$$

$$m_2 = 0.22802 \text{ grams}$$

$$V_{B,1} = 0.2048 \text{ liters}$$

$$V_{B,2} = 0.1986 \text{ liters}$$

$$M_{p,av} = 37.31 \text{ grams/mole}$$

$$P_{B,1} = P_{B,2} = 29.021 \text{ inches Hg} = 0.97 \text{ atm}$$

$$P_t = 29.017 \text{ inches Hg} = 0.97 \text{ atm}$$

$$\dot{V}_{c,a} = 89.2 \text{ std. cm}^3/\text{min}$$

$$\dot{V}_{c,p} = 20.44 \text{ std. cm}^3/\text{min}$$

$$T_{t,a} = 32.8 \text{ C} = 305.9 \text{ K}$$

$$T_{t,p} = 88.8 \text{ C} = 362.0 \text{ K}$$

$$T_o = 111 \text{ C} = 384.2 \text{ K}$$

Substitution of these values into the partially differentiated mass fraction equation yields

$$\delta(\alpha) = 0.0311$$

$$\delta(M_{p,av}) = -0.0099 \text{ grams/mole}$$

$$\delta(\beta) = -0.0004$$

Calculating  $\alpha$  and  $\beta$  yields

$$\alpha = 4.364$$

$$\beta = 0.963$$

Substituting these values into equation (20) yields the uncertainty of the pyrolysate mass fraction

$$\delta(Y_p) = 0.001$$

For the uncertainty of the ignition temperature of the chromel-alumel thermocouple, the minimum ignition temperature is specified as

$$T_{ig} = 797 \pm 1 \text{ C}$$



## APPENDIX B

## DATA REDUCTION SAMPLE CALCULATIONS

This section gives sample calculations for the determination of molecular weight, mass fractions of pyrolysis gases, and minimum ignition temperature. The following calculations were performed on test data taken from experiment number 118 on GIRCFF fabric number 17. A sample data sheet containing the data for test 118 is shown in Table B.1.

Molecular Weight Determination

## Experimental Data:

1. Gross weight of balloon #1: 85.17171 grams
2. Tare weight of balloon #1: 84.93658 grams
3. Gross weight of balloon #2: 77.05576 grams
4. Tare weight of balloon #2: 76.82774 grams
5. Local barometric pressure: 29.021 inches Hg
6. Oven temperature: 111 C

The volumes of the balloons were previously determined to be 0.2048 and 0.1986 liters for balloons number 1 and 2, respectively.

The molecular weight is calculated by using equation (3):

$$M_{p,1} = \frac{m_1 R T_o}{P_{B,1} V_{B,1}} \quad (3)$$

## Table B.1. Sample Data Sheet

## Pyrolysate Minimum Ignition Temperature Data Sheet

- L I T A C A -

Date: 11/9/1975

## Molecular Weight Measurement:

(Pressure Reading: 29.125" Hg at 68°F)

(Pressure Correction Factor: 0.104" Hg)

1. Corrected Barometric Pressure: 29.021" Hg

2. Oven Temperature: 111°C

3. Gross Weight of Balloon #1: 85.17171 g

4. Tare Weight of Balloon #1: 84.93658 g

5. Gross Weight of Balloon #2: 77.05576 g

6. Tare Weight of Balloon #2: 76.82774 g

## Minimum Ignition Temperature Determination:

(Pressure Reading: 29.120" Hg at 68°F)

(Pressure Correction Factor: 0.104" Hg)

7	8	9	10	11	12	13	14	15
Exp #	Pressure ("Hg)	Fuel Scale Rdg (mm)	Float Desig. *	Fuel Temp (IC-mV)	Dry Air Scale Rdg(%)	Float Desig. *	Dry Air Temp (IC-mV)	Ign. Temp (CA-mV)
117	29.016	29 54	2 1	4.66	50	1	1.71	34.496
118	29.017	31.5 58	2 1	4.66	40	1	1.68	33.152
119	29.019	33 61	2 1	4.68	30	1	1.69	33.860
120	29.020	34 61	2 1	4.70	20	1	1.70	33.584
121	29.021	31 58	2 1	4.65	10	1	1.84	32.056

\* 1: glass; 2: stainless steel

Substitution of values yields:

$$M_{p,1} = \frac{(85.17171 - 84.93658)(0.08205)(111 + 273.16)}{\left(\frac{29.021}{29.92}\right)(0.2048)}$$

$$= 37.31 \text{ g/mole}$$

Similarly,

$$M_{p,2} = \frac{(77.05576 - 76.82774)(0.08205)(111 + 273.16)}{\left(\frac{29.021}{29.92}\right)(0.1986)}$$

$$= 37.31 \text{ g/mole}$$

$$M_{p,av} = \frac{M_{p,1} + M_{p,2}}{2} = 37.31 \text{ g/mole}$$

#### Pyrolystate Mass Fraction Determination

Experimental Data:

1. Local barometric pressure: 29.017 inches Hg
2. Fuel scale reading: 31.5 mm (stainless steel float) and 58 mm (glass float)
3. Iron-constantan thermocouple emf at entrance of pyrolystate flow meter: 4.66 mV
4. Dry air scale reading: 40% (glass float)
5. Iron-constantan thermocouple emf at entrance of dry air flow meter: 1.68 mV

6. Mean molecular weight: 37.31 g/mole

Linear interpolation from the calibration table of the dry air flow meter yields the calibrated flow rate of 89.2 std. cm<sup>3</sup>/min. From the equation obtained from the recalibration of the pyrolysis flow tube, the calibrated flow rate obtained was 20.4 std. cm<sup>3</sup>/min for the stainless steel ball and 16.2 std. cm<sup>3</sup>/min for the glass ball. A mean value of 18.3 std. cm<sup>3</sup>/min is used.

By interpolation using tabular data supplied by Omega Engineering, Inc., the pyrolysis inlet temperature is 326.0 K and the dry air inlet temperature is 305.9 K.

The mass fraction of pyrolysis gases is now calculated by using equation (16)

$$Y_p = \left\{ 1 + \frac{2(89.2)}{(0.08205)(18.3)} \left( \frac{\frac{29.017}{29.92}}{\frac{0.23513}{0.2048} + \frac{0.22802}{0.1986}} \right) \right\}$$

$$\left[ \frac{(28.97)(37.31)}{(305.9)(326.0)} \right]^{1/2} = 0.168$$

Hence there is 0.168 grams of pyrolysis per gram of mixture present.

#### Minimum Ignition Temperature Determination

The temperature at which ignition first occurs is obtained by converting the temperature sensing thermocouple's emf into degrees. From the Omega Engineering tables used above, the temperature corresponding to 33.152 mV is 797.0 C.



## APPENDIX C

SUMMARY OF MINIMUM IGNITION TEMPERATURE AND MASS FRACTION  
DATA FOR PROPANE-AIR AND PYROLYSATE-AIR MIXTURES

Listed in Tables C.1 through C.5 is the reduced data obtained from the minimum ignition temperature tests for:

1. Propane,
2. GIRCFF Fabric Number 4,
3. GIRCFF Fabric Number 15,
4. GIRCFF Fabric Number 17, and
5. Wood Chips (fir).

All the data is reduced using a mean molecular weight for the gases being tested.

Table C.1. Summary of Minimum Ignition Temperature and Mass Fraction Data for Commercial Propane

PROPANE MINIMUM IGNITION TEMPERATURES--LITACA

Date: 5/21/1975

Fuel: Propane

Exp. No.	M,1 g/mole	M,2 g/mole	M,av g/mole	V,f cc/s	$\dot{m},f$ g/h	V,a cc/s	$\dot{m},a$ g/h	Y,f g/g	T,ig °C
2	44.00	44.00	44.00	.340	1.739	1.11	4.72	.268	583.3
3	44.00	44.00	44.00	.126	.655	2.79	11.72	.052	598.1
4	44.00	44.00	44.00	.126	.655	2.37	9.96	.061	618.7
5	44.00	44.00	44.00	.133	.688	3.41	14.28	.045	656.3
6	44.00	44.00	44.00	.126	.656	2.56	10.71	.057	650.8
7	44.00	44.00	44.00	.127	.658	4.28	17.78	.035	707.5
8	44.00	44.00	44.00	.133	.690	2.08	8.67	.073	638.4
9	44.00	44.00	44.00	.126	.653	4.85	20.48	.030	705.1
11	44.00	44.00	44.00	.127	.659	1.78	7.40	.081	648.2
20	44.00	44.00	44.00	.239	1.239	2.23	9.38	.116	516.1

Table C.1. (continued)

Date: 6/25/1975

Fuel: Propane

Exp. No.	M,1 g/mole	M,2 g/mole	M,av g/mole	V,f cc/s	$\dot{m},f$ g/h	V,a cc/s	$\dot{m},a$ g/h	Y,f g/g	T,ig °C
21	44.00	44.00	44.00	.231	1.198	2.64	11.09	.097	532.5
22	44.00	44.00	44.00	.235	1.219	3.07	12.86	.086	478.2
23	44.00	44.00	44.00	.231	1.198	1.85	7.76	.133	532.5
25	44.00	44.00	44.00	.230	1.194	1.17	4.97	.193	536.0
100	44.00	44.00	44.00	.051	.265	2.65	11.05	.023	650.3
101	44.00	44.00	44.00	.050	.262	2.65	11.05	.023	626.5
102	44.00	44.00	44.00	.052	.273	1.86	7.71	.034	631.3
103	44.00	44.00	44.00	.050	.262	3.52	14.57	.017	664.6
104	44.00	44.00	44.00	.048	.252	4.73	20.02	.012	724.1
105	44.00	44.00	44.00	.044	.229	6.36	26.87	.008	709.8

Table C.1. (concluded)

Date: 11/20/1975

Fuel: Propane

Exp. No.	M,1 g/mole	M,2 g/mole	M,av g/mole	V,f cc/s	$\dot{m},f$ g/h	V,a cc/s	$\dot{m},a$ g/h	Y,f g/g	T,ig °C
107	44.00	44.00	44.00	.060	.312	1.12	4.71	.062	605.2
145	44.00	44.00	44.00	.068	.354	2.25	9.29	.036	653.7
146	44.00	44.00	44.00	.130	.677	6.44	26.52	.024	769.8
147	44.00	44.00	44.00	.312	1.614	3.09	12.74	.112	566.0
148	44.00	44.00	44.00	.269	1.396	1.51	6.23	.183	605.1
150	44.00	44.00	44.00	.269	1.395	3.95	16.35	.078	521.5
151	44.00	44.00	44.00	.261	1.351	5.19	21.49	.059	549.6
152	44.00	44.00	44.00	.267	1.383	2.25	9.30	.129	562.7
153	44.00	44.00	44.00	.269	1.396	1.86	7.70	.153	559.9
154	44.00	44.00	44.00	.261	1.353	3.09	12.76	.095	513.1



Table C.2. Summary of Minimum Ignition Temperature and Pyrolysis Mass Fraction Data for GIRCEFF Fabric No. 4, 100% Cotton

PYROLYSATE MINIMUM IGNITION TEMPERATURES--LITACA

Date: 11/11/1975

Fuel: Pyrolysis Fabric No. 4

Exp. No.	M,1 g/mole	M,2 g/mole	M,av g/mole	V,f cc/s	$\dot{m},f$ g/h	V,a cc/s	$\dot{m},a$ g/h	Y,f g/g	T,ig °C
126	36.04	36.04	36.04	.370	1.568	3.99	16.18	.088	-----*
	36.04	36.04	36.04	.321	1.360	3.99	16.18	.077	-----*
127	36.04	36.04	36.04	.362	1.536	2.90	11.75	.115	793.2
	36.04	36.04	36.04	.297	1.261	2.90	11.75	.096	793.2
129	36.04	36.04	36.04	.328	1.391	2.90	11.75	.105	736.3
	36.04	36.04	36.04	.275	1.166	2.90	11.75	.090	736.3
130	36.04	36.04	36.04	.348	1.477	2.26	9.25	.137	725.3
	36.04	36.04	36.04	.325	1.381	2.26	9.25	.129	725.3
131	36.04	36.04	36.04	.334	1.417	1.55	6.33	.182	744.8
	36.04	36.04	36.04	.270	1.417	1.55	6.33	.153	744.8

\* No ignition was obtained

Table C.2. (concluded)

Date: 11/11/1975

Fuel: Pyrolysate Fabric No. 4

Exp. No.	M,1 g/mole	M,2 g/mole	M,av g/mole	V,f cc/s	$\dot{m},f$ g/h	V,a cc/s	$\dot{m},a$ g/h	Y,f g/g	T,ig °C
132	36.04	36.04	36.04	.355	1.504	.99	4.06	.269	730.8
	36.04	36.04	36.04	.300	1.272	.99	4.06	.238	730.8
133	36.04	36.04	36.04	.365	1.548	.48	1.95	.441	744.3
	36.04	36.04	36.04	.300	1.271	.48	1.95	.393	744.3
134	36.04	36.04	36.04	.387	1.643	.21	.87	.652	743.4
	36.04	36.04	36.04	.321	1.362	.21	.87	.608	743.4
135	36.04	36.04	36.04	.721	3.059	.94	3.85	.442	724.4
	36.04	36.04	36.04	.597	2.533	.94	3.85	.396	724.4

Table C.3. Summary of Minimum Ignition Temperature and Pyrolysate Mass Fraction  
Data for GIRCFF Fabric No. 15, 65/35% Polyester/Rayon

PYROLYSATE MINIMUM IGNITION TEMPERATURES--LITACA

Date: 11/6/1975

Fuel: Pyrolysate Fabric No. 15

Exp. No.	M,1 g/mole	M,2 g/mole	M,av g/mole	V,f cc/s	$\dot{m}$ ,f g/h	V,a cc/s	$\dot{m}$ ,a g/h	Y,f g/g	T <sub>ig</sub> °C
110	40.44	40.43	40.43	.266	1.265	.48	1.94	.393	832.4
	40.44	40.43	40.43	.239	1.137	.48	1.94	.368	832.4
111	40.44	40.43	40.43	.331	1.574	1.52	6.16	.203	794.5
	40.44	40.43	40.43	.270	1.286	1.52	6.16	.172	794.5
112	40.44	40.43	40.43	.232	1.106	3.12	12.62	.080	842.0
	40.44	40.43	40.43	.210	.999	3.12	12.62	.073	842.0
113	40.44	40.43	40.43	.404	1.921	2.28	9.20	.172	796.1
	40.44	40.43	40.43	.368	1.754	2.28	9.20	.160	796.1
114	40.44	40.43	40.43	.208	.992	2.28	9.20	.097	842.2
	40.44	40.43	40.43	.194	.923	2.28	9.20	.091	842.2
115	40.44	40.43	40.43	.415	1.973	.59	2.41	.449	768.6
	40.44	40.43	40.43	.357	1.701	.59	2.41	.413	768.6
116	40.44	40.43	40.43	.302	1.438	.92	3.73	.278	798.5
	40.44	40.43	40.43	.261	1.243	.92	3.73	.249	798.5

Table C.4. Summary of Minimum Ignition Temperature and Pyrolysate Mass Fraction Data for GIRCFF Fabric No. 17, 65/35% Polyester/Cotton

PYROLYSATE MINIMUM IGNITION TEMPERATURES--LITACA

Date: 11/9/1975

Fuel: Pyrolysate Fabric No. 17

Exp. No.	M,1 g/mole	M,2 g/mole	M,av g/mole	V,f cc/s	$\dot{m}_f$ g/h	V,a cc/s	$\dot{m}_a$ g/h	Y,f g/g	T,ig °C
117	37.30	37.31	37.30	.312	1.372	2.28	9.18	.129	831.5
	37.30	37.31	37.30	.250	1.099	2.28	9.18	.106	831.5
118	37.30	37.31	37.30	.337	1.482	1.52	6.15	.193	796.9
	37.30	37.31	37.30	.269	1.181	1.52	6.15	.160	796.9
119	37.30	37.31	37.30	.353	1.551	.92	3.72	.294	814.8
	37.30	37.31	37.30	.284	1.246	.92	3.72	.250	814.8
120	37.30	37.31	37.30	.364	1.598	.48	1.94	.450	807.8
	37.30	37.31	37.30	.284	1.246	.48	1.94	.390	807.8
121	37.30	37.31	37.30	.332	1.459	.19	.78	.651	770.2
	37.30	37.31	37.30	.269	1.181	.19	.78	.602	770.2



Table C.4. (concluded)

Date: 11/9/1975

Fuel: Pyrolysate Fabric No. 17

Exp. No.	M,1 g/mole	M,2 g/mole	M,av g/mole	V,f cc/s	$\dot{m},f$ g/h	V,a cc/s	$\dot{m},a$ g/h	Y,f g/g	T,ig °C
122	37.30	37.31	37.30	.442	1.940	.19	.78	.712	768.2
	37.30	37.31	37.30	.375	1.646	.19	.78	.677	768.2
123	37.30	37.31	37.30	.607	2.664	.19	.78	.772	-----*
	37.30	37.31	37.30	.510	2.238	.19	.78	.740	-----*
124	37.30	37.31	37.30	.455	1.999	.19	.78	.719	745.5
	37.30	37.31	37.30	.365	1.602	.19	.78	.672	745.5
125	37.30	37.31	37.30	.323	1.419	3.15	12.53	.101	-----*
	37.30	37.31	37.30	.251	1.102	3.15	12.53	.080	-----*

\* No ignition was obtained

Table C.5. Summary of Minimum Ignition Temperature and Pyrolysisate Mass Fraction Data for Wood Chips (Fir)

PYROLYSATE MINIMUM IGNITION TEMPERATURES--LITACA

Date: 11/19/1975

Fuel: Wood Chips (fir)

Exp. No.	M,1 g/mole	M,2 g/mole	M,av g/mole	V,f cc/s	$\dot{m},f$ g/h	V,a cc/s	$\dot{m},a$ g/h	Y,f g/g	T <sub>ig</sub> °C
139	35.50	36.67	36.08	.302	1.217	1.00	4.03	.231	747.4
	35.50	36.67	36.08	.210	.848	1.00	4.03	.173	747.4
140	35.50	36.67	36.08	.331	1.337	2.04	8.21	.139	740.7
	35.50	36.67	36.08	.236	.952	2.04	8.21	.103	740.7
141	35.50	36.67	36.08	.331	1.337	2.96	11.87	.101	753.5
	35.50	36.67	36.08	.245	.988	2.96	11.87	.076	753.5
142	35.50	36.67	36.08	.331	1.337	3.75	15.05	.081	761.9
	35.50	36.67	36.08	.245	.988	3.75	15.05	.061	761.9
143	35.50	36.67	36.08	.362	1.463	.73	2.93	.333	734.0
	35.50	36.67	36.08	.259	1.044	.73	2.93	.262	734.0
144	35.50	36.67	36.08	.322	1.299	.44	1.79	.419	745.2
	35.50	36.67	36.08	.245	.990	.44	1.79	.355	745.2

## APPENDIX D

## CALIBRATION OF BROOKS R-2-15-AAA FLOW TUBE

The Brooks R-2-15-AAA flow meter, used for determining volumetric flow rates of the pyrolysate gases, gave erroneous readings when used in conjunction with the supplied calibration curves. For the same flow rates, the glass and stainless steel floats yielded different results. The method used for recalibration will now be described.

A supply of dry air was connected to the entrance of the flow tube and a 50 ml graduated pipette was connected in series with the flow tube exit by a glass "t". The end of the pipette was opened to the atmosphere. A soap-water solution was supplied at the other stem of the "t" junction. Several bubbles are initially produced by allowing the solution level to rise, thereby coating the inner tube wall with a thin soap film. This permits all future bubbles to propagate the length of the tube without bursting. The tube was then cleared by passing air through it. A single bubble enters the graduated calibration pipette, and the time necessary for it to traverse a given distance was recorded. This distance corresponds to a volume on the graduated pipette. By dividing this volume by the time, the flow rate is found in  $\text{cm}^3/\text{min}$  for the corresponding flow meter readings.

Corrections were made to convert these readings to standard condition flow rates (std. cm<sup>3</sup>/min). It was assumed that the pressure drop across the bubble's surface is negligible. Two expressions relating the standard condition flow rates to the flow meter readings were obtained for the glass and stainless steel floats. The least squares method of curve fitting was used. These expressions are, for the glass float:

$$\text{Std. cm}^3/\text{min of Air} = 3.424 + 0.146 b + 1.326 \times 10^{-3} b^2$$

where b is the flow meter reading in mm. For the stainless steel float:

$$\text{Std. cm}^3/\text{min of Air} = 4.781 + 0.399 b + 3.724 \times 10^{-3} b^2$$



## BIBLIOGRAPHY

1. Wulff, W. and Durbetaki, P., "Fabric Ignition and the Burn Injury Hazard," Heat Transfer in Flames, N. H. Afgan and J. M. Beer, Editors, Scripta Book Co., Washington, D. C., (1974) pp. 451-461.
2. "America Burning," The National Commission on Fire Prevention and Control, U. S. Government Printing Office, Washington, D. C., Stock Number 5200-00004, May, 1973.
3. Alkidas, A., Champion, E. R., Giddens, W. E., Hess, R. W., Kumar, B., Nevada, O. A. A., Durbetaki, P., Williams, P. T., and Wulff, W., "Study of Hazards from Burning Apparel and the Relation of Hazards to Test Methods," Second Final Report, NSF Grant GI-31882, School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, December, 1972, National Technical Information Service Document Number PB-242-597/AS.
4. "Study of Hazards from Burning Apparel and the Relation of Hazards to Test Methods," Government-Industry Research Committee on Fabric Flammability, A statement prepared by the Research Committee, Dr. E. Passaglia, Chairman, National Bureau of Standards, June 5, 1970.
5. "The Flammable Fabrics Program," NBS Technical Note 596, Washington, D. C., 1970.
6. "The Flammable Fabrics Program," NBS Technical Note 749, Washington, D. C., 1971.
7. Chumas, S. J., "Tabulation of Voluntary National Standards, Industry Standards, International Recommendations and Certification Programs for Consumer Products," NBS Technical Note 705, Washington, D. C., 1971.
8. Chumas, S. J., "Tabulation of Voluntary Standards and Certification Programs for Consumer Products," NBS Technical Note 762, Washington, D. C., 1973.
9. Tribus, M., "Decision Analysis Approach to Satisfying the Requirements of the Flammable Fabrics Act," Paper presented at the Textile and Needle Trades Division, American Society of Quality Control, Greensboro, N. C., February 12, 1970.

10. Annamalai, K., Durbetaki, P., Matson, G. L., "Prediction of Fire Hazard in Buildings," Semiannual Progress Report No. 2, School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, March 31, 1975.
11. Alkidas, A., Hess, R. W., Kirkpatrick, C. S., Kirkpatrick, M. J., Bergles, A. E., Wulff, W., and Zuber, N., "Study of Hazards from Burning Apparel and the Relation of Hazards to Test Methods," Progress Report No. 1, School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, April 1, 1975.
12. Evans, R. B., Wulff, W., and Zuber, N., "The Study of Hazards from Burning Apparel and the Relation of Hazards to Test Methods," Research Proposal, School of Mechanical Engineering, Georgia Institute of Technology, Submitted to the Government-Industry Research Committee on Fabric Flammability, 1970.
13. Durbetaki, P. and Wulff, W., "The Study of Hazards from Burning Apparel and the Relation of Hazards to Test Methods," Research Proposal submitted to the National Science Foundation by the School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, September, 1972.
14. Durbetaki, P., Wulff, W. et al., "Fabric Ignition," Third Annual Report, NSF (RANN) Grant No. GI-31882, School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, 1974, National Technical Information Service Document No. PB-242-740/AS.
15. Wulff, W., Private Communication, 1975.
16. Holmer, F. R. and Shaw, C. J. G., Journal of Applied Chemistry, Vol. 11, 1962, p. 210.
17. Tang, M. M. and Bacon, Roger, "Carbonization of Cellulose Fibers--I Low Temperature Pyrolysis," Journal of Carbon, Vol. 2, 1964, pp. 211-220.
18. Madorsky, S. L., Hart, V. E. and Strauss, S., Res. Nat. Bur. Standards, Vol. 56, 1956, p. 343; Vol. 60, 1958, p. 343.
19. Major, W. D. TAPPI, Vol. 41, 1958, p. 530.
20. Parker, W. J. and Lipska, A. E., "A Proposed Model for the Decomposition of Cellulose of the Effect of Flame Retardants," TR-69, U. S. Naval Radiological Defense Laboratory, San Francisco, California, 1969.



21. Williams, P. T., "Ignition Temperatures of Pyrolysate-Air Mixtures," M. S. Thesis, School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, October, 1974.
22. Scott, G. S., Jones, G. W. and Scott, F. E., "Determination of Ignition Temperatures of Combustible Liquids and Gases," Anal. Chem., Vol. 20, 1948, p. 238.
23. Jones, G. W. and Scott, F. E., "Estimation of Propane and Butane Flames by Dichlorodifluoromethane," Bureau of Mines Report of Investigations 3908, 1946, p. 8.
24. Coward, H. F. and Jones, G. W., "Limits of Flammability of Gases and Vapors," U. S. Bureau of Mines Bulletin 503, 1952.
25. Belles, Frank E. and Swett, Clyde C., "Basic Considerations in the Combustion of Hydrocarbon Fuels with Air--Chapter III Ignition and Flammability of Hydrocarbon Fuels," NACA Report 1300, 1959, p. 83.
26. Alger, Raymond, "Pyrolysis and Combustion of Cellulosic Materials," National Bureau of Standards, Washington, D. C., Inst. for Materials Research, NBS SP 357, June, 1972, pp. 171-178.
27. Colburn, Robert E., Fire Protection and Suspension, McGraw Hill Book Company, New York, 1975.