IGNITION TEMPERATURES OF PYROLYSATE-AIR MIXTURES

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

By

Paul Thomas Williams

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Mechanical Engineering

Georgia Institute of Technology

October, 1974

IGNITION TEMPERATURES OF PYROLYSATE-AIR MIXTURES

Approved:

P. Durbetaki, Chairman

R. B. Evans

W. C. Tincher

Date approved by Chairman: 10/28/1974

ACKNOWLEDGMENTS

The author would like to thank Dr. Wolfgang Wulff for suggesting this thesis topic and, along with Dr. Pandeli Durbetaki, contributing a great amount of advice and assistance throughout this research effort. The author also appreciates the many constructive suggestions made by the other members of his reading committee, Drs. Robert B. Evans and Wayne C. Tincher, during the completion of this thesis.

The author would like to thank Mr. Don Lillie, the glassblower in the School of Chemistry at Georgia Tech, for his skill and patience in the construction of the ignition tube. The efforts and assistance of the technical staff of the School of Mechanical Engineering are greatly appreciated.

The original design of the Pyrolysate Generating Furnace was done by Mr. James Brazell, instructor in the School of Mechanical Engineering, and his contribution is also greatly appreciated.

The author would like to thank the National Science Foundation for funding this research under NSF Grant No. GI-31882A#1.

This thesis is dedicated to the author's family in gratitude for their continual support and encouragement.

TABLE OF CONTENTS

Chapter Page

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

A	cross sectional flow area cm^2
B	dimensionless modulus equation (13)
G	volumetric flowrate $cm^3 min^{-1}$
M	molecular weight g $g\text{-}mole^{-1}$
$\dot{m}$	mass flowrate g s^{-1}
m	mass g
P	pressure atm
R_u	universal gas constant liter atm $g\text{-}mole^{-1}K^{-1}$
T	temperature K
V	volume cm^3
v	velocity cm s^{-1}
ρ	density g cm^3
$\emptyset$	dimensionless modulus equation (12)
χ_ρ	mass fraction of the pyrolysate
τ	time s

Subscripts

a	dry air
b	at test conditions
c	at calibration conditions
d	without condensibles present
f	flowmeter float
bal	glass balloon
p	pyrolysate

w	with condensibles present in pyrolysate
1	position at entrance of flowmeter tube
2	position at the float inside flowmeter
ig	ignition

SUMMARY

This work is part of a research program on fabric flammability being carried out at the School of Mechanical Engineering, Georgia Institute of Technology. This research is an outgrowth of the Flammable Fabrics Act of 1953 as amended in 1967 and is funded by the National Science Foundation.

The fire hazard of a system such as a garment is expressed in terms of its burn-injury probability which is a function of pertinent subsidiary probabilities, one of which is the probability of ignition after given exposure. The ignition probability depends on the ratio of exposure time over mean ignition time. The prediction of ignition time requires a universally valid ignition criterion.

A new ignition criterion has been proposed [9] which requires the measurement of the lowest ignition temperatures of pyrolysate-air mixtures, as a function of pyrolysate mass fractions.

This work is concerned with the design, construction, and use of an apparatus which has been designed to:

(a) thermally decompose pyrolyzing materials,

(b) store the pyrolysates,

(c) mix pyrolysates with dry air at controlled mass fractions, and

(d) measure the minimum mixture temperature at which self-ignition occurs.

Tests were run with propane and three different cotton fabrics. The results of these tests are presented in terms of ignition temperature as a function of mass fraction. The average molecular weights of the pyrolysates were also measured.

This work was supported by a National Science Foundation Grant No. GI-31882A#1 under the RANN Program.

CHAPTER I

INTRODUCTION

Relevance of Flammability Research

The United States leads all the major industrialized countries in the world in per capita deaths and property loss from fire with a deaths-per-million-population rate nearly twice that of second-ranking Canada (57.1 versus 29.7). Nearly 12,000 lives are lost and 300,000 Americans are injured annually due to fire. The economic cost of destructive fire has been estimated to be 11.4 billion dollars per year which includes property loss, fire department operations, burn injury treatment, operating cost of the insurance industry, and productivity loss [1].* A major portion of these deaths and injuries are related to clothing and fabric fires. The U. S. Department of Health, Education, and Welfare (HEW) estimates [2] "that there are annually 3,000 to 5,000 deaths and 15,000 to 250,000 injuries from burns associated with flammable fabrics and that the directly related financial loss exceeds a quarter billion dollars."

There are two avenues of approach in attacking this

---

*Numbers in brackets refer to the Bibliography.

very serious problem of destructive fire hazard: (1) educational campaigns for the public with the goals of recognizing and preventing potential fire hazards, and (2) the setting of standards for materials which have the potential of being involved in destructive fires. These standards should be rational and reasonable and based on a scientific foundation laid down through basic research. The congress has responded to this need for reasonable standards by amending, in 1967, the Flammable Fabrics Act of 1953. The amended Act demands of the Secretary of Commerce [3] "to conduct research on the flammability of products, fabrics and materials, conduct feasibility studies on reduction of flammability, develop flammability test methods and offer appropriate training in the use of flammability test methods." The National Bureau of Standards was given the above responsibilities, and, with the cooperation of the United States textile industry, it established the Government-Industry Research Committee on Fabric Flammability (GIRCFF) whose responsibility was to formulate and administer research programs in the area of fabric flammability with joint funding from textile trade associations and the National Science Foundation under the RANN program (Research Applied to National Needs). GIRCFF monitored the work for the first two years starting with November, 1970. The School of Mechanical Engineering at the Georgia Institute of Technology was one of the participants in this research

effort along with the Massachusetts Institute of Technology, The Factory Mutual Research Corporation, and The Gillette Company Research Institute. The work carried out in the Fire Hazard and Combustion Research Laboratories of the School of Mechanical Engineering at Georgia Tech was funded during the first year (1971) under NSF grant No. GK-27189, and during the following two years under NSF grants No. GI-31882 (1972) and GI-31882A#1 (1973). The research project is presently in its fourth year and is now involved in studying the fire hazard of building materials.

Previous Efforts and Accomplishments

The Government-Industry Research Committee has stated [4] that the central problem of fabric flammability studies is the "determination of the relationship between fabric behavior in a test method, on the one hand, and the hazard that the fabric presents in actual use, on the other." Tribus [5] was first to propose that the above relationship could be formulated in terms of the burn injury probability as derived from a decision tree and associated subprobabilities. Two of these subprobabilities were singled out by the Government-Industry Research Committee as being of particular importance, the probability of ignition given exposure, P(I/E), and the probability of burn injury given ignition, P(B/I). Evans, Wulff and Zuber [6] showed how modeling analysis and experiments can be used to obtain

these two probabilities.

The probability of fabric ignition for a given exposure, P(I/E), is related to the ratio of the time the fabric is exposed to a given ignition source, or its exposure time τ_e, over the time it takes the fabric to ignite under the given exposure conditions, the ignition time τ_i [7].

$$P(I/E) = f(\tau_e/\tau_i)$$

Wulff, et al., states that [8]:

> While the exposure time τ_e depends on human response and reaction the ignition time τ_i depends on (1) physical fabric properties; (2) process parameters describing the interactions between fabric, heating source and environment, and (3) fundamental physicochemical processes such as heat and mass - transfer and chemical reactions.

The School of Mechanical Engineering at the Georgia Institute of Technology has been carrying on a combined analytical and experimental program in fabric flammability research, and one of their goals has been to develop an analytical model which will predict the mean ignition time under given exposure conditions. In pursuit of that goal, Wulff has proposed [9] a new ignition criterion for pyrolyzing solids, which is predicated on the assumption that ignition occurs in a boundary layer at the pyrolyzing solid. In this boundary layer the combustible volatiles, or pyrolysates,

generated by the thermal decomposition of the solid fuel, mix with oxygen from the air and the thermal reaction between oxygen and pyrolysates accelerates itself. It has also been postulated that this thermal excursion begins when, locally, a concentration-dependent minimum ignition temperature $T_{ig}(\chi_\rho)$ is reached, where T_{ig} is the minimum ignition temperature of the pyrolysate at a particular mass fraction of pyrolysate χ_ρ. Wulff has stated that [10]:

> There are two possibilities by which the system can reach ignition conditions, depending on the type of external heating imposed on the system: During convective heating the gas mixture temperature is for all $\tau>0$ time after exposure large enough, at least at the outer edge of the boundary layer (or else ignition is impossible) and the pyrolysate concentration at the solid surface must reach a minimum value. On the other hand, during radiative heating the pyrolysate concentration at the surface increases from zero to one, requiring at first infinitely large, then decreasing and finally again increasingly large solid surface temperatures. This follows from the concave shape of the curve representing $T_{ig}(\chi_\rho)$. Therefore, ignition by radiative heating occurs when the surface temperature reaches a minimum value.

The above ignition criterion takes into account the heating history, degree of decomposition and air flow dynamics near the heated surface. The key to the successful application of this new ignition criterion is the experimental determination of the $T_{ig}(\chi_\rho)$ curve for the pyrolysates that are generated by the thermally decomposing solid fuel.

In summary, it has been shown that the burn injury hazard can be measured by the burn injury probability. The burn injury probability depends on the ignition probability

P(I/E) and other probabilities. In order to predict the ignition probability, one needs to predict ignition time through modeling analysis, in terms of material properties and process parameters. Any successful modeling analysis of ignition requires an ignition criterion. The ignition criterion newly proposed by Wulff [10] is based on the minimum ignition temperatures measured on pyrolysate-air mixtures as a function of pyrolysate concentration. The thesis presented here deals with such measurements.

Purpose and Statement of Problem

The purpose of this thesis is to develop experimental techniques to measure minimum ignition temperatures of pyrolysate-air mixtures at controlled pyrolysate concentrations. This enables one to describe through an ignition analysis the preignition history of a pyrolyzing solid fuel in terms of the processes of (i) material heating, (ii) thermal decomposition, and (iii) external fluid dynamics (dynamics of mixing), and, finally, to predict the instant of ignition.

Towards this end, an apparatus has been designed, constructed and assembled which:

(i) thermally decomposes pyrolyzing materials,

(ii) stores the pyrolysates,

(iii) mixes pyrolysates with dry air at controlled mass fractions, and

(iv) measures in an isothermal environment the minimum mixture temperature at which self-ignition occurs.

The result is an empirically determined curve of ignition temperature versus pyrolysate mass fraction, $T_{ig}(\chi_p)$.

Literature Survey

This literature survey is concerned with the measurement of minimum ignition temperatures of combustible gases and their flammability limits. Definitions and methods of determination will be discussed.

Ignition and Ignition Temperature

Setchkin has defined [11] ignition to be "a self-perpetuating exothermic reaction that is initiated at the temperature of incipient oxidation, and that increases the temperature of the reactants above their initial temperature until an explosion, flame, or sustained glow occurs." One of the key words in this definition is "self-perpetuating," because, if a reaction is to be considered an ignition process, it must be capable of propagating a flame. This is important, because flame propagation is a requisite in both the definitions of ignition temperature and a flammable mixture.

The ignition temperature has been defined by Belles and Swett [12] to be the lowest temperature at which the heat lost from the flammable mixture is balanced by the heat

generated by chemical reaction. The rate of chemical reaction increases at the ignition temperature, and as a result, the temperature is increased to the flame temperature. A flammable mixture is one which is capable of propagating a flame indefinitely away from, and in the absence of, a source of ignition. When it is desired to determine ignition temperatures, it becomes necessary to use various types of apparatus which in themselves do not give the true temperature of the gas but rather a temperature of part of the apparatus. Sortman has cautioned [13] that:

> The so-called spontaneous-ignition temperature of a combustible liquid is not a definite property but varies according to the method of test. However, the application of one suitable test method to different combustibles will give comparative results which may be of considerable significance.

There are four important methods for determining surface ignition temperatures of fuels. They are:

(1) crucible methods, static and dynamic,

(2) heated surfaces of various geometries,

(3) adiabatic compression method, and

(4) bomb method.

The crucible method, which has been critically evaluated and refined by Setchkin [14], is used most widely to obtain ignition temperatures of liquid fuels. A drop of fuel is introduced into a heated container which is filled with either air or oxygen. In a static test the air is quiescent, while, in a dynamic test, it is flowing through

the combustion chamber. By observing the conditions when the drop bursts into flame, the ignition temperature and ignition lag can be determined. There are two main disadvantages to this method: (1) the mixture composition is not known and (2) the heat of vaporization is supplied by the crucible. The temperature of the surface of the crucible is recorded as the ignition temperature. Scott, et al. [15] modified the drop method apparatus so that the ignition temperatures of both liquids and gases could be determined. Gases are liquified by means of dry ice or liquid nitrogen and are tested in the same manner as ordinary liquids. The designers claim that "gases whose ignition temperatures in oxygen have not been determined because of the violence of the explosions may be liquified and tested in this apparatus with safety."

The dynamic heated-tube method, as described by Dixon and Higgins [16], consists of two quartz or Pyrex tubes, separately heated, in which the combustible gas and supporting atmosphere are flowing. The combustible gas is mixed with the supporting atmosphere at a controlled rate by means of a small orifice in the end of the small tube which contains the flammable gas. The measured ignition temperature is the mixture temperature at which the flame appears after a measured time lag. With this method, the mixture composition is known and controllable.

When it was first developed by Tizard and Pye [17],

the adiabatic compression method was supposed to be suitable to eliminate the effects of the surface on ignition temperature. The resulting ignition temperature would be equal to those for homogeneous gas-phase ignition. The apparatus was constructed with a piston that moved forward very quickly, thus, compressing a volume of fuel-air mixture in a cylinder. At the end of the stroke, the piston was locked. Calculations by Tizard and Pye showed the time required for any appreciable heat transfer to the cylinder walls from the gas was much greater than the observed ignition time lags. The ignition temperature is determined from the pressure ratio which has been measured. However, the experiments of Tizard and Pye showed that significant heat transfer to the walls did take place. Lewis and von Elbe [18] have pointed out that all experimenters have found it necessary to condition the walls of the reaction chamber in order to obtain consistent results. Therefore, a wall effect does exist, and the adiabatic-compression method gives an apparatus dependent temperature rather than an absolute ignition temperature.

In the bomb method [19], the flammable mixture is injected into an evacuated chamber which has been preheated to a known temperature. Errors may result from possible catalytic effects of the chamber and from the fact that the gas mixture must be heated before ignition can occur.

In discussing the above methods for determining the

ignition temperature, Belles and Swett [12] have stated that "data from all these methods cannot be compared because of the difference in experimental apparatus and technique; however, data from one source can be used to show the trends of different variables."

Flammability Limits

Coward and Jones [20] define the dilution limit of flammability, or, more simply the flammability limit, as the borderline composition, which, with a slight change in one direction produces a flammable mixture and in the other direction an inflammable one. There are two limits of flammability, a lower and a higher. The lower, or lean, limit is the minimum concentration of combustible gas that will propagate a flame, and the higher, or rich, limit is the maximum concentration. These limits are, therefore, physico-chemical constants (at given temperatures and pressures) of gases and vapors.

After studying the literature, Coward and Jones have concluded that "normal variations of atmospheric pressure do not appreciably affect the limits of flammability, as has been shown both by direct observation and by deduction from the course of curves showing the variation of limits over much wider variations of pressure than that of the atmosphere" [20].

White [21] has shown by experiment that, for most mixtures, there is a straight-line relation between the

limit of flammability and the initial temperature of the mixture. In order to propagate a flame, the layer of unburned gas next to the burning layer must be brought to the ignition temperature. If the temperature of the unburned gas is increased before the passage of the flame front, then less heat has to be supplied by the burning layer. The result of this increase in initial unburned gas temperature is a decrease in the lower limit and an increase in the upper limit, i.e. the range of flammability should be widened at both limits by an increase of temperature.

Egerton and Powling [22] in a study on the effects of various dilutents on the upper and lower flammability limits of various combustible gases, have concluded that, "whether combustion takes place or not is dependent upon the temperature of the flame being sufficient to maintain a certain boundary flame temperature which provides a certain concentration of active radicals in the boundary region." Ignition is produced in the unburnt gas mainly from the radicals derived from the flame. A flame which is traveling through a combustible gas mixture can be described as consisting of (1) a region in which the gas mixture, initially cold, is being heated by conduction, (2) a region in which combustion is occuring, and (3) a region in which the products are cooling. Egerton and Powling's experiments have led them to conclude that the influence of reactions in the preflame zone is not of major importance. The

initiation of the flame at the edge of the preflame zone is due to the unburnt gas meeting, as it enters the flame zone, active radicals and molecules with high energy which come from the flame itself. When the combustible gas encounters "a region of high enough temperature containing sufficient concentration of these radicals the combustion is initiated and then proceeds rapidly."

The U. S. Bureau of Mines [20] uses the following method for determining the flammability limits of volatile liquids and gases. A glass tube in which the mixture is tested is first evacuated by a vacuum pump. A measured amount of vapor of gas is then introduced into the tube, after which air or another supporting atmosphere is admitted through a drying tube until atmospheric pressure is reached. The air and test gas are then thoroughly mixed by circulation for 10 to 30 minutes. After sufficient mixing, the heretofore closed tube is opened to the atmosphere, and the mixture's flammability is tested by attempting spark ignition or by passing a small flame across the open end of the tube.

Powling [23] has designed a burner which can be used for determining low burning velocities and limits of flammability. The burner stabilizes slow burning flames, beyond the range of other burners, and produces a flat reaction zone free from all surface contact. A description of the burner is given below. The premixed explosive gas

mixture enters a water cooled burner tube from below, and the flow is distributed uniformly across its whole diameter of 6 cm by a diffuser which is positioned near the top of the copper burner tube. The diffuser consists of a short length of glass beads followed by a series of fine gauzes. The gases are then conducted almost to the burner port through a vertically laminated matrix made from a roll of alternatively plain and corrugated metal tape through which the flow is streamlined. By adjusting the position of this packing, the velocity distribution can be made to be quite uniform except for friction effects at the edges. These are corrected just above the port by a suitable current of inert gas which is introduced at the exit of the burner by means of a sliding glass jacket, positioned around the outside of the burner. Powling used the burner for experimentally determining burning velocity versus composition curves for various hydrocarbon gases to their lower limits. The determination of the lower limit from these curves was found to be quite precise, the error being less than ± 0.02 per cent.

As has been stated before in the preceding section of this chapter, the purpose of this thesis is to develop the experimental apparatus and techniques necessary for the determination of the minimum ignition temperature of combustible fuel-air mixtures as a function of their mass fraction. As can be seen from the foregoing discussion of flammability

limits and ignition temperatures, the results of this thesis will also be a method for determining the flammability limits of a combustible gas. For the expected U shaped curve of ignition temperature versus mass fraction of fuel, the flammability limits are the two vertical asymptotes of the curve.

Scope of Thesis

The instrumentation and equipment along with a discussion of their design criteria is presented in Chapter II of this thesis. The experimental procedures and the methods of data reduction are described in detail in Chapters III and IV, respectively, and the results of tests on propane and three cotton fabrics are presented in Chapter V. A discussion of these results is also given in Chapter V. Conclusions and some recommendations are presented in Chapter VI. The Appendix contains sample calculations.

CHAPTER II

INSTRUMENTATION AND EQUIPMENT

Purpose and Design Criteria

An apparatus called the Lower Ignition Temperature and Concentration Apparatus (LITACA) was designed, constructed, and assembled to

(i) thermally decompose pyrolyzing materials,

(ii) store the pyrolysates,

(iii) mix pyrolysates with dry air at controlled mass fractions,

(iv) measure the minimum mixture temperature at which self-ignition occurs, and

(v) afford pyrolysate sampling for molecular weight determinations.

The major criteria which this apparatus had to meet are (1) the integrity of the pyrolysate composition should be insured by preventing water vapor condensation in the apparatus, and (2) the temperature measured should be the true minimum ignition temperature to within $\pm 5°C$. The apparatus also had to have the provision to let a sample of pyrolysate be drawn off for density measurements.

Major Components and Operating Principles

Figure 1 is a flow diagram for LITACA, which is shown

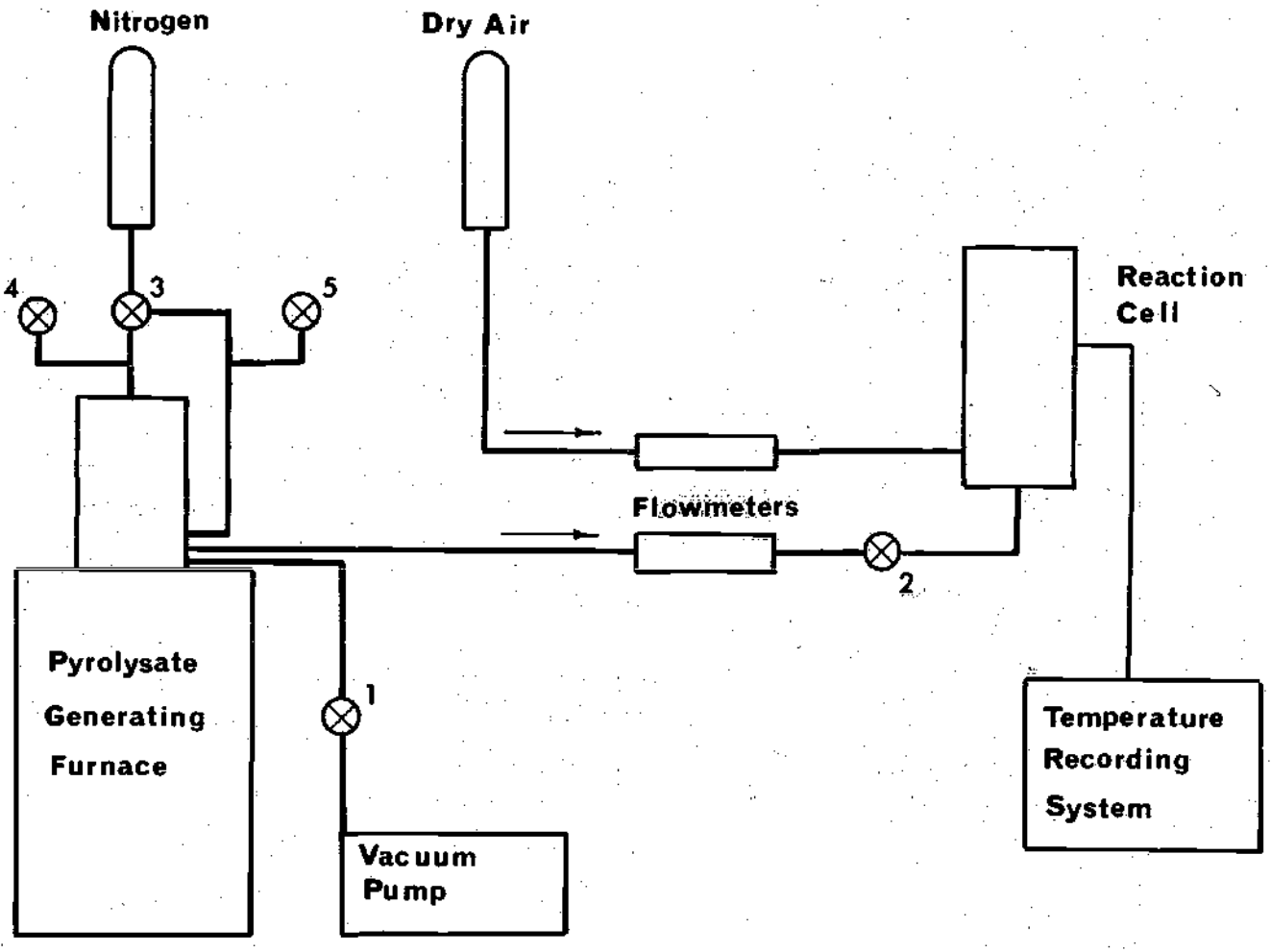


Figure 1. Flow Diagram for Lower Ignition Temperature and Concentration Apparatus (LITACA).

in Figure 2. Its six components are:

(i) Pyrolysate Generating Furnace with Accumulator, to decompose up to 100 grams of thermally degradable materials and to store the decomposition gases,

(ii) Supply of dry air, to be mixed at a controlled rate with the pyrolysate gases,

(iii) Supply of nitrogen gas, to pressurize the top side of the accumulator piston which causes the ejection of pyrolysate from the generating furnace at a controlled rate and to flush the air from the system during the preparatory stages of the experimental procedure,

(iv) Flow Metering System, to measure the volumetric flowrates of the dry air and of the pyrolysate in order to determine and vary the mass fraction of pyrolysate-air mixture,

(v) Reaction Cell, in which the dry air and pyrolysate are mixed and in which this mixture is heated and its temperature is monitored,

(vi) Temperature Recording Facility, to monitor the pyrolysate temperature.

These major components along with auxiliary components are described in the following sections.

Pyrolysate Generating Furnace

Figure 3 is an assembly drawing of the Pyrolysate Generating Furnace, with its accompanying parts list given in Table 1. The furnace is mounted inside the cabinet of

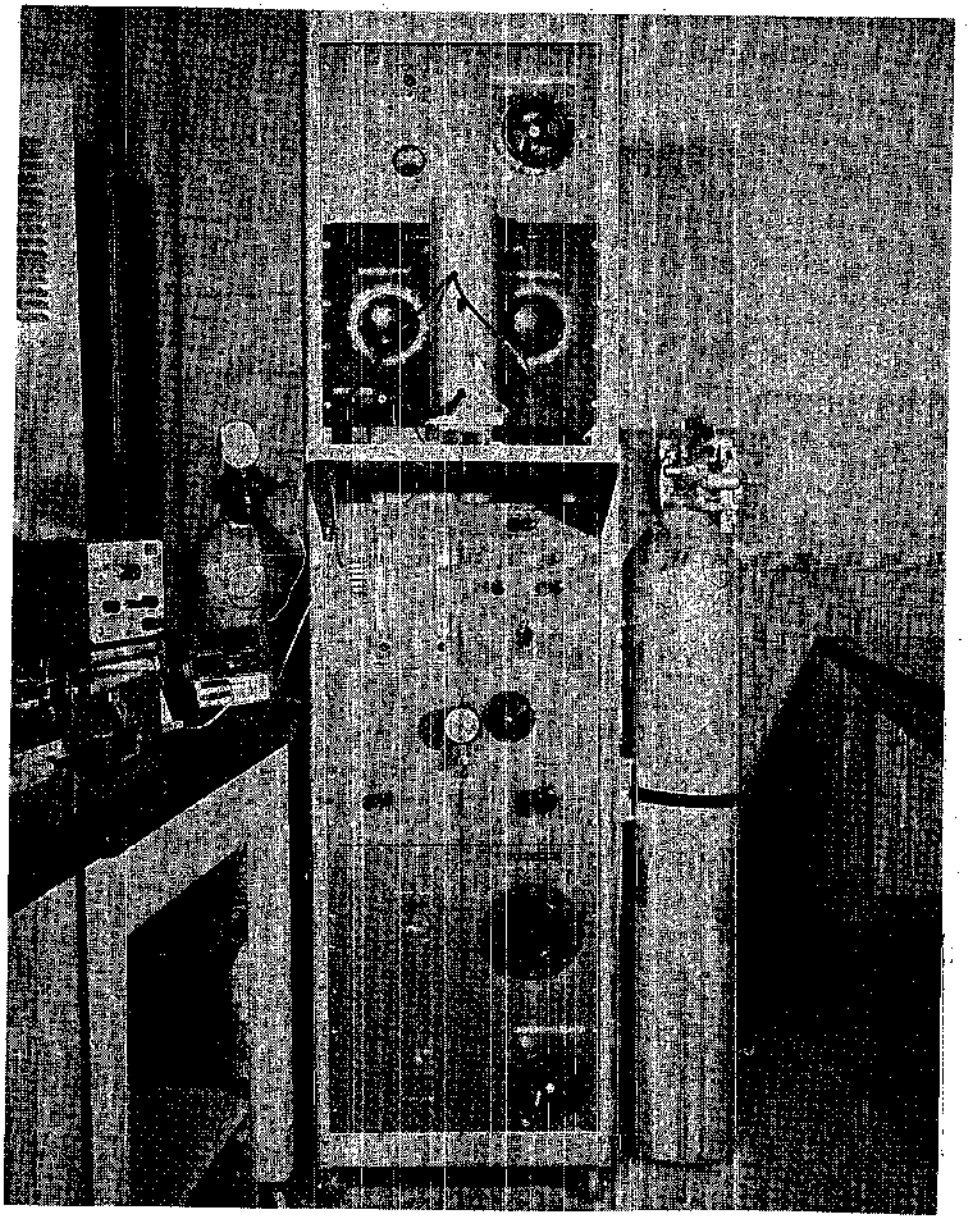


Figure 2. Lower Ignition Temperature and Concentration Apparatus (LITACA)

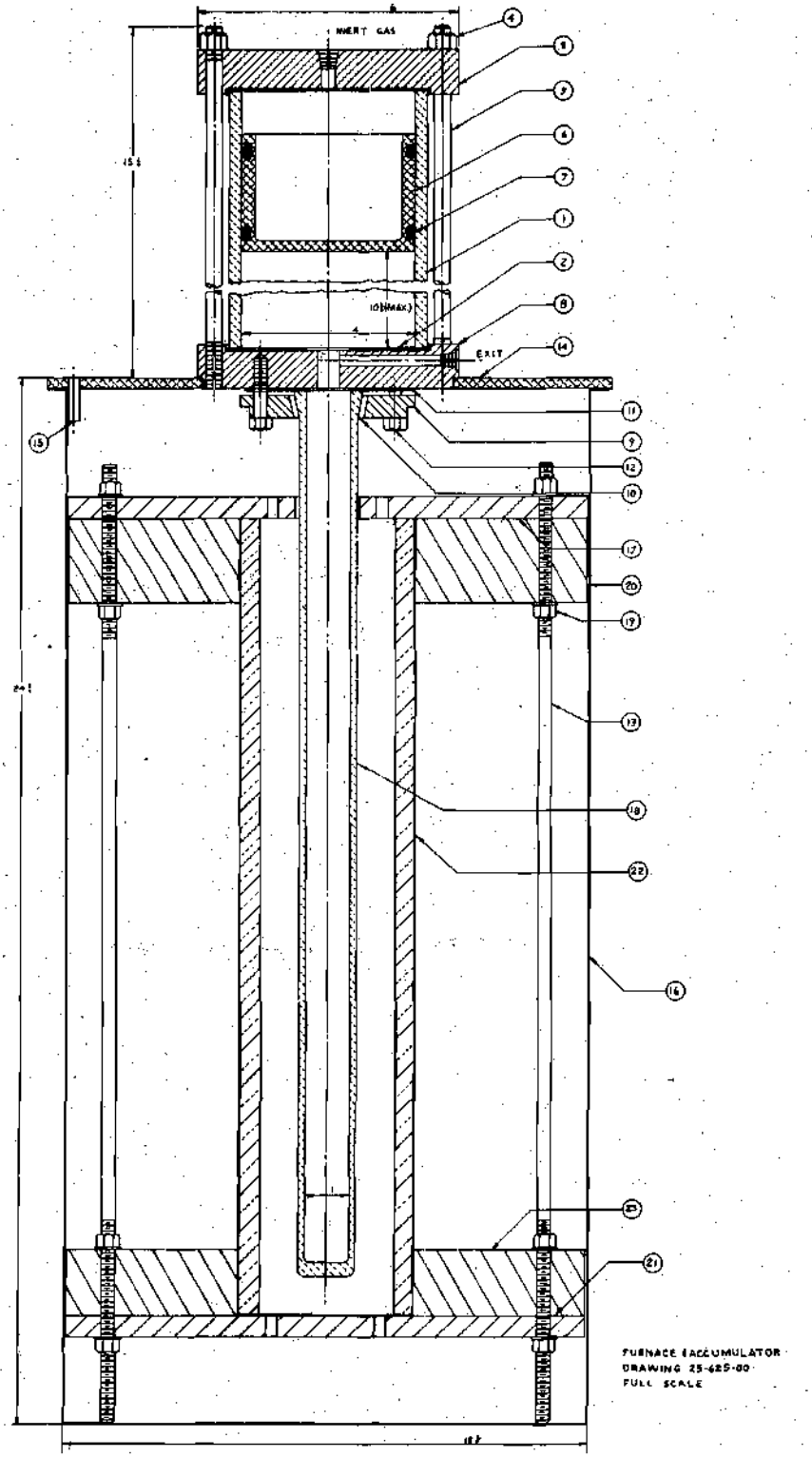


Figure 3. Cross Section of Furnace and Accumulator for LITACA.

Table 1. Parts List for Figure 3

Part No.	Description	Material	Req'd
1	Accumulator Barrel	Pyrex Glass	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	Neoprene	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	Furnace Test 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

Figure 2. The heat sources for the furnace consist of two cylindrical half-shell, 1720 watt-230 volt, Model RH 256 heaters from Thermal Corporation, Huntsville, Alabama. The heaters are wired in parallel. The heating elements have the upper operating temperature limit of 2,200°F and are chrome-aluminum-iron resistance wires, helically wound and placed in ceramic backings. These backings are then embedded in a ceramic core. The test tube which holds the sample is made of "Vitreosil" fused quartz. It is 20-1/2 inches long and has a 1-inch internal diameter. The stainless steel manifold allows access to the furnace from five points in the system, namely the vacuum pump, the gas sampling glass balloon, the nitrogen supply, the pyrolysate flow meter, and the pressure gauge. The accumulator barrel, made of pyrex glass, is positioned on top of the manifold and has a maximum capacity of approximately two liters. It is sealed by a nitrogen gas pressurized piston, made of aluminum with two neoprene "O" rings. The pressurized piston controls the pressure in the accumulator. The accumulator together with the inner core of the furnace is shown in Figure 4.

The power input to the furnace is controlled by two 20 amp-115 volt variable-autotransformers, wired in series. All gaskets used in the furnace are made of 1/16 inch thick Dupont Teflon. A chromel-alumel thermocouple is positioned near the center of the furnace core to monitor the temperature of the furnace.

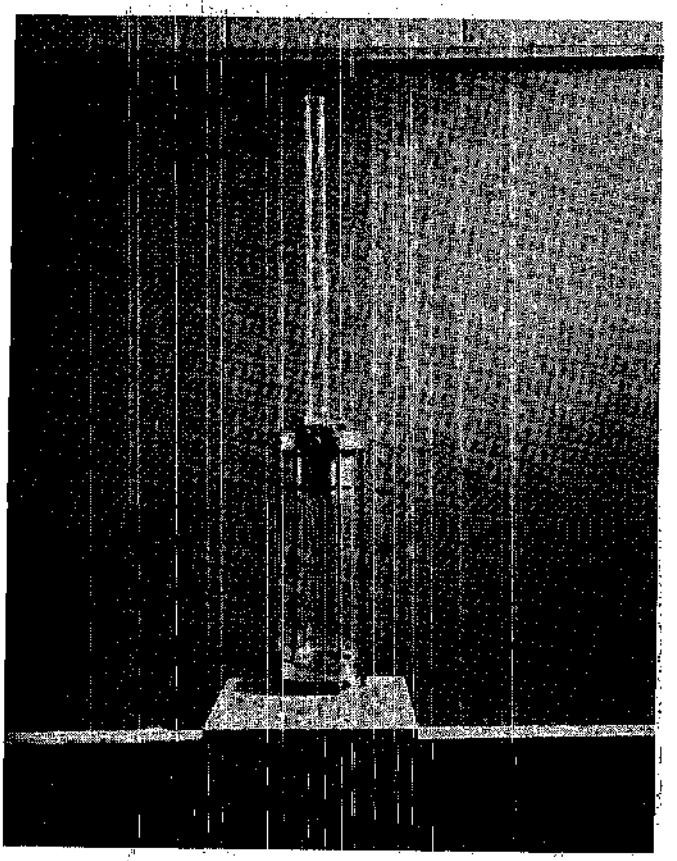
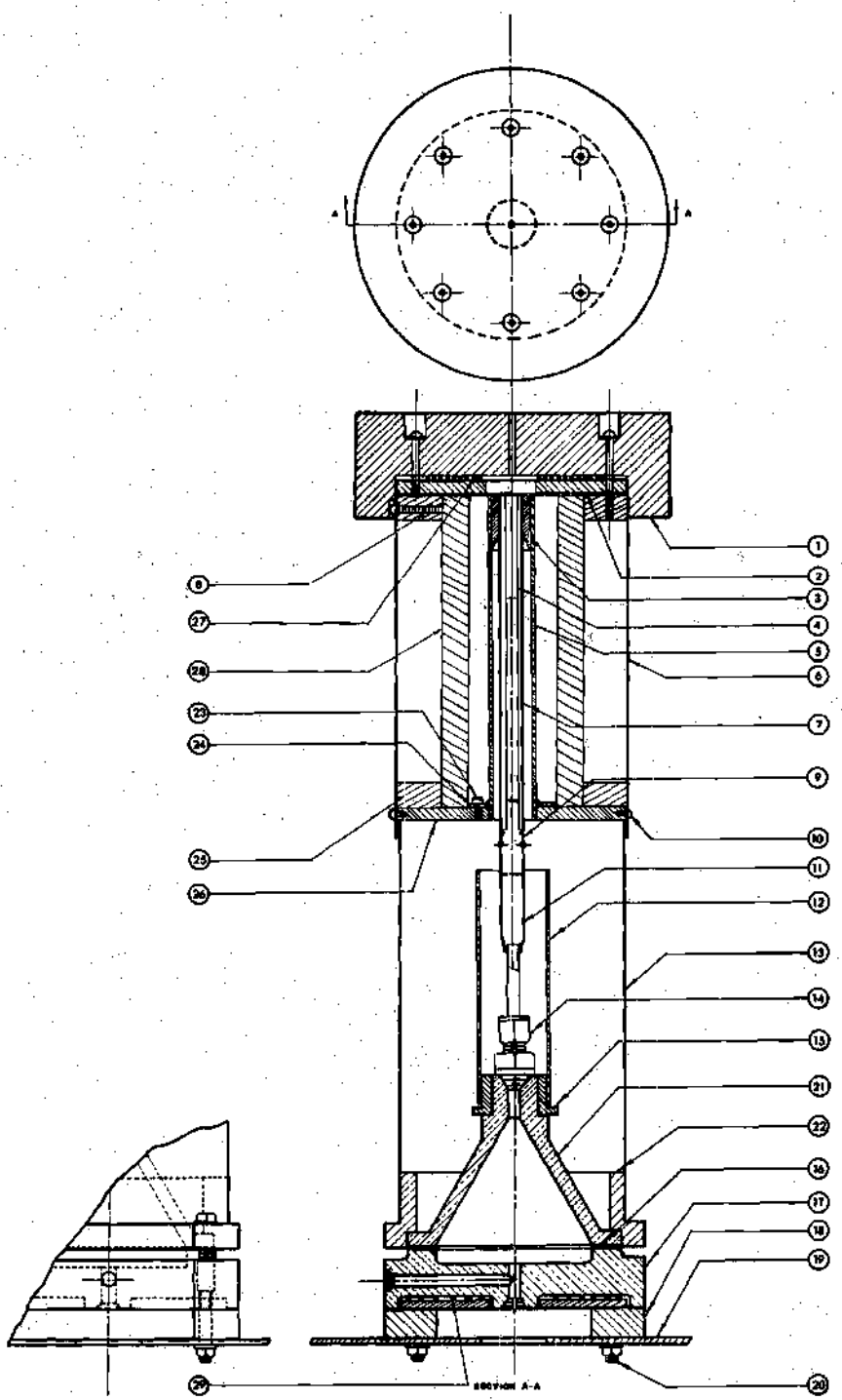


Figure 4. Furnace Core and Accumulator, Overall Height is 90 cm.

Reaction Cell

Figure 5 is an assembly drawing of the Reaction Cell in which the pyrolysate is mixed with dry air and then heated to the mixture's ignition temperature while its temperature is being monitored. Table 2 is the accompanying parts list. Figure 6 is a photograph of the reaction cell. Both the mixing chamber and the flame arresting chamber are made of chrome plated brass with a nickel undercoating. The mixing chamber has a guard heater positioned underneath it to prevent condensation in the mixing and flame arresting chambers. The flame arresting chamber is filled with 3 mm diameter glass beads which prevent the upstream propagation of the flame and at the same time enhance the mixing of the gases. A guard heater encloses most of that part of the ignition tube which is in the lower section of the Reaction Cell. This heater prevents condensation in the cooler, lower half of the ignition tube and can also act as a pre-heater if necessary. The ignition heater, positioned in the upper half of the Reaction Cell, consists of two 515 watt, 115 volt cylindrical half-section heaters, Model RH 221 from Thermal Corporation, Huntsville, Alabama, wired in parallel. The 2,200°F capacity heating elements are also chrome-aluminum-iron wires, helically wound and placed in ceramic backings, which are then embedded in a ceramic core. The power supply to the heater is controlled by a 15 amp-115 volt variable auto-transformer. A guard heater



GEORGIA INSTITUTE OF TECHNOLOGY	REACTION CELL ASSEMBLY	DR BY:	SCALE: FULL
			DATE: 10-17-78

Figure 5. Cross Section of Reaction Cell for LITACA.

Table 2. Parts List for Figure 5

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	Lower Guard Htr 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 Floor	Transite	1
27	Upper Guard Heater	Nichrome Wire	1
28	Ignition Heater	Chrome-Al-Fe Wire	1
29	Lower Guard Heater	Nichrome Wire	1

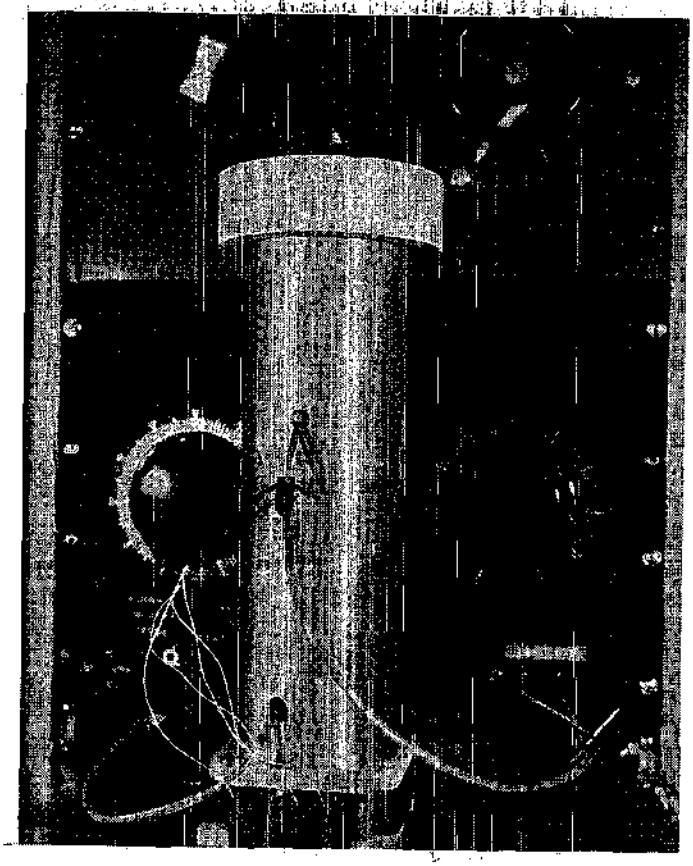


Figure 6. Reaction Cell for LITACA.

is built into the top insulating cap of the Reaction Cell by embedding a 10 ohm coil of nichrome wire in Sauereisen Insa-Lute adhesive cement. This heater is positioned between the insulating cap and the transite lid in order to suppress heat losses from the top.

The key component of the Reaction Cell is the ignition temperature thermometer. This thermometer unit is made up of four basic parts: (i) ignition tube, (ii) quartz tube bundle, (iii) nickel resistance wire, and (iv) the chromel-alumel thermocouple.

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

(ii) The quartz tube bundle is made up of 19 quartz tubes, each with a 2 mm O.D. and a 1 mm I.D. Seventeen of the tubes are 30 mm long and are bound together (by means of two stainless steel wire rings) with two 144 mm long tubes which support the bundle and act as conduits for the stranded nickel leads. The top of the bundle is 6 mm from the top of the ignition tube.

(iii) Approximately 570 mm of 0.005 inch diameter nickel wire (type A, purchased from Sigmund Cohn Corp., Mr. Vernon, New York) was passed through the tubes. The five conductor stranded nickel leads, which are positioned

inside the quartz tube legs of the bundle, are spot-welded to the ends of the single strand wire at the bottom of the bundle. The other ends of these stranded leads are silver soldered to tungsten pins which are sealed into (and exit) the pyrex section of the ignition tube. On the outside of the ignition tube, two leads are attached to each of the tungsten pins. These four leads then proceed to the resistance measuring facility.

(iv) A chromel-alumel thermocouple with ceramic insulation was positioned in the center of the tube bundle, with its leads exiting the Reaction Cell through the top.

The tube bundle was placed so that it occupies that section of the ignition tube that experiences the highest temperature. This position was determined from the results of a temperature traverse along the axis of the ignition tube. With an air flow of 87 SCCM, the stainless steel ignition tube shield (part number 5, Figure 5) was brought to an equilibrium temperature of 431°C, and the centerline temperature of the ignition tube was measured at different points from the top of the reaction cell by a chromel-alumel thermocouple. Figure 7 shows the results of that temperature traverse.

Flow Metering System

Two Brooks Instrument flowmeters (Model 1355, meter size #2) are used for measuring volumetric flowrates. For the pyrolysate, an R-2-15-AAA flow tube with glass and

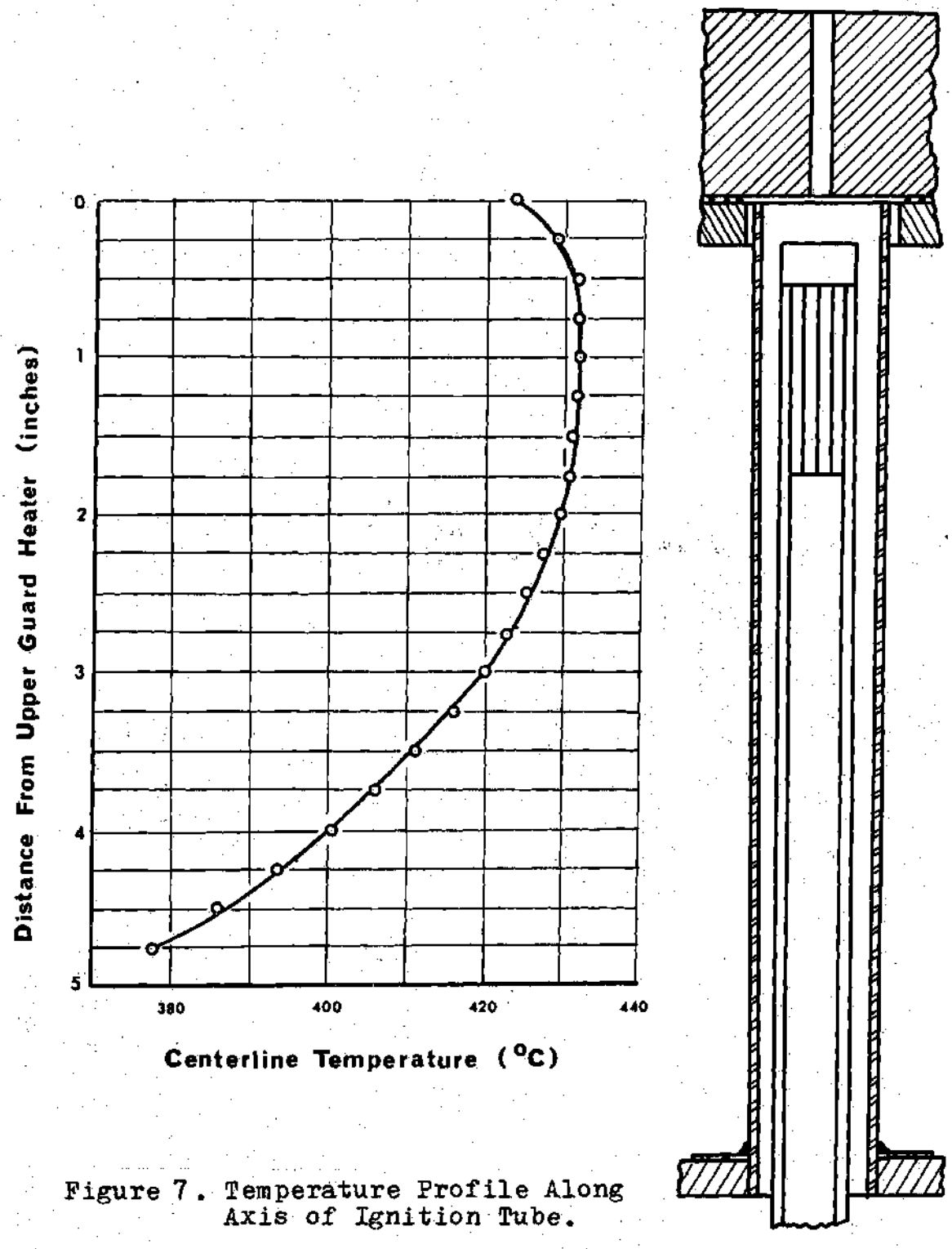


Figure 7. Temperature Profile Along Axis of Ignition Tube.

stainless steel floats (maximum capacity of 49 SCCM and 147 SCCM, respectively) are used. For dry air, three flow tubes are available with both glass and stainless steel floats: (1) R-2-15-AAA, (2) R-2-15-D providing a maximum capacity of 375 SCCM and 830 SCCM with glass and stainless steel floats respectively, and (3) R-2-15-B with 5.0 SCFH and 9.8 SCFH maximum capacity. Iron-constantan thermocouples are positioned in the flowstream at the entrances of both flow meters. These temperatures are necessary for the conversion of the calibrated flow meter readings from standard conditions to the test conditions. A U-tube manometer was used to determine if it would be necessary to make pressure conditions in the flow readings; however, it was found that the static gage pressure in the flow lines was near atmospheric and no corrections were necessary.

Resistance and Thermocouple Recording Facilities

The resistance recording facility for the nickel wire resistance thermometer consists of:

(i) one Hewlett-Packard Model 34703A DCV/DCA/OHM Meter which provides eight ranges of resistance measurement, from 1 ohm full scale to 10 mega ohms full scale,

(ii) one Hewlett-Packard Model 34705A Five Digit Display Unit,

(iii) one Hewlett-Packard Model 34721A BCD Module which provides nonisolated BCD output for operation with printers and other devices,

(iv) one Hewlett-Packard Model 581A Digital to Analog Converter which accepts the 4 line BCD Module output, and sends out a DC signal to the recorder,

(v) one Hewlett-Packard Model 680 Strip Chart Recorder.

The Digital to Analog Converter allows the display of any set of three adjacent digits to be recorded with automatic range stepping.

A two-channel Leeds and Northrup Speedomax X/L 680 Recorder is used in conjunction with an Omega Thermocouple Ice Point Reference Chamber to measure and record the thermocouple emf's of the system. A Hewlett-Packard 3420B DC Differential Voltmeter is also used to monitor and measure thermocouple signals.

Auxiliary Systems and Components

The gas lines used in LITACA are all 1/8 inch O.D. SS316 stainless steel tubing. All valves with which the pyrolysate gases come into contact are made of SS316 stainless steel with teflon packings, while the valves on the air side are brass.

The vacuum pump used to evacuate the system prior to pyrolysis is a Vac-Torr Model D-25, which is a two-stage pump with a 1/3 horsepower motor, vented exhaust, 25 liter per minute free air displacement and guaranteed vacuum of 0.0001 torr Hg. The furnace pressure gage reads both positive and negative gage pressure with a range of from 30

inches of Hg up to 30 psig.

All of the pyrolysate gas lines are wrapped with chromel-alumel thermocouple wire which are hooked up to a 115 volt-5 amp variable-autotransformer to act as a guard heater. These two guard heaters are used to keep the pyrolysate gas lines and the accumulator barrel at 120°C during testing to prevent condensation of any of the pyrolysate mixture.

In order to measure the density of the pyrolysate gases, it is necessary to collect a known sample volume of the gas from the furnace. This sample is collected in a glass balloon made of blown glass for that purpose.

Construction Difficulties

In order to pass on some of the experience the author gained during the construction and preliminary testing phases of this work, some of the major problems that were encountered will be discussed.

Pyrolysate Generating Furnace

The original design of the Pyrolysate Generating Furnace called for 12 General Electric tungsten filament lamps to be used as the heating elements. The 12 radiative heaters were placed vertically in the furnace and formed a cylinder around the furnace test tube. During the first test of the furnace after its construction, the furnace temperature was raised to 700°C. The resulting thermal

stresses caused the quartz casings around the tungsten coils to break. The heaters described in the preceding sections of this chapter were then acquired and installed.

Reaction Cell

The greatest difficulties in the fabrication of the Reaction Cell were encountered with the resistance thermometer. The first thermometer built used 0.005 inch diameter platinum wire with 18 gauge platinum exit pins. A thin coating of gold had been electroplated onto the platinum in order to prevent the possibility of the bare platinum acting as a catalyst. Since the resistance versus temperature relation for platinum and gold are well established, it was unnecessary to use a thermocouple in the tube bundle. The exit pins and the 0.005 inch diameter platinum wires were spot welded together. After ignition tests were run with propane, the Reaction Cell was disassembled, and it was found that the gold had evaporated from the platinum.

It was then decided to use nickel as the resistance wire with tungsten exit pins. Above 351°C, nickel cannot be used as a resistance thermometer because of oxidation; a thermocouple was then incorporated into the design. Difficulties were encountered in joining the nickel wire to the tungsten pins. Both spot welding and silver soldering were attempted and found to be unacceptable. The final solution, as described previously, was to silver solder stranded nickel wire, which runs from the bottom of the tube

bundle to the pins, to the tungsten pins.

During the test runs on fabric samples, the copper hook-up wire to the ignition heater inside the upper cell housing disintegrated due to the high temperatures. This copper wire was then replaced by stranded nickel-chrome wire with ceramic fish spine beads from Thermal Corporation, Huntsville, Alabama, used as electrical insulation.

CHAPTER III

EXPERIMENTAL PROCEDURE

This chapter details the experimental procedures used to obtain the ignition temperatures of propane-air mixtures, pyrolysate-air mixtures, and the pyrolysate density. The calibration of the nickel resistance thermometer will be discussed first.

Calibration of the Thermometer

A calibration of the nickel resistance thermometer was carried out, using the ignition and guard heaters to bring the Reaction Cell to thermal equilibrium. Three thermocouples, positioned at the lower guard heater, the ignition tube shield, and the centerline of the ignition tube were used to monitor the temperature inside the Reaction Cell. When these three thermocouples experienced temperatures within 2°C of each other, a calibration point was recorded. Prior to the calibration test, the ignition heater was taken up to a temperature of 435°C and allowed to slowly cool back down to room temperature. This annealing of the wire (which was not annealed by the manufacturer) served to relieve any work hardening stresses which might have been formed during the threading of the tube bundle and to allow a thin protective oxide film to form on the

surface of the nickel. After the annealing, four calibration points were taken at different temperatures. During the initial testing with propane-air mixtures, it was discovered that the resistance thermometer did not respond to ignition, and, therefore, the results of the calibration were not used.

Ignition Temperature Measurement

This section describes the procedures used for running an ignition temperature test on propane-air mixtures and pyrolysate-air mixtures.

Propane-Air Mixtures

The Pyrolysate Generating Furnace and pyrolysate gas lines are filled with propane after being evacuated by the system vacuum pump. In these tests none of the guard heaters outside of the Reaction Cell are used. The procedures for the attainment and the recording of ignition temperatures of propane-air mixtures are the same as those described later in this chapter for pyrolysate-air mixtures.

Pyrolysate-Air Mixtures

This section describes the procedures used in running ignition tests on fabrics.

Preparation of Fabric Sample. A fabric sample of approximately 28 grams is prepared by cutting the cloth into 2 to 3 inch squares and packing it into the fused quartz test tube of the furnace core. By the flushing procedure

described next and by desiccation prior to insertion into the furnace, the fabric moisture was removed.

Flushing Procedure. With the fabric sample in place in the test tube and the furnace core installed in the furnace, the system is now ready for flushing. The valve numbers used below refer to the valves shown in Figure 1. With valves 1, 2, 3, 4, and 5 closed, the vacuum pump is allowed to evacuate the system for 1 to 2 minutes. After this period, valve 1 is closed. Valve 3 is a three-way valve which allows access from the nitrogen supply either to the top side of the accumulator piston or to the furnace test tube and pyrolysate gas lines through the accumulator manifold. The system is filled with nitrogen to a slightly positive gage pressure by turning valve 3 to the proper position. After filling the system with nitrogen, valve 3 is closed, and valve 1 is opened to re-evacuate the system. This flushing and evacuating procedure is repeated five times, and a final vacuum is pulled on the system. Valve 1 is then closed, and the vacuum pump is turned off. The system is now ready for the pyrolytic process to begin.

Pyrolysis of Fabric. The pyrolysis of the fabric and the accumulation of pyrolysates will now be described. The furnace is energized and brought to a temperature of approximately 360°C. The pyrolysis of the fabric can be monitored by observing the rise in furnace pressure. During the early stages of pyrolysis, the nitrogen pressure on the

top side of the accumulator barrel is kept at atmospheric pressure by keeping the piston vent, valve 4, open and the nitrogen pressure regulator turned off. As the pressure in the furnace rises above atmospheric pressure, the piston rises in the accumulator barrel until it reaches its maximum displacement; at which time, the piston vent is closed. The guard heater on the accumulator barrel prevents the condensation of volatile vapors and tars on the walls of the glass barrel and on the bottom of the piston.

It takes the furnace 15 to 20 minutes to reach 360°C. The rise in furnace pressure due to pyrolysis occurs at 355°C, and pyrolysis is complete after a period of 25 minutes.

Guard Heater Control. During the period in which the furnace is generating pyrolysates, the guard heaters are turned on to warm up the necessary components in the system. The pyrolysate gas lines are brought to a temperature of approximately 110°C, and the lower guard heater rises to about 200°C. The ignition heater and upper guard heater are set so that the upper half of the Reaction Cell reaches a temperature of 300°C, and the accumulator barrel guard heater is set at 120°C.

Flow Rate Control and Measurement. When the pyrolysate generation is completed, dry air is passed through the ignition tube at a selected flowrate, and the input power to the ignition heater is stepped up such that the

Ni-resistance thermometer shows the desired steady increase in temperature. Finally, the pyrolysate is introduced at a preselected and measured flowrate. The temperatures of the dry air and pyrolysates are measured by iron-constantan thermocouples at the inlets of both flowmeters. These temperatures are used to convert the calibrated flow rate measurements from standard to test conditions.

Attainment and Recording of Ignition Temperature. For an increasing heat flux into the gas mixture during its passage through the ignition tube, the gas will reach its maximum temperature at the tube bundle. The nickel wire and the thermocouple junction represent, because of their higher absorptance in relation to quartz and the gas, the highest temperature in the ignition tube. Thus, when the resistance wire or the centerline thermocouple in the tube bundle shows a sudden excursion from its steady rise, ignition of the mixture should have taken place on the wire.

The steady rise in the ignition tube temperature is induced by a step increase in power input to the ignition heater. Prior to this step increase, the guard heaters will have been allowed to come to equilibrium. At the time of the step increase in power, the air flow is set and measured; the pyrolysate is mixed with the air at a preselected flowrate when the ignition tube centerline temperature reaches a temperature approximately 100°C below the estimated minimum ignition temperature, which in

the case of GIRCFF fabrics is obtained from data presented in Reference [8] or experience gained from previous test runs.

At the point of ignition, the resistance of the nickel wire and the emf output from the centerline thermocouple will show a sudden rise, and repeated popping noises may be heard from the inside of the Reaction Cell. When this occurs, the emf of the centerline thermocouple in the Reaction Cell is recorded at the time at which the disturbance occurs and defined to be the ignition temperature for that concentration of pyrolysate.

Pyrolysate Density Measurement. The average molecular weight of the pyrolysates can be calculated from density measurements at a known pressure and temperature. At the end of the pyrolysis process, a sample of the pyrolysate is drawn off into a 3 inch diameter evacuated glass balloon. After filling with pyrolysate, the stopcock to the container is quickly opened and closed to allow the pyrolysate to come to barometric pressure. The balloon is then placed in a drying oven, which is set at 120°C, for two hours. At the end of this time, the balloon is removed from the oven and its stopcock again quickly opened and closed. The glass balloon with pyrolysate sample is then weighed on an analytical balance. Since the volume and tare weight of the glass balloon are known from previous measurements, the density can therefore be calculated. With the measured

barometric pressure, temperature, and density of the gas, its average molecular weight can be calculated by using the equation of state for a perfect gas.

Cleaning Procedure

After disassembly, the pyrolysate gas lines, manifold, accumulator barrel, flow tubes, and ignition tube can be cleaned of tars with the use of acetone, soap, and water. The carbonaceous deposits on the inside of the furnace test tube can be removed by placing it into the furnace without the manifold so that the test tube's mouth is open to the air. The furnace is then energized and brought to a temperature of 600°C for a period of one hour. The oxygen in the air will oxidize the carbon deposits.

CHAPTER IV

DATA REDUCTION

This chapter describes the methods used to calculate the mass fractions of pyrolysate from the flow metering data.

Calculation of Mass Fraction

The mass fraction χ_ρ of the pyrolysate in the mixture is defined by equation (1):

$$\chi_\rho = \frac{\dot{m}_p}{\dot{m}_p + \dot{m}_a} , \qquad (1)$$

where $\dot{m}_p$ and $\dot{m}_a$ are the mass flowrates of the pyrolysate and air, respectively.

The flowmeters used in LITACA were calibrated for air at the standard conditions of temperature equal to 21°C and a pressure of one atmosphere. The result of this calibration is a curve of volumetric flowrate versus flow tube scale reading. The procedure for correcting this flowrate to a different density gas and temperature will now be described.

A momentum balance is taken on a control volume which encompasses the float and that portion of the flowtube upstream of the float. The results are shown in equation (2):

$$\dot{m}_c(v_2-v_1)_c = m_f g$$

$$\dot{m}_b(v_2-v_1)_b = m_f g, \tag{2}$$

where $\dot{m}_c$ and $\dot{m}_b$ are mass flowrates at calibrated and test conditions respectively, v_2 is the velocity of the gas at the annular opening around the float, v_1 is the velocity of the gas at the entrance of the flow tube, m_f is the mass of the float, and g is the acceleration of gravity. Applying the conservation of mass equation at points 1 and 2 results in:

$$v_1 = \frac{m}{\rho A_1}$$

$$v_2 = \frac{m}{\rho A_2}, \tag{3}$$

which holds for both calibration and test conditions. Combining equations (2) and (3), one gets:

$$m_c\{(m_c/\rho_c)[(1/A_2) - (1/A_1)]_c\} =$$

$$m_b\{(m_b/\rho_b)[(1/A_2) - (1/A_1)]_b\}. \tag{4}$$

The areas A_1 and A_2 are the cross-sectional areas through which the gas flows at points 1 and 2, and thus for the same scale reading:

$$[(1/A_2) - (1/A_1)]_c = [(1/A_2) - (1/A_1)]_b; \tag{5}$$

therefore, equation (4) reduces to equation (6):

$$\dot{m}_b = \dot{m}_c \left[\frac{\rho_b}{\rho_c}\right]^{1/2} \tag{6}$$

The volumetric flowrate G, which is defined by

$$G = \frac{\dot{m}}{\rho} , \tag{7}$$

can now be introduced into equation (6) with the result:

$$G_b = G_c \left[\frac{\rho_c}{\rho_b}\right]^{1/2} . \tag{8}$$

By introducing the equation of state for a perfect gas and assuming that the test and calibration pressures of the gas are equal, equation (8) can be transformed into:

$$G_b = G_c \left[\frac{M_c T_b}{M_b T_c}\right]^{1/2} , \tag{9}$$

where M_c and M_b are the molecular weights and T_c and T_b are the absolute temperatures of calibration and test gases respectively. Using equation (7), equation (1) can be put in the form of densities and volumetric flowrates:

$$\chi_\rho = \frac{1}{1 + (G_{ba}\rho_a / G_{bp}\rho_p)} , \qquad (10)$$

where the subscripts a and p represent dry air and pyrolysate respectively. Equation (9) and the perfect gas law can be substituted into equation (10) with the result:

$$\chi_\rho = \frac{1}{1 + \phi B} , \qquad (11)$$

where

$$\phi = (G_{ca}/G_{cp}), \qquad (12)$$

and

$$B = \left[\frac{M_a T_p}{M_p T_a}\right]^{1/2} . \qquad (13)$$

In order to determine the mass fraction of pyrolysate in the mixture, equations (11) and (13) show that it is necessary to experimentally determine the molecular weight of the pyrolysate. This is described in the next section.

Calculation of the Molecular Weight of Pyrolysate

As described in Chapter III, the density of the pyrolysate is measured by collecting a vapor sample in a glass balloon whose volume is known. The gas sample is weighed after the determination of its temperature and

pressure. The density of the pyrolysate ρ_p at the known temperature and pressure is defined as:

$$\rho_p = \frac{m_p}{V_{bal}} , \tag{14}$$

where m_p is the weight of the gas sample, and V_{bal} is the volume of the glass balloon.

The average molecular weight of the pyrolysate M_p can be determined by using the equation of state for a perfect gas:

$$M_p = \frac{\rho_p T_p R_u}{P_p} , \tag{15}$$

where T_p and P_p are the temperature and pressure of the pyrolysate at which the density ρ_p has been determined, and R_u is the universal gas constant.

Summary

Equation (15) is the equation that was used in calculating the molecular weight of the pyrolysate, and equation (11) was used to calculate the mass fraction of the pyrolysate. As stated before, the ignition temperature for each fuel composition tested was defined to be the temperature registered by the emf response of the centerline thermocouple in the ignition tube when the thermocouple showed a sudden change in its emf.

CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION

In the previous three chapters, the Lower Ignition Temperature and Concentration Apparatus (LITACA), its operating procedures, and methods of data reduction have been described. The results of ignition tests run on LITACA for propane and three cotton fabrics will now be presented and discussed.

Propane Tests

Ignition temperatures of a number of propane-dry air mixtures were determined with LITACA. The data is given in Table 3 and shown graphically in Figure 8.

Scott, et al. [15], using the modified drop method described on the literature survey of Chapter I, measured a minimum ignition temperature for propane in air of 493°C. This is 173°C lower than the minimum ignition temperature of 666°C determined by LITACA. One possible reason for this difference is the quenching effect of the quartz tube bundle on the mixture. For the tests shown in Table 3, the tube bundle was 3 cm long. This tube bundle was then replaced bu a tube bundle 8 cm long, and the tests of Table 3 were rerun. The resulting minimum ignition temperature was 714°C, which is a 48°C increase over the shorter tube bundle. If

Table 3. Propane Ignition Temperature Data for B^{*}=0.811

Dry Air, G_{ca} SCCM	Propane, G_{cp} SCCM	Mass Fraction of Propane, χ_p	$T_{ignition}$ °C
90	7	0.087	693
90	4	0.051	666
110	4	0.042	670
130	4	0.036	673
180	4	0.026	681
235	4	0.020	690
280	4	0.017	698
330	4	0.014	704
375	4	0.013	712

$$^{*}B = \left[\frac{M_a\ T_p}{M_p\ T_a}\right]^{\frac{1}{2}}, \text{ Eqn.(13) and}$$

$$\chi_p = \frac{1}{1 + (G_{ca}/G_{cp})B}, \text{ Eqn.(11).}$$

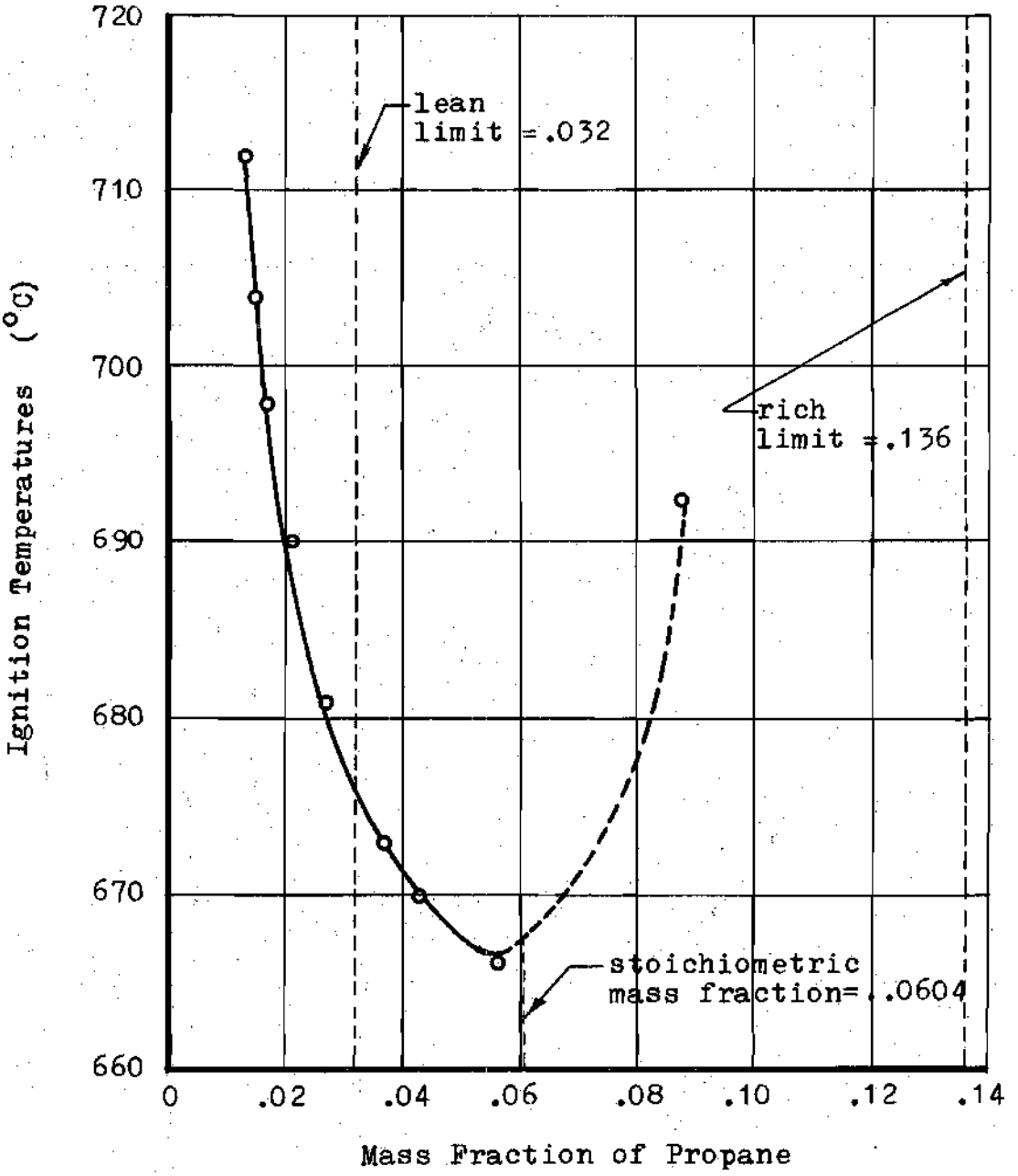


Figure 8. Ignition Temperatures of Propane-Air Mixtures. Lean and rich limits were taken from Reference [24].

the quenching length of the tubes were an important variable, this result would be expected.

The stoichiometric mass fraction for propane and air is 0.0604. It can be seen from Figure 8, that the minimum ignition temperature occurs near this stoichiometric value.

Jones and Scott [24], using the U. S. Bureau of Mines apparatus described in the literature survey of Chapter I, report the flammability limits of propane in air to be 2.15 and 9.05 per cent by volume for the lean and rich limits respectively. Converting these volume per cents to mass fractions, they become 0.0323 for the lean limit and 0.136 for the rich limit. The asymptotes for the U shaped curve in Figure 8 correspond to the lean and rich limits of flammability. This curve appears to be approaching a lean limit asymptote on the order of 0.01 and a rich limit asymptote on the order of 0.10. Therefore, in the case of propane at least, LITACA predicts lean and rich limits lower than that of the U. S. Bureau of Mines data.

Pyrolysate Tests

Ignition tests were run on three 100% cotton fabrics. Two of the fabrics tested were among those selected by the Government-Industry Research Committee on Fabric Flammability (GIRCFF). They were:

(i) GIRCFF No. 5, a white jersey T-shirt, and

(ii) GIRCFF No. 4, a blue denim fabric.

Properties of these fabrics can be found in Reference [8]. The third fabric tested was a 100% cotton, specially prepared by Dr. Wayne Tincher of the School of Textile Engineering at Georgia Tech such that no chemical additives were used during its fabrication. For purposes of identification, this fabric will be called Fabric A in this thesis.

In the initial tests on the cotton fabrics, the author was unable to get self-ignition of pyrolysate-air mixtures. It was believed that the presence of large amounts of water vapor in the pyrolysate products inhibited ignition; therefore, a cold trap type condenser was installed in the plumbing system between the accumulator manifold and the inlet to the pyrolysate flow meter. The cold trap consisted of a hollow glass sphere approximately three inches in diameter with inlet and exit glass tubes. This sphere was immersed in an ice-water bath. The ignition temperature data for pyrolysates reported in this thesis are for gas mixtures which have had condensibles removed by this cold trap.

Table 4 shows the results of the density measurements taken during the three fabric tests. The subscripts w and d designate, respectively, with and without condensibles present in the pyrolysate. The values of M_d were used in equation (13) when calculating the pyrolysate mass fractions. In an initial test with Fabric A in which ignition tests were not run, M_w was measured at 43.5 and M_d was found to

Table 4 . Average Molecular Weights of Pyrolysates.

Fabric Description	Molecular Weights	
	M_w*	M_d**
Fabric A 100% Cotton***	37.4	15.0
GIRCFF No.5 100% Cotton T-Shirt	36.2	37.7
GIRCFF No.4 100% Cotton Blue Denim	48.8	39.4

*With condensibles present in pyrolysate

**With condensibles removed from pyrolysate

***No chemical additives were used in the preparation of this fabric.

be 17.2.

Table 5 presents the data for the ignition tests run on GIRCFF No. 5. Figure 9 is a graphical representation of the data on GIRCFF No. 5. Table 6 and Figure 10 give the data for GIRCFF No. 4, and Table 7 and 8 and Figure 11 show the results of the tests on the Fabric A.

Ignition temperatures for GIRCFF No.'s 4 and 5 are reported in Reference [7] for both self- and pilot-ignition. The reference describes how a Setchkin furnace was used to obtain these temperatures for the fabric itself. For GIRCFF No. 4 the self-ignition temperature was found to be 288°C and to be 314°C for GIRCFF No. 5. From Figures 9 and 10, it can be seen that the self-ignition temperatures of the fabrics are much lower than that of their pyrolysates as measured by LITACA. The author believes that the quenching effect of the quartz tube bundle may be responsible for much of this large difference in temperature.

With the propane tests, ignition was determined by the onset of a popping noise inside the Reaction Cell. No such sounds were heard while running ignition tests on the pyrolysate; however, ignition could be determined by recording the centerline thermocouple on a Leeds and Northrup Speedomax recorder. At the point of ignition, large fluctuations in the thermocouple's output were observed. A typical centerline thermocouple ignition response is shown in Figure 12. In both the propane and pyrolysate tests, no

Table 5. GIRCFF No.5 Ignition Temperature Data for B^{*}=.927

Dry Air, G_{ca} SCCM	Pyrolysate, G_{cp} SCCM	Mass Fraction of Pyrolysate, χ_p	$T_{ignition}$ C
130	19.7	0.140	757
90	19.7	0.191	738
130	22.7	0.158	740
130	26.0	0.177	736
130	29.7	0.197	720
130	33.0	0.215	715
130	35.0	0.225	713
130	44.5	0.269	701
130	54.0	0.309	685
130	64.5	0.348	684
130	75.0	0.383	702
130	86.0	0.416	720
130	110.0	0.477	730
90	86.0	0.507	745

$$^{*}B = \left[\frac{M_a\ T_p}{M_p\ T_a}\right]^{\frac{1}{2}}$$, Eqn. (13) and

$$\chi_p = \frac{1}{1 + (G_{ca}/G_{cp})B}$$, Eqn.(11).

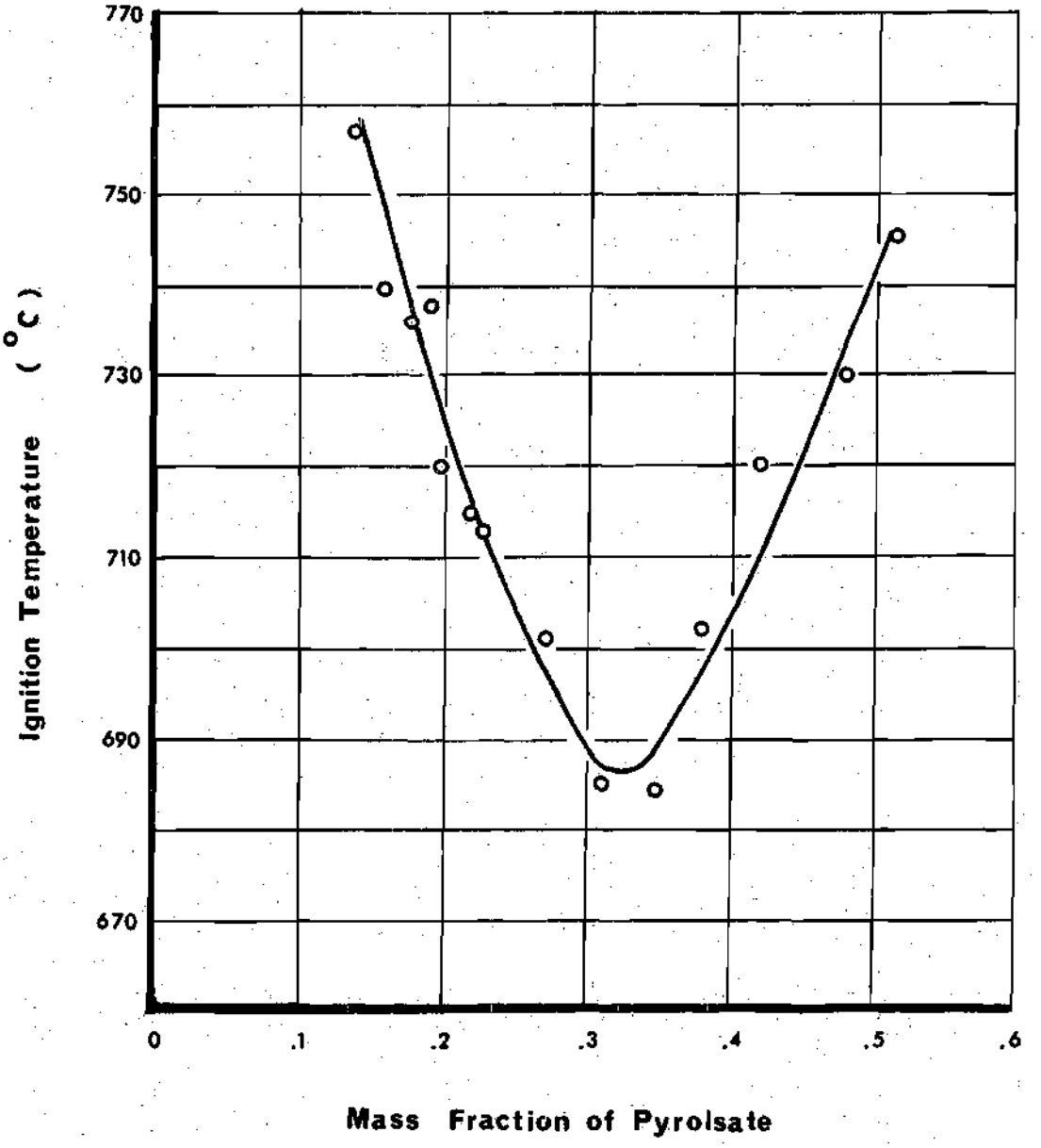


Figure 9. Ignition Temperatures of GIRCFF No. 5 Pyrolysate-Air Mixtures.

Table 6. GIRCFF No.4 Ignition Temperature Data for $B^{*}=.906$

Dry Air, G_{ca} SCCM	Pyrolysate, G_{cp} SCCM	Mass Fraction of Pyrolysate, x_ρ	$T_{ignition}$ °C
52	26.0	0.356	716
70	26.0	0.291	721
90	26.0	0.242	729

$$^{*}B = \left[\frac{M_a\ T_p}{M_p\ T_a}\right]^{\frac{1}{2}}, \text{ Eqn.(13) and}$$

$$x_\rho = \frac{1}{1 + (G_{ca}/G_{cp})B}, \text{ Eqn.(11).}$$

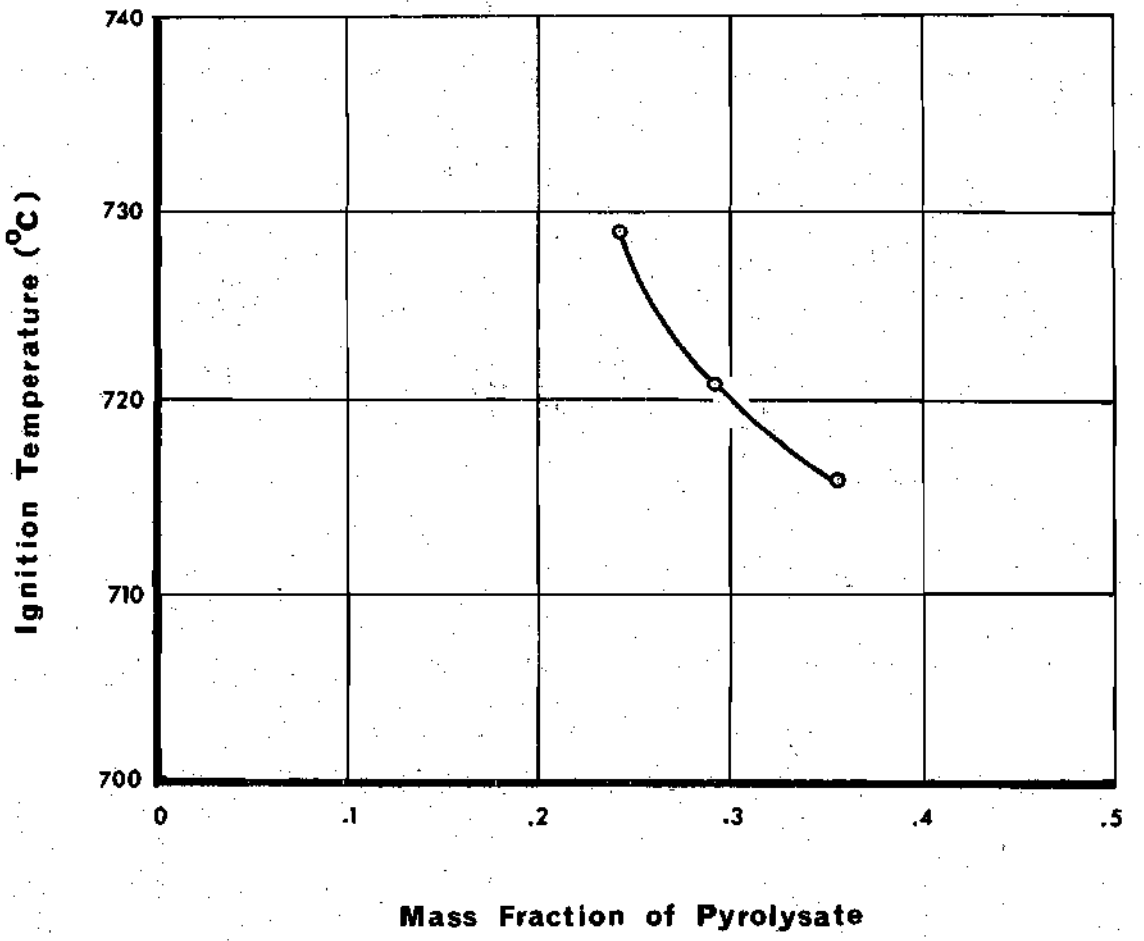


Figure 10. Ignition Temperatures of GIRCFF No.4 Pyrolysate-Air Mixtures.

Table 7. Fabric A** Ignition Temperature Data for $B^* = 0.996$

Dry Air, G_{ca} SCCM	Pyrolysate, G_{cp} SCCM	Mass Fraction of Pyrolysate, χ_p	$T_{ignition}$ C
180	33.0	0.156	692
235	30.0	0.114	709

Table 8. Fabric A** Ignition Temperature Data for $B^* = 1.45$

Dry Air, G_{ca} SCCM	Pyrolysate, G_{cp} SCCM	Mass Fraction of Pyrolysate, χ_p	$T_{ignition}$ C
375	55.0	0.092	714
375	65.0	0.107	712
375	55.0	0.092	712
375	45.0	0.076	716

$$^*B = \left[\frac{M_a \, T_p}{M_p \, T_a} \right]^{\frac{1}{2}}$$, Eqn. (13) and

$$\chi_p = \frac{1}{1 + (G_{ca}/G_{cp})\,B}$$, Eqn. (11).

**This fabric is a 100% cotton which was specially prepared by the School of Textile Engineering such that no chemical additives were used during its fabrication.

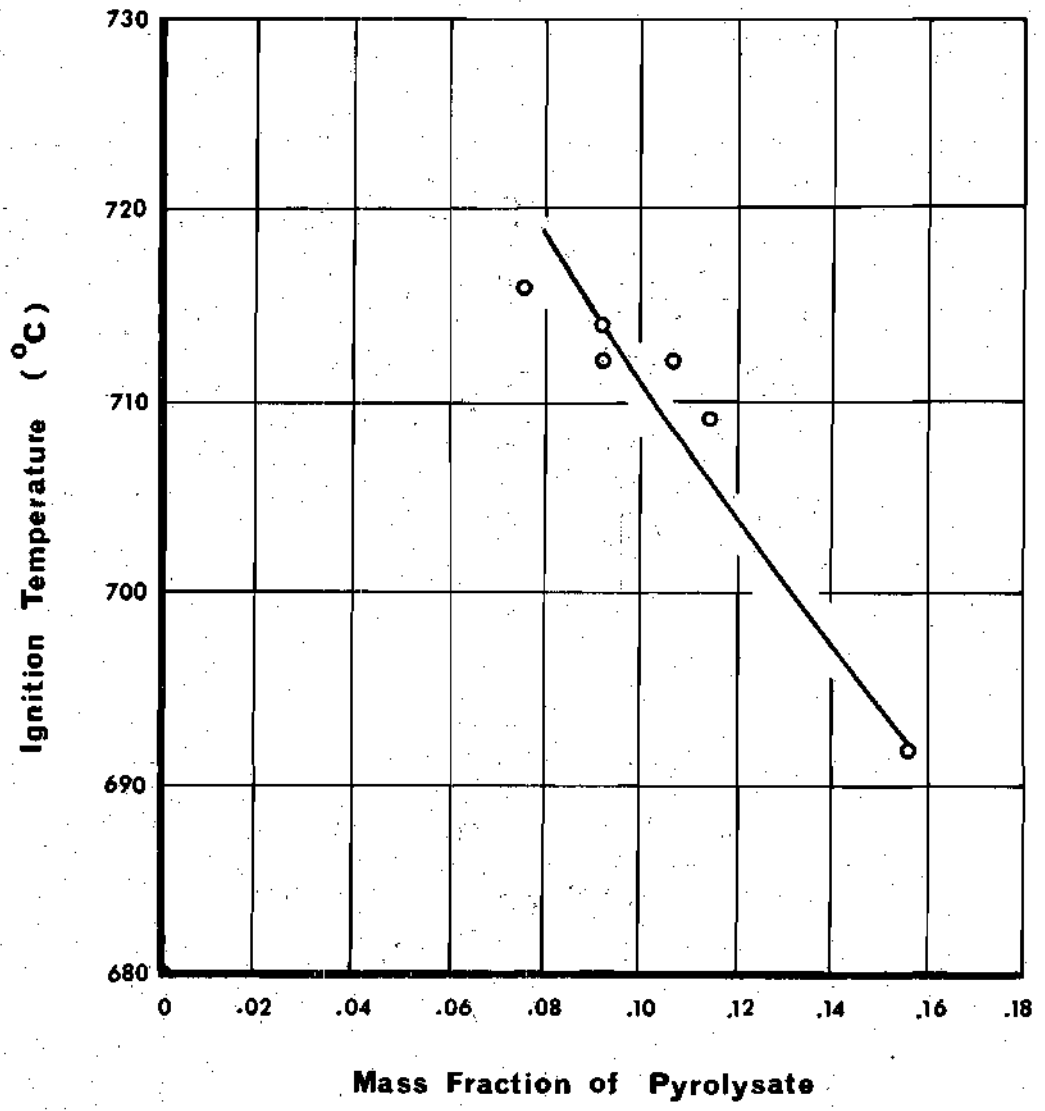


Figure11. Ignition Temperatures of Fabric A Pyrolysate-Air Mixtures.

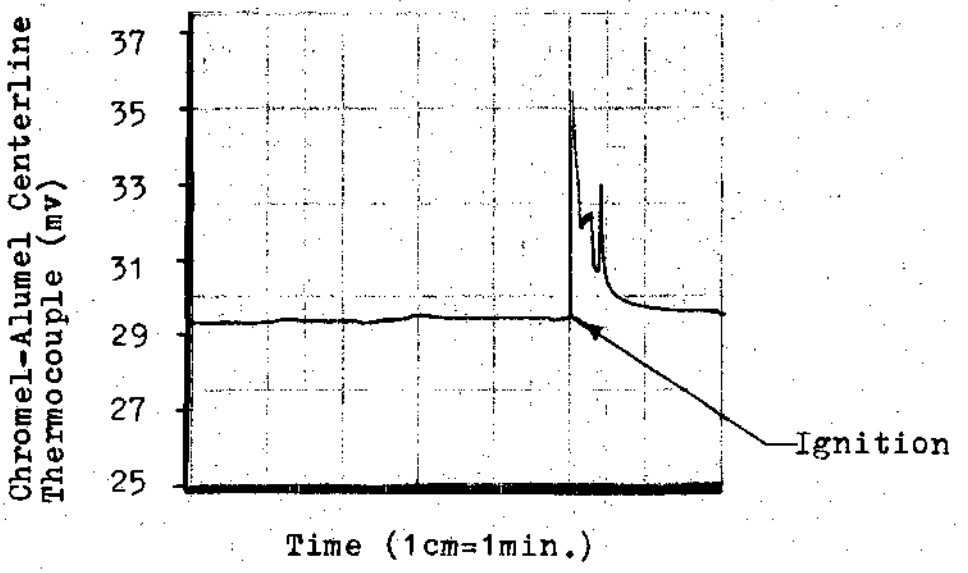


Figure12. Typical Ignition Signal. Centerline Thermocouple emf versus Time.

response was observed from the Ni-resistance thermometer at ignition. When propane tests were run with the longer tube bundle, described earlier in this chapter, a sharp rise in resistance was observed at the point of ignition. This longer tube bundle was not used in later tests because of the high ignition temperatures it measured.

All of the cotton fabrics were pyrolyzed at a furnace temperature of 360°C. The temperature was selected because according to Schwenker and Pacsu [25], in their work on the pyrolytic degradation of cellulose, true pyrolysis was found "to begin at 250°C and adjuged complete at 360°C."

Estimation of Experimental Error

Mass Fraction Determination

Estimates will now be given for the accuracy of the measurements taken to determine the mass fraction of fuel.

The flowmeters can be read within an accuracy of $\pm$2.5 SCCM for the air flow and $\pm$0.5 SCCM for the fuel. The inlet temperatures are known within $\pm$1°C for both flowmeters. When equation (11) was partially differentiated, and the above error estimates along with a data point from the Fabric A cotton were substituted into the resulting equation, an estimate for the error in the value of the fuel mass fraction was calculated to be 0.001 or $\pm$0.0005.

Ignition Temperature

The centerline chromel-alumel thermocouple in the ignition tube can be read with an accuracy of $\pm$5°C.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The objective of this thesis was to develop an apparatus and the experimental techniques which will measure the ignition temperatures of pyrolysate-air mixtures as a function of the concentration of pyrolysate. The Lower Ignition Temperature and Concentration Apparatus (LITACA) as described in this thesis meets this objective.

The tasks of design, construction, and successful testing have been achieved. LITACA can be used to:

(i) thermally decompose pyrolyzing materials,

(ii) store the pyrolysates,

(iii) mix pyrolysates with dry air at controlled concentrations,

(iv) measure the minimum ignition temperature at various concentrations of pyrolysate, and

(v) measure the density of pyrolysate for molecular weight determinations.

It is recommended that further study be carried out on LITACA to determine the effect of the quenching length of the quartz tube bundle. The author also believes that since ignition was not obtained with the complete pyrolysate composition, further ignition temperature studies should be

carried out with the different components of the pyrolysis products.

APPENDIX

SAMPLE CALCULATIONS

This Appendix contains sample calculations for a data point with GIRCFF No. 5.

The following calculations were performed on test data taken from ignition experiments run on GIRCFF No. 5.

Molecular Weight Calculations

A sample of the pyrolysate was taken from the downstream side of the cold trap. This sample and glass balloon container were placed in a preheated drying oven for a period of two hours. At the end of that time the temperature inside the oven was measured and found to be 407°K. When the gas sample was removed from the oven, the stopcock was opened and closed quickly to allow the pressure of the pyrolysate to assume barometric pressure. The barometric pressure was measured on a mercury barometer and found to be 29.14 inches of Hg or 0.974 atmospheres. The volume of the glass balloon had been previously determined to be 0.1862 liters. A Christian Becker analytical balance was used to weigh the gas sample which was 0.1910 grams. The density of the gas sample is calculated from equation (14):

$$\rho_p = \frac{0.1910}{0.1739} = 1.098 \frac{\text{grams}}{\text{liter}} .$$

The molecular weight is calculated from equation (15):

$$M_p = \frac{(1.098)(0.08205)(407)}{0.974} = 37.7 \ \frac{\text{grams}}{\text{gram-mole}}$$

Mass Fraction Calculations

The flowmeters were set at the calibrated flowrates of 130 SCCM for air and 22.7 SCCM for the pyrolysate, and ignition occured at a centerline thermocouple output of 30.80 mv which for a chromel-alumel thermocouple is 740°C. The inlet iron-constantan thermocouple at the flowmeters measured 340.0°K for the pyrolysate and 304.5°K for the dry air. From equation (13),

$$B = \left[\frac{(29)(340)}{(37.7)(304.5)}\right]^{1/2} = 0.927 \ ,$$

and from equation (12),

$$\phi = \frac{130}{22.7} = 5.73 \ .$$

Therefore, the mass fraction χ_ρ of pyrolysate is, from equation (11):

$$\chi_\rho = \frac{1}{1 + (5.73)(0.927)} = 0.158 \ .$$

BIBLIOGRAPHY

1. The Report of the National Commission on Fire Prevention and Control, America Burning, U. S. Government Printing Office, 1-2 (1973).

2. Fourth Annual Report by the U. S. Department of Health, Education, and Welfare, "Studies of Deaths, Injuries, and Economic Losses Resulting from Accidental Burning of Products, Fabrics, or Related Materials-Fiscal Year 1972."

3. NBS Technical Note 498, "Bibliographies on Fabric Flammability," February, 1972.

4. Government-Industry Research Committee on Fabric Flammability, "Study of Hazards from Burning Apparel and the Relation of Hazards to Test Methods." A work statement prepared by the Research Committee, Dr. E. Passaglia, Chairman, National Bureau of Standards, June 5, 1970.

5. 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, North Carolina, February 12, 1970.

6. 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 submitted by the School of Mechanical Engineering, Georgia Institute of Technology, to the Government Research Committee, July, 1970.

7. Alkidas, A., Hess, R. W., Wulff, W., and Zuber, N., "Study of Hazards from Burning Apparel and the Relation of Hazards to Test Methods," First Annual Report, NSF Grant No. GK-27189, GIT, Atlanta, Georgia, December, 1971. National Technical Information Access No. COM-73-10954.

8. Alkidas, A., Champion, E. R., Durbetaki, P., Giddens, W., Hess, R. W., Kumar, B., Naveda, O. A. A., 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 No. GI-31882, GIT, Atlanta, Georgia, December, 1972. National Technical Information Access No. COM-73-10956.

9. Durbetaki, P. and Wulff, W., "The Study of Hazards from Burning Apparel and the Relation of Hazards to Test Methods," a research proposal submitted to the National Science Foundation by the School of Mechanical Engineering, Georgia Institute of Technology, September, 1972.

10. Acree, R. L., Champion, E. R., Durbetaki, P., Lee, C. K., Naveda, O. A. A., Wedel, G. L., Williams, P. T., and Wulff, W., "Fabric Ignition," Third Annual Report, NSF Grant No. GI-31882A#1, GIT, Atlanta, Georgia, March, 1974.

11. Setchkin, Nicholas P., "A Method and Apparatus for Determining the Ignition Characteristics of Plastics," Research Paper RP2052, National Bureau of Standards, Vol. 43, 1949, p. 592.

12. 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.

13. Sortman, Charles W., Beatty, Harold A., and Heron, S. D., "Spontaneous Ignition of Hydrocarbons-Zones of Non-Ignition," Ind. and Eng. Chem., Vol. 33, 1941, p. 357.

14. Setchkin, Nicholas P., "Self-Ignition Temperatures of Combustible Liquids," Journal Res. Nat. Bur. Standards, Vol. 53, 1954, pp. 49-66.

15. 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.

16. Dixon, H. B. and Higgins, W. F., "On the Ignition-Point of Gases at Different Pressures," Memoirs and Proc. Manchester Phil. Society (Manchester Memoirs), Vol. 70, 1925-26, pp. 29-36.

17. Tizard, H. T. and Pye, D. R., "Experiments on the Ignition of Gases by Sudden Compression," Phil. Mag. and Journal Sci., Vol. 44, July, 1922, pp. 79-121.

18. Lewis, Bernard and von Elbe, Guenther, Combustion, Flames and Explosion of Gases, Academic Press, Inc., 1951, p. 162.

19. Mason, Walter and Wheel, Richard Vernon, "The Ignition of Gases, Pt. IV Ignition by a Heated Surface. Mixtures of the Parafins with Air," Journal Chem. Soc. Trans. (London), Vol. 127, 1925, pp. 672-684.

20. Coward, H. F. and Jones, G. W., Limits of Flammability of Gases and Vapors, U. S. Bureau of Mines Bulletin 503, 1952.

21. White, A. G., "Limits for the Propagation of Flame in Inflammable Gas-Air Mixtures. III. The Effect of Temperature on the Limits." Journal Chem. Soc. of London, Vol. 127, 1925, pp. 672-684.

22. Egerton, Sir Alfred and Powling, J., "The Limits of Flame Propagation at Atmospheric Pressure. II. The Influence of Changes in the Physical Properties," Proc. Royal Soc. of London, Vol. 193A, 1948, pp. 190-209.

23. Powling, J., "A New Burner Method for the Determination of Low Burning Velocities and Limits of Inflammability," Fuel, Vol. 28, 1949, pp. 25-28.

24. 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.

25. Schwenker, R. F., Jr. and Pacsu, E., "Pyrolytic Degradation Products of Cellulose," Ind. and Eng. Chem., Vol. 2, No. 1, January, 1957, p. 83.