COMPUTER CONTROL AND ON LINE

DATA ACQUISITION FOR

THERMOGRAVIMETRIC

ANALYSIS

By

RAGHUNATHAN LAKSHMANAN

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Bharathiar University

Coimbatore, India

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Thesis Approved:

Arlund H. Johannes

Thesis Adviser

Barry L. Fonte

Martin S. High

Thomas C. Collins

Dean of the Graduate College

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CHAPTER I

INTRODUCTION

Thermogravimetric analyzers (TGA's) are versatile
instruments that have been used for a diverse set of
applications. They have been used to study physical
properties of materials as a function of pressure and
temperature in isothermal and non-isothermal environments.
Examples of some reactions studied using TGA's are
oxidation/reduction, corrosion, decomposition, dehydration,
adsorption, pollution analysis, surface tension, thermal
degradation of polymers, etc.

Thermogravimetry(TG) is a technique whereby the weight
of a substance in an environment, heated or cooled at a
controlled rate is recorded as a function of time or
temperature. Thus, the two basic requirements of TG are a
method of heating or cooling and a means of weighing. TG
has been developing over a number of years as a research
tool for characterizing weight loss behavior of organic,
inorganic and polymeric materials. TG is being increasingly
used as a rapid automated gravimetric separation technique
The basic instrumental requirements for TG are :
a precision balance with a control unit and a furnace with a
programmable temperature controller.

Recently, Cahn Instruments has developed very sophisticated high pressure and high temperature TGA's. The high pressure(Cahn 1100) and the low pressure(Cahn 2000) TGA's combined together can be used to study all of the above reactions, both under high and low pressures and at temperatures ranging from ambient upto 1000°C. The new high pressure TGA permits studies ranging from vacuum (10^{-5} torr) up to 1500 psi covering both the critical and the supercritical regions too. Previously, low pressure data was extrapolated to explain the kinetics of the high pressure processes, usually without any success. The high pressure TGA now eliminates this problem.

The analog outputs coming from the TGA's are nothing but just a continuous voltage signal that is directly proportional to the weight change of the sample, being analyzed. When connected to a strip chart recorder, a plot is made out of this raw data from the system. This has major limitations. Extra data manipulations such as interpolations and derivatives have to be calculated and plotted manually. This is time consuming and highly imprecise. To overcome this limitation, the output signal from the TGA can be interfaced to a computer.

Therefore, the objectives of this study are:

1) to set up the high pressure TGA along with its control unit,

2) to interface the low pressure and the high pressure TGA's to a computer and perform online data

acquisition, and

3)   to test the TGA's and online data acquisition system using thermal degradation of polyethylene, which is the standard test procedure.

CHAPTER II

LITERATURE REVIEW

The recent trend in laboratory data acquisition has been towards automatic control of experiments, digitization and computerized reduction and storage of data. As the cost of personal computers has continued to drop, their use in laboratory applications has risen. Their flexibility makes them a highly desirable piece of equipment to have in a modern day laboratory.

Computer interface studies on TGA's have been carried out since the early 70's. Kleineberg et al. (1) carried out a kinetic study on the thermal degradation of high polymers, utilizing a computerized thermogravimetric analyzer - mass spectrometer system. A HP 2100A computer with a 4K 16 bit word core memory and a digital tape unit with 9 tracks for storage of data was used. A software package, which consisted of basic routines for acquiring and processing of the data was also used along with a HP programmable calculator to study the kinetics of the degradation. They concluded that the results from the data acquisition study, were good enough to characterize the complex reaction.

Cassel and Gray (2) used a Tektronic 31 programmable calculator to interface a differential scanning calorimeter and a TGS-2 TGA for polymer characterization studies.

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Programs were developed for sample purity and thermal stability determination, statistical treatment, curve fitting and plotting of data. They encountered data storage problems before sufficient data had been collected.

Ulerich et al. (3) coupled a DuPont 951 thermobalance controlled by a console to a data acquisition system, that was controlled by a Mostek microprocessor. They collected data from the system to study the effects of pore volume-pore size distribution on the sulfation of calcined limestone. The microprocessor was programmed by a calculator to control the flow of weight and temperature data. A multichannel interface was used where the signals were digitized. The calculator was equipped with a 16K of memory and cassette tapes were used to store the data.

With the advent of inexpensive microprocessors, and support circuits, it became possible to dedicate low cost programmable machines to experiment control, data acquisition and simple data processing. Taylor et al. (4) published the hardware design and software of the programmable laboratory equipment controller (PLEC), and its advantages. The system consisted of an Intel 8080A 8 bit microprocessor CPU with 1024 of RAM. He used a board containing an additional 2048 bytes of RAM to increase the program and data storage capacity. A paper tape puncher was used for recording the data. An 8-bit successive approximation A/D converter was used to allow the analog signal input to the PLEC. This configuration worked

successfully for lab controlled experiments. He concluded that the 8-bit resolution limited the accuracy of the system and suggested using a 12-bit A/D for higher resolution and accuracy.

Danielson et al. (5) developed a general purpose interface for minicomputers, oriented towards laboratory data acquisition and experimental control applications. FORTRAN, for the first time was used as a compatible interface language. Their design eliminates the need for the user to have a prior knowledge of the interface electronics. The interface used a 16 channel analog multiplexer with a 6 µsec, 12-bit A/D converter. They achieved a higher resolution than past studies using an 8-bit board. FORTRAN was preferred over other languages, because of its greater speed and capability of adding very fast assembly language subroutines. The interface worked well in many different applications.

Chadwick and Bernasek (6) used a minicomputer for the first time to carry out thermal desorption studies on molybdenum crystals. They had a data acquisition chassis consisting of a 12-bit A/D board with a 16 channel multiplexer. By this time, the use of a multiplexer along with an A/D board had become very effective and efficient. Software for the interface was written in assembly language. With this system, it was possible for them to obtain a great deal of accurate and reproducible thermal desorption data from complicated heterogeneous systems.

The use of a microprocessor controller to direct changes in temperature and pressure allowed a new dimension in TG analysis. In their second paper, Cassel and Gray (7) describe a new microprocessor controlled TGA from a hardware standpoint. They used a Perkin Elmer TGA with a System 4 microprocessor controller. They studied the gravimetric separations of volatiles, organics and fillers in polymers. Some of the new advancements done in the control were multiple step programming, automatic purge change over, automatic temperature calibration and recall of stored data. They confirmed the capability of their microprocessor controller and concluded that it was faster, simpler and more reliable than past methods.

Gardner et al. (8) reviewed the thermogravimetric measurement techniques at high pressures. They developed a thermobalance capable of operation at temperatures upto 1370 K and pressures upto 100 atm. They interfaced it to a HP 3000 minicomputer and used a microprocessor to provide data acquisition and control and thus, serve as a communication link between the experiment and the computer. This was the first time an interface with a high pressure TGA was attempted.

Tsung et al. (9) added a new phase to the TGA interface world by using mainframe computers for the first time. They used a Motorola 6800 microprocessor for control and data acquisition of a DuPont 951 TGA which was used as a microreactor to study the gas/solid reaction kinetics of

coal combustion and sulfation of lime. The interface was equipped with an 8 channel 12-bit A/D board with an analog multiplexer. Modems were used to establish communication with the mainframes. Programs for the interface were written in assembly language because they tend to occupy 30% less memory than the other high level languages. They concluded that the inherent flexibility of the TGA could be used to interface with future generation computers for small lab experiments.

After this work, other researchers started working on interfacing the TGA's with other different instruments. Prime and Shushan (10) coupled a mass spectrometer with a TGA and performed data acquisition analysis using a minicomputer. Graphics packages were used for the first time to analyze the data. Filsinger and Bourrie (11) followed the interface work with an integrated thermal and IR spectral analyzer. Many other computer interface studies were carried out later by Parker et al. (12), Zhang et al. (13), and Parlouer et al. (14) with the TGA's, and all of them described the ease and efficiency of handling the digitized data resulting from the conversion.

All of the above studies show that by providing direct digitization and storage of data for further analysis, one can eliminate tedious and imprecise conventional data handling problems and thereby achieve an overall higher accuracy with the modern day data acquisition and computer control systems. This idea forms the objective of my

experimental undertaking to interface both a low pressure and a high pressure TGA simultaneously to a computer. This work will enable one to carry out both high pressure and low pressure experiments easily and effectively. An IBM PC AT has been used for the first time to carry out this interface work in a lab scale environment. The data acquisition and control software Labtech Notebook was used for the interface and analysis work.

Thermal degradation experiments on polyethylene were carried out as a standard test procedure for the TGA's. A kinetic study on the thermal degradation reaction of polyethylene has been carried out by Anderson and Freeman (19).

CHAPTER III

DATA ACQUISITION AND CONTROL

Data acquisition systems interface between the real world of physical parameters which are analog and the artificial world of digital computation and control. The devices which perform the interfacing function between the analog and digital worlds are the analog to digital (A/D) and the digital to analog (D/A) converters. Together they are known as data converters.

Theory of Data Acquisition System

The input to the system, physical parameters like temperature, weight and pressure, are analog quantities. They are first converted into an electrical signal by a transducer. Once in electrical form, all further processing is done by electronic circuits. Next, an amplifier boosts the amplitude of the output signal from the transducer. The active filter then takes this signal and eliminates any interference noise and smooths the data. The processed analog signal is next sent to a multiplexer which sequentially switches between a number of different analog input channels as shown in Figure 1.
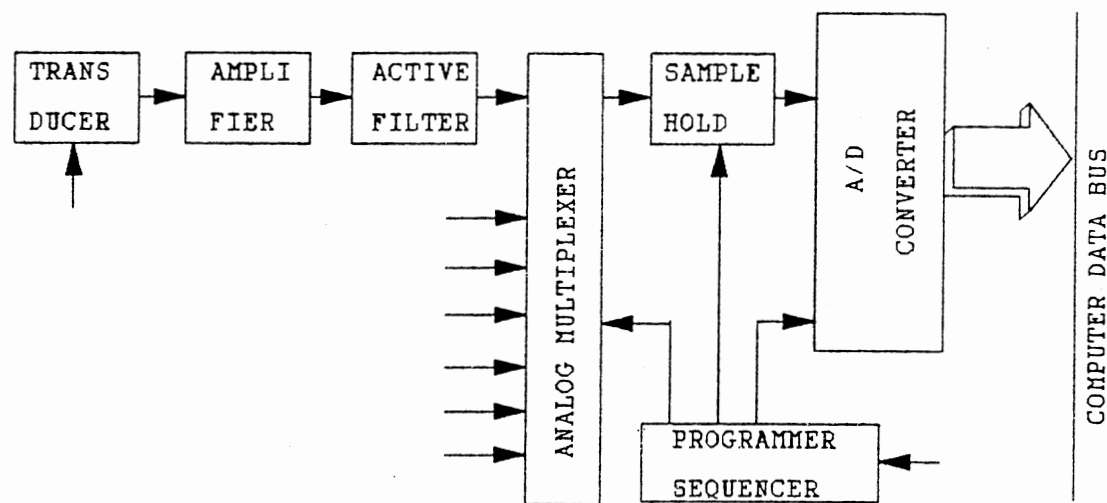
Figure 1.   Data Acquisition System

Each input is then in turn connected to the output of the multiplexer for a specified period of time by the multiplexer switch. During this connection time, a sample hold circuit acquires the signal voltage and holds its value, while an A/D converter converts the value to digital form. The resultant digital word is then sent to a computer data bus. Thus, the analog multiplexer together with the sample hold shares the A/D converter, with a number of analog input channels. The timing and control of the complete data acquisition system is done by a digital circuit called a programmer sequence which in turn, is under the control of the computer.

CHAPTER IV

INSTRUMENTATION

Low Pressure TGA

The heart of the Cahn Low Pressure TGA System 113 is the Cahn Recording Electrobalance. When high sensitivity with small samples is required, the Cahn 2000 Electrobalance is the balance of choice, and is the main unit of Cahn TGA System 113. The electrobalance is a very sensitive weight measurement device. It is designed for weight up to 2.5 grams and is sensitive to weight and force changes as small as 0.1 µg. The instrument contains two units - the control unit and the weighing unit. In brief, it converts a weight change into an electrical signal, which can be read from a digital output.

The system consists of an external microprocessor controlled furnace with a temperature programmer, called the Micricon, which ensures accurate digital control of the sample temperature, and offers good programming flexibility. The furnace can operate from below $100^{\circ}C$ up to $1100^{\circ}C$. A type K Chromel-Alumel thermocouple, positioned below the sample pan of the balance, monitors the temperature at the sample and by a feedback system controls the furnace. The

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system operates in pressures as low as 10^{-4} to 10^{--5} Pa (10^{-6} to 10^{-7} torr).

The control unit of the Cahn 2000 electrobalance includes a TDC, ARE and a strip chart recorder. The TDC, which is the time derivative computer, is designed to convert the weight change signal to the rate of weight change with respect to time signal. The ARE (automatic range expander) keeps the output between two fixed limits and the percentage sample weight attachment simply outputs the weight change as a function of % weight loss or gain.

High Pressure TGA

Unlike the low pressure TGA System 113, the Cahn's High Pressure TGA does not have a built-in furnace and a microprocessor controlled temperature programmer. The following units were assembled together to make up the high pressure TGA as shown in Figure 2:

1) a Cahn C1100 Pressure Balance which consists of a C1000 Recording Balance and a pressure housing,

2) a special high pressure stand,

3) a single zone vertically mountable split tube furnace,

4) a standard one channel Micristar temperature controller, and

5) a single phase power controller.

THE C1100 Pressure Balance can be used for the analysis of high mass samples under high pressures and high temperature conditions. The operating features include:

- Vacuum capability up to 10^{-5} torr.

- Pressures up to 107 atm.

- Temperatures up to 700°C.

- Solid control of the Cahn 1000 balance allows up to 100 grams maximum capacity.

- 0.1 mg sensitivity at high temperatures and pressures.

- 10 µg sensitivity at normal conditions.

The C1100 Pressure Balance consists of two sections. One is the control unit where all the controls and outputs are maintained. The other section is the weighing unit which detects the actual weight or force. This section may be operated in a variety of environments such as vacuum, flowing gas, or atmospheric conditions.

The C1100 Balance is a force to current converter consisting of a balance beam mounted to, supported by and pivoting about the center of a taut ribbon, a torque motor coil located in a permanent magnetic field and mounted to the taut ribbon, sample suspension fixtures, a beam position sensor system and controls. It also includes a long reactor tube of about 92 mm on the sample side of the beam and a small counter weight compartment on the tare side. The whole weighing unit is enclosed in a housing and secured to a leveling plate with socket screws.

The whole assembly weighs about 50 lbs. The reactor tube has openings for vent at the top and for reaction gas and thermocouple feed at the bottom. The weighing unit is connected to the control unit through a connecting cable.

The control unit of the Cahn 1000 is very much the same as that of the Cahn 2000. It has three analog outputs of 1, 10, and 100 mv. When interfacing into a digital readout, the 100 mv output of the C1000 was used, because of the restriction of the DAS-8 board's capability in handling the input analog voltage.

Some of the controls of the C1000 are:

OUTPUT SWITCH: This switch is used to indicate a reading from the balance.

COARSE ZERO: This control is used to electrically tare out a significant weight value.

MRR RANGE: This is the meter and recorder range which determines the amount of weight that is displayed across the control unit meter.

WS RANGE: This is the weight suppression range, which determines the maximum amount of weight that may be suppressed electrically with the WS switch. This is digital and allows any desired fraction of any sample weight to be suppressed, so that the remaining can be blown-up and displayed full scale.

High Pressure Stand

This is a three legged stand that holds the whole balance assembly. It also aids in the centering of the sample pan and the hangdown wire. The legs of the stand

need to be set in boxes filled with sand, which helps in absorbing all the high frequency vibrations of the floor.

Split Tube Furnace

This is a single zone vertically mountable unit. It can heat up to $1900^{o}F$ ($1037^{o}C$) and has provisions for holding the long reactor tube of the C1100 Pressure Balance.

Micristar Temperature Controller

This is a standard one channel, digital PID (proportional, integral and derivative) heat processing controller, designed to provide closed loop control with thermocouple inputs. It has two panels - an outer operator panel and an inner primary panel. The operator panel displays the parameters and the status of events.

The primary panel permits all operator panel actions plus allows one to program a recipe and change the configuration of the controller. This temperature controller is specified for the K-type thermocouple with an input range from $-26.6^{o}C$ to $1371.5^{o}C$.

The Micristar temperature controller contains three circuit boards. They are the input/output board, the cpu board and the power supply board. There are four analog output types available on the input/output board. The controller can be configured for an auto start, where one can prevent the Micristar from returning to its default conditions if power is lost or removed. The controller

control unit
cahn 1000

control unit
Cahn 2000
system 113

system 113

exp-16

c-1800 cable

das-8

notebook

high pressure tga

(1) tripod stand

(2) furnace

(3) reactor tube

(4) sample pan

(5) k-type t/c

(6) power controller

(7) temp. controller

low pressure tga
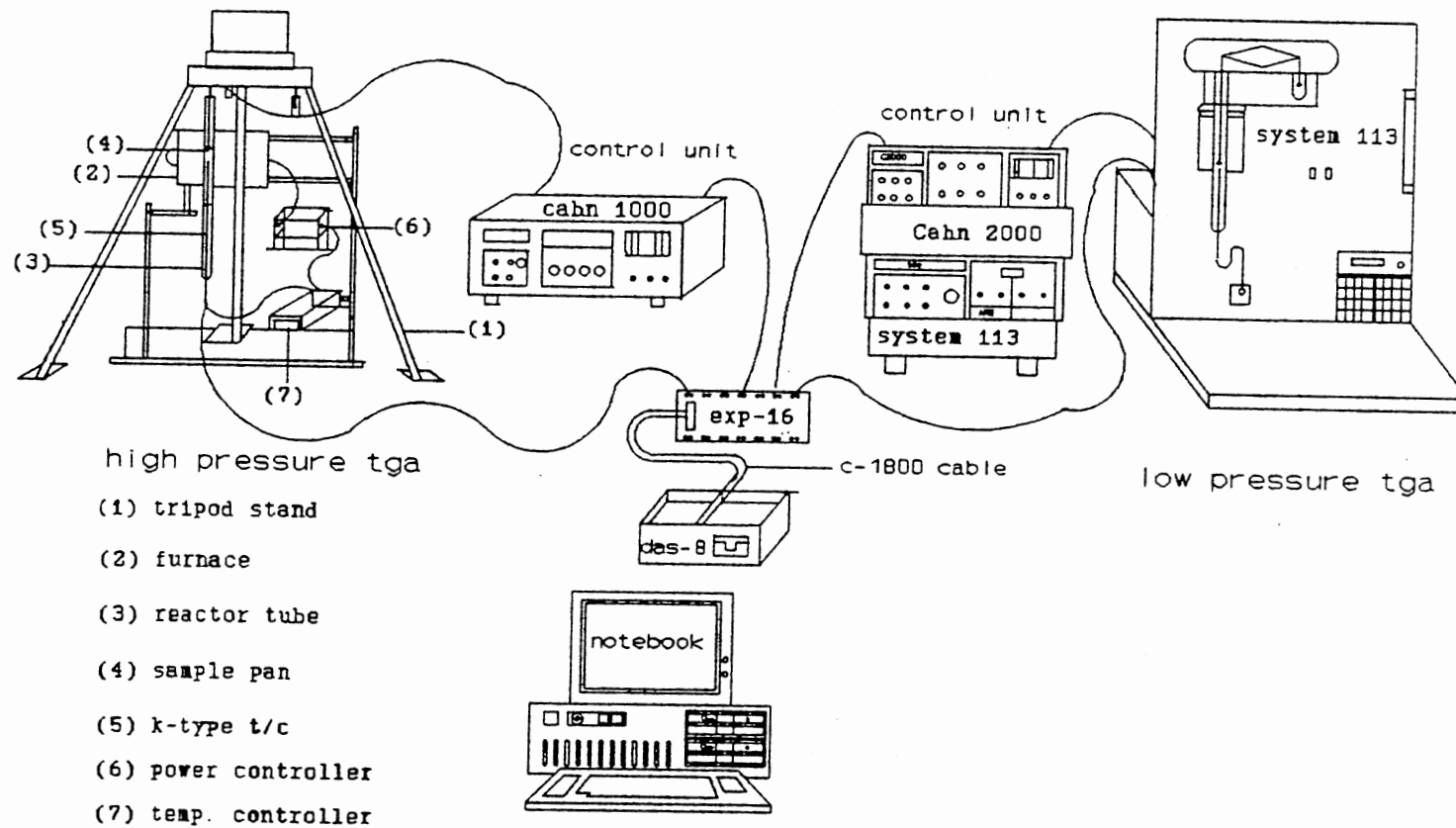
Figure 2.   Experimental Setup of the TGA Systems.

provides the PID control with direct, reverse or bimodal control action. The gain, reset and the rate values respectively define the PID control parameters - proportional, integral and the derivative, which are essential for the fine tuning of the setpoint control action. Finally, the temperature controller is capable of being programmed to carry out a planned recipe.

Power Controller

This is a single phase power controller, designed to control power from an a.c. source. It uses silicon controller rectifiers (SCRs) to control power to the load (which is the furnace in the experiment). It derives its operating power from the control signal (which is the Micristar temperature controller in the experiment).

CHAPTER V

EXPERIMENTAL SETUP

The first instrument to be installed was the Cahn 2000 Low Pressure TGA System 113. The unit was mounted on a marble table and the leveling screws at the base were adjusted to ensure that the whole unit was straight and uniform. The weighing unit was connected to the control unit using the provided cable. Hangdown wires were then installed on both the sample and tare sides of the balance. Sample pans were then let hang from both the hangdown wires. The balance was then warmed for about two hours to avoid frequent recalibration and rezeroing. Zeroing of the balance was then performed to achieve an equilibrium state of the balance. This was done using the zero controls provided.

The next instrument to be installed was the Cahn C1100 Pressure Balance. The high pressure balance stand was first assembled. Three sand boxes were made to hold the legs and they were then filled with sand upto 5 inches to absorb the vibrations from the floor. The weighing unit was then removed and the balance assembly was opened. The hangdown ribbons were then installed on both sides of the beam. The weighing mechanism was then closed. The leveling plate was then placed on the top of the stand and positioned

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accordingly by adjusting the three leveling screws. The weighing mechanism was secured to the base plate, which in turn was secured to the bottom plate. All the socket screws were tightened and the unit was tested for leaks. Using a nichrome wire, a long hangdown was cut with a pliers and a 45 degree hook was made at both the ends of the wire. The wire was attached to the hangdown hook of the sample side. A smaller length wire was cut and attached to the tare side of the beam. Stainless steel pans were then hung from each of the hangdown wires and the leveling screws were adjusted to make sure that the wires appeared perpendicular to the leveling plate. The long reactor tube was then installed using the couplings and fittings to the sample side. The counter weight compartment was then attached to the tare side of the beam. This completed the main installation of the Cahn C1100 Pressure Balance.

Next, an angular iron structure was built to house the split tube furnace, the power controller and the temperature controller. We had to make sure that the center of the long reactor tube was within the furnace to ensure that the sample is being uniformly heated. So, to accomplish this, we had to lift the furnace. This was done by adding thick long wooden slabs to the legs of the angular iron housing. The furnace was then secured to the housing and provision was made for opening the doors of the furnace to freely access the reactor tube. The power controller was then installed on the bottom floor of the housing. Holes were

drilled on the floor to permit free ventilation. The furnace (load) was then connected to the power controller and its power supply lines were also connected. A slot was cut in the front bottom of the housing to hold the Micristar temperature controller.

The temperature controller's connections were next. The input/output(I/O) board was removed from the controller and the jumpers were set for the (0-20) mA analog output configuration. The board was then replaced and the front panels were closed. The back panel of the Micristar temperature controller was then opened to work on the wiring connections. The AC power line connection was made. The positive and negative leads of the K-type thermocouple wire were connected to the input terminals of the controller PV1 and PV2. The other end of the thermocouple goes into the bottom feedthrough of the reactor tube to measure the temperature of the sample. The control signal connection was the last to be made, which connects the power controller and the control output of the temperature controller. Having completed the whole installation of the high pressure unit, the weighing unit was finally connected to the control unit C1000 through the connecting cable.

Computer Interface of the TGA's

An IBM PC AT computer was used for the interfacing of the thermogravimetric analyzers. The interface was used for recording temperature, weight and time data from the Cahn

C1000 and the Cahn C2000 recording balances. Labtech Notebook software provided the interface between the computer and the TGA's. Labtech Notebook was designed to work with a variety of Metrabyte's data acquisition and control boards. Thermocouple measurements are among the most common of all data acquisition inputs. We used the Metrabyte's DAS-8/EXP-16 boards for providing the hardware interface.

Specifications of the computer

The computer used was an 80286 machine with an 80287 math coprocessor and an EGA video adapter. It had one parallel port and two serial ports. The AT class computer has a total conventional memory of 640 K and 384 K of extended memory.

Metrabyte's das-8 board

This is an 8 channel, 12 bit high speed A/D converter and timer/counter board for the IBM PC. The input resolution of data acquisition system is usually specified in bits. The conversion from bits of resolution to actual resolution is given by

$$\text{resolution} = \text{one part in } 2^{(\# \text{ of bits})}.$$

Therefore, a 12 bit A/D converter has an actual resolution of 2^{12} (4096). The board is 5" long and can be fitted in a

half slot. All connections are made through a standard 37 pin male D connector. The board is IBM PC bus compatible and features a high speed successive approximation, with a conversion time of 25 microseconds, resulting in data throughput rates in excess of 30 khz. The card has a highly advanced 8254 timer/counter providing 3x16 bit countdown registers. The board has an input scan rate of 4000 samples per sec. It provides a fixed input of +/-5 v dc input with a resolution of 0.00244 volts using a common ground, ie., 2.44 mv is the smallest input voltage that the system can detect. Applications include data logging, process control, signal analysis, etc.

The DAS-8 capability can be greatly enhanced by the addition of an EXP-16(expansion multiplexer and instrumentation amplifier) board.

Metrabyte's exp-16 board

This is a 16 channel amplifier/multiplexer featuring differential analog inputs and switch selectable gains. Low level transducers such as thermocouples require significant amplification before applying to the high level of A/D inputs like DAS-8. The EXP-16 expansion multiplexer incorporates an instrumentation amplifier that can provide stable amplification and also includes circuitry that allows cold junction compensation of thermocouples. It allows multiplexing of 16 different analog signals to a single DAS-8 analog input. The gain switch on the EXP-16 configures

the entire board for the gain selected. Each type of thermocouple has its own gain setting. The K-type thermocouple in our case, has a gain of 50. Thermocouple measurements are handled easily with the EXP-16's. The board includes a compensation circuitry that provides a scaling of 24.4 mv/^{o}C. This enables easy compensation in software. The EXP-16 can be connected directly to DAS-8 using the C-1800 cable.

Hardware Installation

This section describes the installation of the DAS-8 and the EXP-16 boards to the IBM PC. Figure 3 gives a schematic representation of the installation of the boards. The DAS-8 A/D connections were made using a 37 pin male D connector, projecting out of the rear of the computer housing. Software was provided along with the DAS-8 board for its installation. DAS-8 requires 8 consecutive address locations in I/O space. The I/O base addresses may be set by the base address DIP switch to any 8 bit boundary in the IBM PC decoded I/O space. This I/O address space encompasses a decimal code. The software was used for installation of the base address. The UTIL executable file was run to generate a file DAS-8.ADR containing the base I/O address. For the DAS-8/EXP-16 systems, the base address was 768 or Hex 300. The base address DIP switch was then set accordingly by suitable selection of the jumpers. This

completed the installation of the DAS-8 A/D board in the IBM PC.

The next part of the installation was that of the EXP-16. The simplest way to get power to the EXP-16 was to connect it to the DAS-8 with the C-1800 cable. The EXP-16 had to be calibrated using a digital voltmeter. There was provision for the calibration of the EXP-16 in the included software. When the software was run a voltage test appears on the screen which tells one how to calibrate the board. A gain switch of 50 was then selected for the K-type thermocouple. The two zero out potentiometers on the board were then adjusted until they read 0 volts dc. The CJC potentiometer was adjusted to 24.4 mv/^{o}C. The basic installation of the two boards was thus completed.

Figure 4 gives a schematic representation of the A/D conversion. The DAS-8/EXP-16 boards have a maximum voltage output of +/-5 v. The A/D board must have the ability to handle the input analog voltage coming from the recording balance. Due to the limited voltage configuration of the boards, the 100 mv output of the control unit was chosen. With a gain factor of 50 for the K-type thermocouple, a 100 mv output is amplified to give a 5000 mv (5 v), which matches the DAS-8 voltage capability. The amplified analog signal goes to A/D converter and then to the data register, finally to give digitized data which is received by the computer.
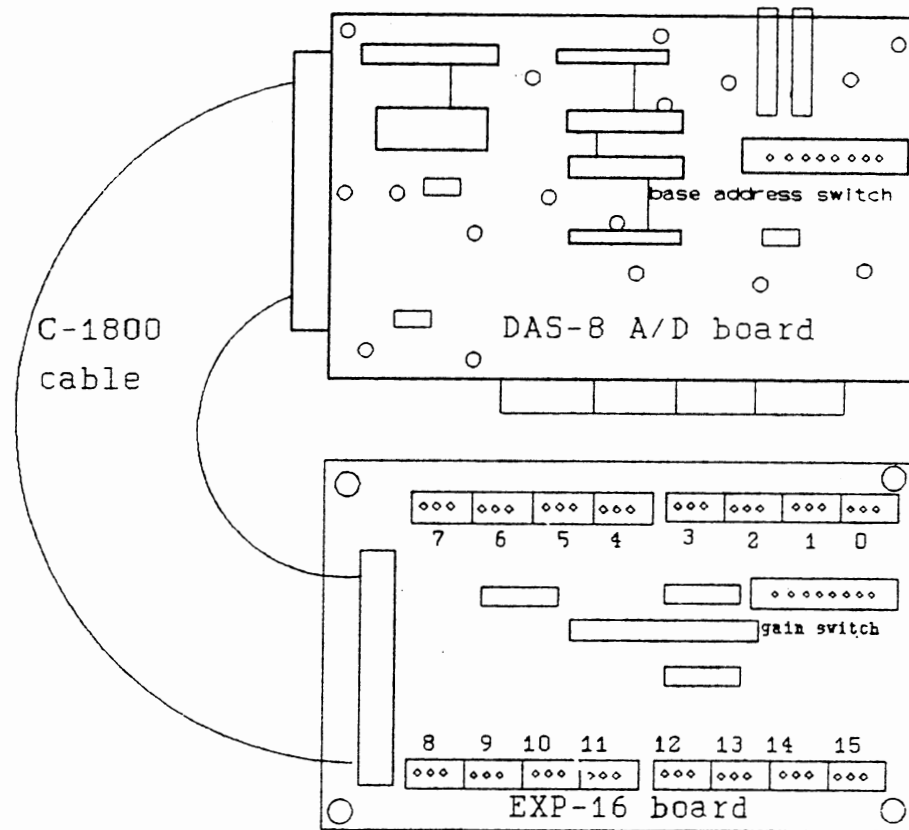
Figure 3. Hardware Installation of the Acquisition
           Boards.
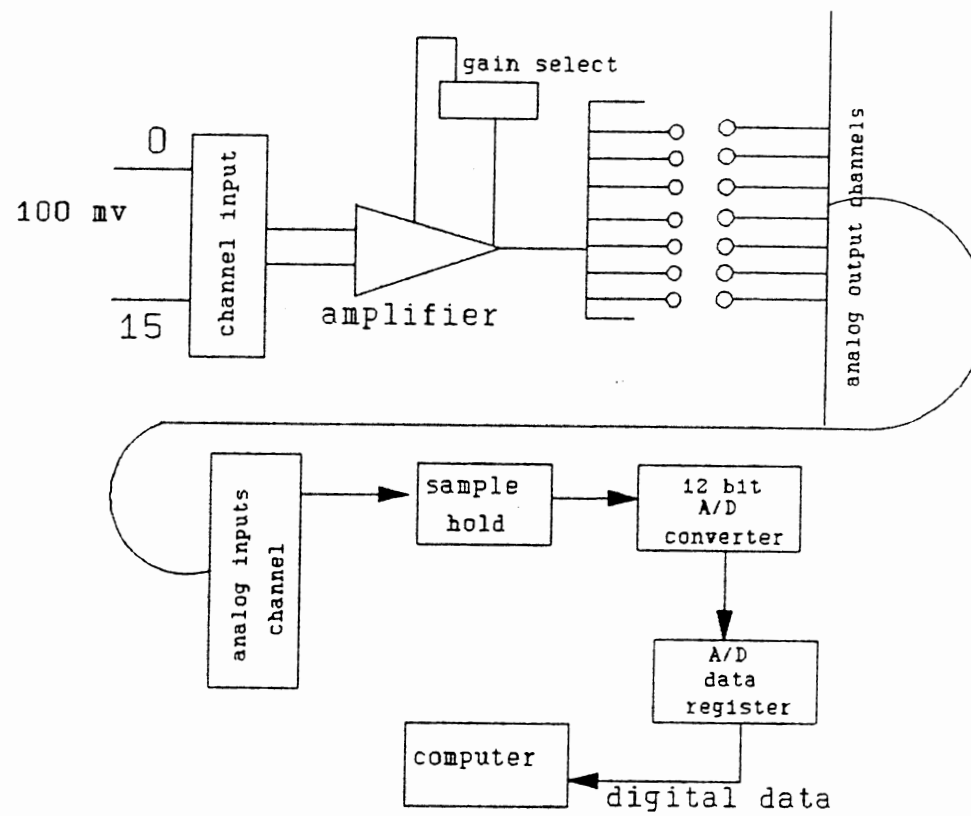
Figure 4.   Schematic representation of the A/D
             Conversion.

Interfacing of Cahn Recording Balances
to the IBM PC

The analog output signals coming from the Cahn C1000 and Cahn C2000 recording balances are now ready for conversion. When interfacing the C1000 to the computer, the 100 mv output range of the control unit was selected. For the C2000 the 10 mv output range was selected. These values represent the voltage output when the balance senses an untared weight equal to the selected weight span. When using the 100 mv output, the C1000 has a 2 v full scale signal that can be resolved down to 100 μv and on the C2000 using the 10 mv output, the 1 v full scale signal can be resolved down to 1 μv.

A wire was run from the 10 mv output of the C2000 and connected to Channel 1 of the EXP-16 board. Another wire was used for the time computation, which was connected to Channel 2 of the EXP-16. The K-type thermocouple wire coming from the temperature controller was connected to Channel 0. This completed the interface of the low pressure TGA.

For the high pressure TGA, Channels 4 and 5 were used for the temperature and weight readings. Since the temperature controller was a standard control unit there was no provision for outputting the signal to the EXP-16. So, alternatively, the K-type thermocouple wire was connected

directly to the thermocouple assembly itself (ie., an additional thermocouple wire was connected to the one going to the temperature controller which was the input to the temperature controller). The other end of the wire was connected to channel 4 of the EXP-16 board. The whole hardware interface installation was thus completed.

The software package, Notebook by Labtech, was used for acquiring, storing and manipulating the incoming data.

Labtech Notebook

It is a very user friendly piece of software. It's completely menu-driven. By using the menus, one can design a format for a data acquisition run by entering the sample rates, run duration, scaling factors, etc. Labtech Notebook version 4.3 was used in this experimental work.

Installation

The Notebook software was installed on the hard disk of the computer. The Notebook system included a hardware key that is required to run the notebook's data acquisition and control code, GO.EXE. The male end of the parallel hardware key was plugged into the parallel port LPT1 of the computer and secured with screws. The installation was completed and the software was tested.

Notebook's main menu contains the following commands: SETUP, GO, ANALYZE, CURVE-FIT, FFT, INSTALL, PROGRAM & QUIT.

Setup

This command has several sub menus that help in setting up data acquisition runs. One can assign the number of channels being used, the channel type and the corresponding interface channel number. There are also provisions for specifying the stage duration and the sampling rate for each channel. All these specifications can be saved and stored in a file, so this file can be loaded or modified as required.

Go

The GO command is used to initiate the data acquisition and control runs. When GO is selected from the main menu, the appropriate files will be loaded into RAM and the run will commence. As the run progresses, a trace representing the acquired data will be drawn across the window from left to right. When the run is over, the display will disappear and one will be returned to the main menu.

Analyze

Data analysis programs like Lotus 1-2-3 are required for data reduction and graphing of the results. Once the data acquisition phase of the experiment is completed, one would like to organize and analyze the data accumulated. This is where data analysis programs like Lotus 1-2-3 are ideal. The Analyze command is used to call the data

analysis program from the Notebook's main menu. When invoked, the Analyze sends the name of the analysis program file to the DOS operating system for execution, the name of the analysis program file having been previously entered during setup. This command is very useful in reducing data and plotting the same according to the model required. One can also perform all the basic mathematic calculations using Lotus.

Curvefit

This is one of Notebook's built in data analysis routines. Using curvefit, one can perform non linear regression analysis on the experimental data collected.

FFT

This FFT (Fast Fourier Transform) is another of Notebook's built in data analysis routines. Using this feature, one can perform a fast fourier transform on a data file.

Install

This command is used to make changes to the system configuration.

Program

This command provides access to the magic/1

language provided as part of Notebook. One can use this
command to execute DOS commands and to review the
experimental data files created.

<u>Quit</u>

This command lets one to leave the Notebook's
main menu and return to the DOS prompt.

CHAPTER VI

EXPERIMENT PROCEDURE

Having completed the equipment and interface setup, the next stage was to conduct experiments to test the equipment.

Both TGA's were hooked to the computer interface. The pipe fittings, flowmeter and the tubing connections to the TGA's were completed. All the fittings were checked for gas leaks using gas leak detector under a helium atmosphere. The balance mechanism for both TGA's required purging and the gas selected for this purpose was helium.

First, experiments were conducted with the low pressure TGA (Cahn C2000 unit). The balance system was purged with helium for about one hour. Helium at about 60 psia was introduced through the flowmeter into the system to ensure a clean, dry and non corrosive atmosphere. The system was then placed under vacuum at about 27 in. of Hg for one hour. The sample to be treated was polyethylene. About 8.0 mg of polyethylene was weighed. The control unit was then switched on and the control parameters were specified. The vacuum pump was then switched off to insert the sample. The furnace was opened and the glass assembly was removed. The sample was placed on the sample pan and then placed in position. The glass assembly was then replaced and the furnace was closed. The vacuum pump was then started again,

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to evacuate the system with the sample at about 27 in. of Hg for one hour. The Micricon temperature controller was then programmed to a temperature of about 900°C. Parameters like the setpoint, heating rate and segment time were specified for each segment. For our experiment, the program was split into five segments and at the end of the fifth segment, the program stops, indicating that the setpoint has been reached at the specified time. The polyethylene sample was programmed to be heated from the room temperature up to 900°C.

The Labtech Notebook on the computer was then switched on to record the experimental data. Entering the main menu, all the parameters were assigned the setup menu and saved in the files menu. The trace and window screens were specified for the required length of time. Three channels were assigned, one for weight, time and thermocouple temperature. The interface channel numbers were then assigned corresponding to the EXP-16 multiplexer board. The stage duration was then fixed and the screen was set for execution.

The furnace was then switched on and the program on the Micricon controller and the Labtech GO were also switched on simultaneously. That step started the recording of the weight and temperature data versus time for the sample polyethylene subjected to high temperature under high vacuum. The experiment ended when the program was over and the notebook had also finished collecting the data.

We carried out a similar data acquisition run with the high pressure TGA under the same vacuum conditions as the low pressure TGA. Before running the experiment, however, we had to fine tune the control unit. The C1000 control unit was very sensitive to vibrations. In order to obtain meaningful results, the balance has to be zeroed. Sufficient warm up time was allowed for a stable zero setting. After sufficient warm up, the balance power was switched on. There are two empty pans within the weighing unit of the C1100 Pressure Balance. The coarse zero knob was used for zeroing the balance. This is one of the crucial steps in operating the C1000 unit. The zero setting of the balance control unit does not change when the sensitivity or the recorder range is changed. The balance was then calibrated with a 100 mg calibration weight accurate to a few micrograms on the 100 mg range. The calibration then holds over all the ranges.

Having zeroed the instrument, the next step was to insert the sample into the sample pan. About the same amount of polyethylene (8.0 mg) was weighed and placed on the pan. The long reactor tube was then replaced and the tubings and fittings were again tightened in place. The balance was purged with helium for about one hour. Similar to the low pressure TGA, here again, the temperature controller was programmed to run the experiment. All the parameters were assigned and stored in a file. Two channels were assigned, one for the thermocouple and one for the

analog weight. PID control values were assigned to the program and the furnace was switched on to warm up to the room temperature. The Notebook GO and the Micristar program were then executed simultaneously. The program was set in auto mode for the controller to take over the experiment. At the end of the program, the controller automatically comes back to the manual mode and shuts off the power to the furnace. Weight and temperature data were thus recorded as a function of time by the Labtech Notebook and were ready to be analyzed.

CHAPTER VII

EXPERIMENTAL RESULTS

Experimentation consisted of using the TGA's for the thermal degradation of polyethylene.

Many experimental runs were carried out using the above polyethylene, as a learning experience, prior to the following three typical runs.

Three 8.0 mg samples of polyethylene were subjected to TGA at linear heating rates of $1^{o}C$, $2^{o}C$ and $3^{o}C$/min. Different heating rates were used to check for consistency in the performance of the equipment. Degradation was carried out under vacuum. The actual weight loss occurred between 400 and $470^{o}C$. Therefore, an arbitrary initial weight of plastic (7.46 mg) was chosen from the TGA data in this temperature range where examination of the curves showed the major weight loss to begin.

The degradation results can be seen in Figures 5, 6 and 7. The tabulated data for the three experiments can be seen in Appendix A. Figure 5 gives the TGA curves for the three samples subjected to three different heating rates. The $60^{o}C$/hr. heating rate experiment was carried out using the high pressure TGA and the other two heating rate experiments were carried out using the low pressure TGA. The graph shows the polyethylene sample losing weight with increase in

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temperature. The mechanism involved is that of a random breaking of the molecule chains.

Figures 6 and 7 give the weight and temperature plots versus time respectively for the sample heated at $60^{\circ}C/hr$. From Figure 6, one can conclude that the weight decrease is almost uniform with time. But in Figure 7, a thermal lag is inherent which shows up as a fluctuation with respect to time. From the tables in the appendix, one can observe that a scale factor of 1000 has been used to scale the analog weight signal coming from the control unit.

From the table, one can conclude that there is a heavy fluctuation in the temperature and weight signal readings. This could be due to the following reasons:

(a) the analog signal coming from the thermocouple goes directly to the EXP-16 board due to the limitation of the standard temperature controller.

(b) a complete calibration of the EXP-16 board could not be achieved with a multimeter.

(c) convection effects in between the furnace and the reactor tube creates a thermal lag.

Data Analysis

Notebook provides the menu for organizing and analyzing the accumulated experimental data. Lotus 1-2-3 spreadsheet package was used for the analysis.

During the experimental run, I observed a slight deviation in the temperature readings of the digital readout

from that of the actual temperature controller readout. The deviation was about $0.2^{O}C$. This could be attributed to the absence of the direct signal link between the controller and the EXP-16 board.
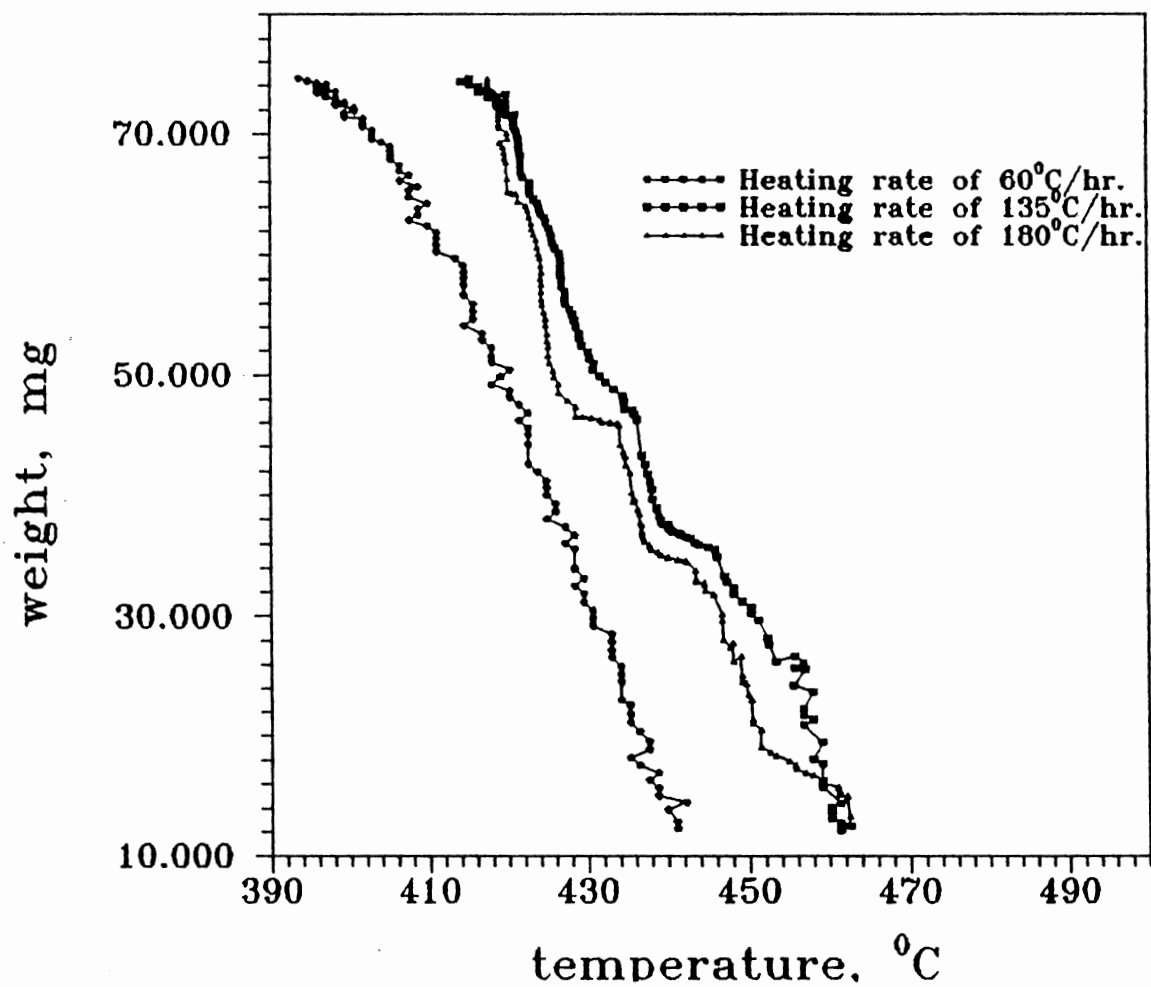
Figure 5. TGA curves for polyethylene samples
subjected to different heating rates.
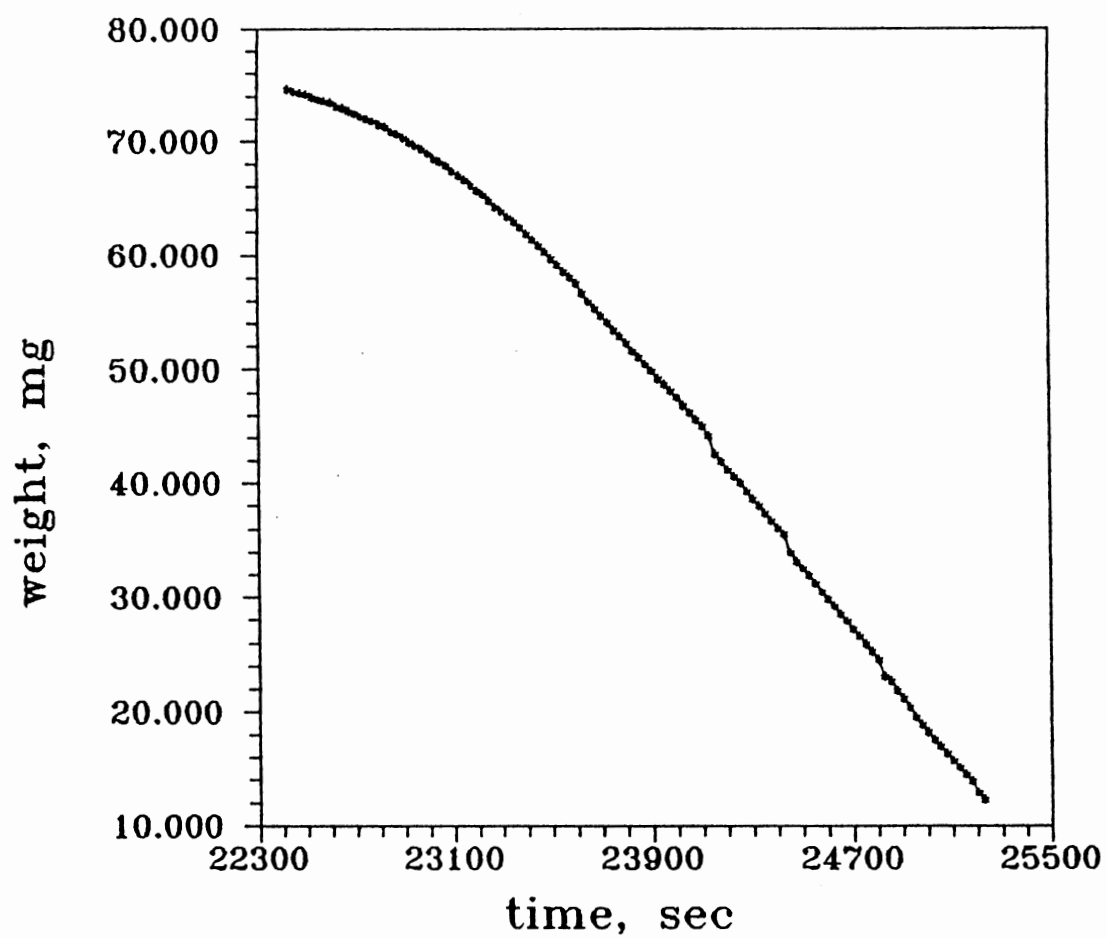
Figure 6. Plot of weight vs time for a sample
the polyethylene heated at 60°C/hr.
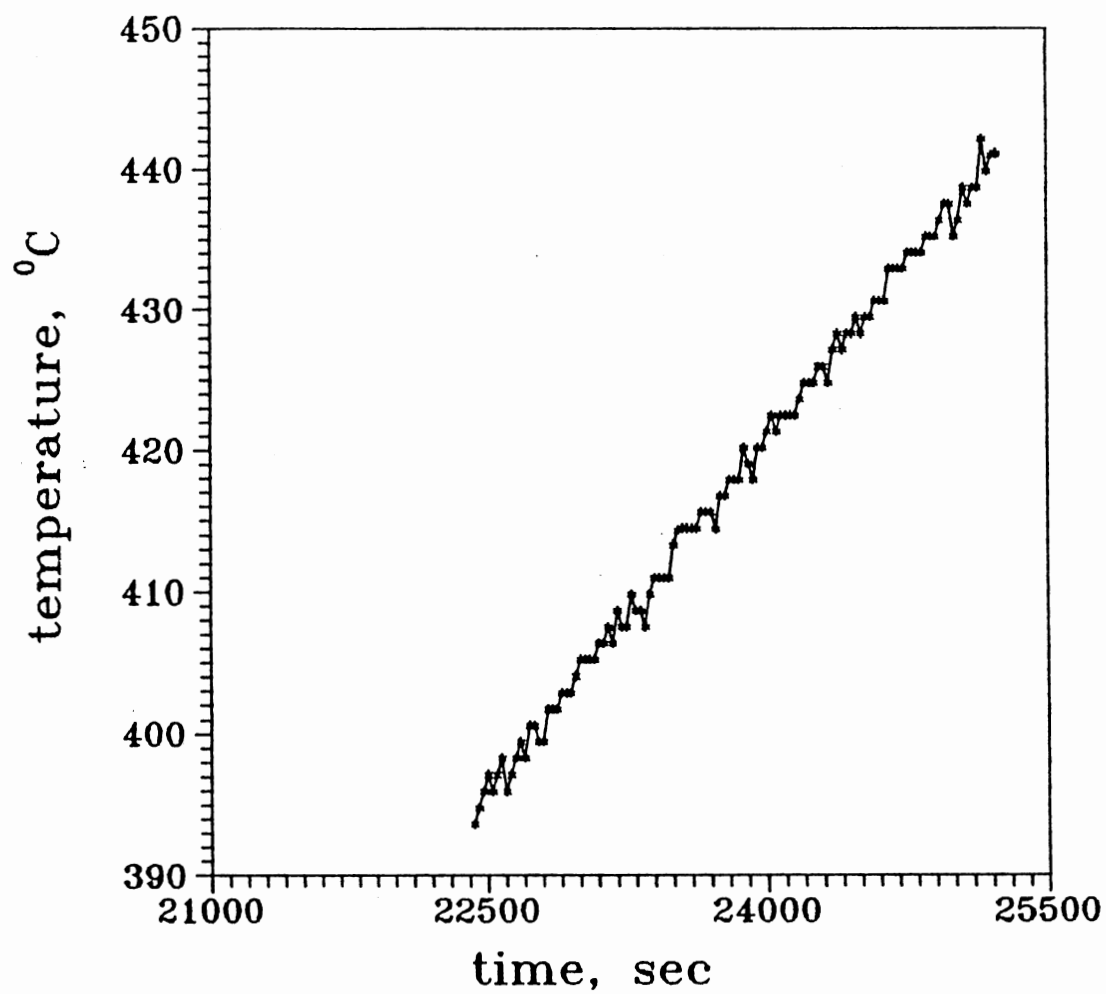
Figure 7. Plot of temperature vs time for the sample of polyethylene heated at 60°C/hr

CHAPTER VIII

DISCUSSION

Kinetics of thermal degradation of solids have been
evaluated from the TGA at linear rates of temperature rise
in a number of studies. Freeman and Carroll (18) used the
technique of differential thermal analysis for estimating
the kinetic parameters. Their technique was modified by the
Anderson-Freeman (19) group to evaluate the rate parameters
for the thermal decomposition of polyethylene and
polystyrene.
Doyle (20) and Ozawa (21) have also studied the thermal
degradation of a large number of plastics using different
mathematical treatments.

This study follows Friedman's technique (17) for
evaluating the kinetic parameters, which describe the
thermal degradation of the plastics using the TGA data.
Kinetic calculations were based on an intercomparison of
three experiments, which were carried out at three different
heating rates. In all of the earlier studies, calculations
were based on experiments performed at a single rate of
temperature rise.

Petrothene (Linear Low Density Polyethylene) pellets
belonging to the polyolefin family were used for this study.

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They were obtained from the Quantum Chemical Corporation.
Some of the physical properties of the pellets are:

(a) Crystalline, white to opaque in color and insoluble in water.

(b) Odorless and are in pellet form.

(c) Generally stable and have an ignition temperature of about $645^\circ F$.

Polyethylene is a typical homochain polymer that undergoes random degradation. When these polymers degrade, bonds in chains may be broken at random. Thus all bonds still intact at any one stage of the degradation, have the same probability of being broken.

Kinetic Analysis

Theory and Derivation

The rate of decomposition for the degradation reaction of polyethylene is a function of both temperature and weight. The rate of decomposition is a function of a temperature dependent rate constant k and a temperature dependent function X.

$$\frac{dX}{dt} = k\ f(X)$$

X (the decomposition) $= 1 - (W/W_o)$, where W_o is the initial weight and W is the weight at any time. Therefore, the

residual fraction $(1 - X) = W/W_0$ and the rate of decomposition is

$$\frac{dX}{dt} = -\frac{1}{W_0} \frac{dW}{dt}$$

Therefore,

$$-\frac{1}{W_0} \frac{dW}{dt} = k \ f(X)$$

$$-\frac{1}{W_0} \frac{dW}{dt} = k \ f(\frac{W}{W_0})$$

where $k = A \ e^{-E/RT}$

The temperature dependency of the rate constant k was modeled using an Arrhenius equation, similar to a work done by (17).

This kinetic equation was used for the analysis:

$$-\frac{1}{W_0} \frac{dW}{dt} = A \ e^{-\frac{E}{RT}} \ f(\frac{W}{W_0}) \qquad (1)$$

where   W = weight of the organic material (mg)

W_o = original weight of the organic material

(mg)

t = time

A = pre-exponential factor (/hr.)

E = activation energy (kcal/mol)

R = gas constant (1.987 cal/ mol K)

T = absolute temperature (K)

$f(W/W_o)$= a function of the weight of material

Taking the logarithm of (1),

$$\ln\left[\left(-\frac{1}{W_o}\right)\left(\frac{dW}{dt}\right)\right] = \ln A + \ln f\left(\frac{W}{W_o}\right) - \frac{E}{RT} \qquad (2)$$

The function $f(W/W_o)$ is assumed to be constant for constant values of W/W_o .

Since the weight loss occurred in the temperature range of 390 to 420°C, ten values of W/W_o for the three heating rates ranging from 0.2 to 0.95 were selected. Values of $(1/W_o)(dW/dt)$ and T were found for each W/W_o, for each experiment. Plots of $\ln[(-1/W_o)(dW/dt)]$ vs $(1/T)$ were made (Figure 8) which gives a slope of $-E/R$ and an intercept of $\ln[A\, f(W/W_o)]$. Ten values of $-E$ ranging from 40.09 to 116.9 kcal/mol were obtained. An average value of 82 kcal/mol, was calculated from these values.
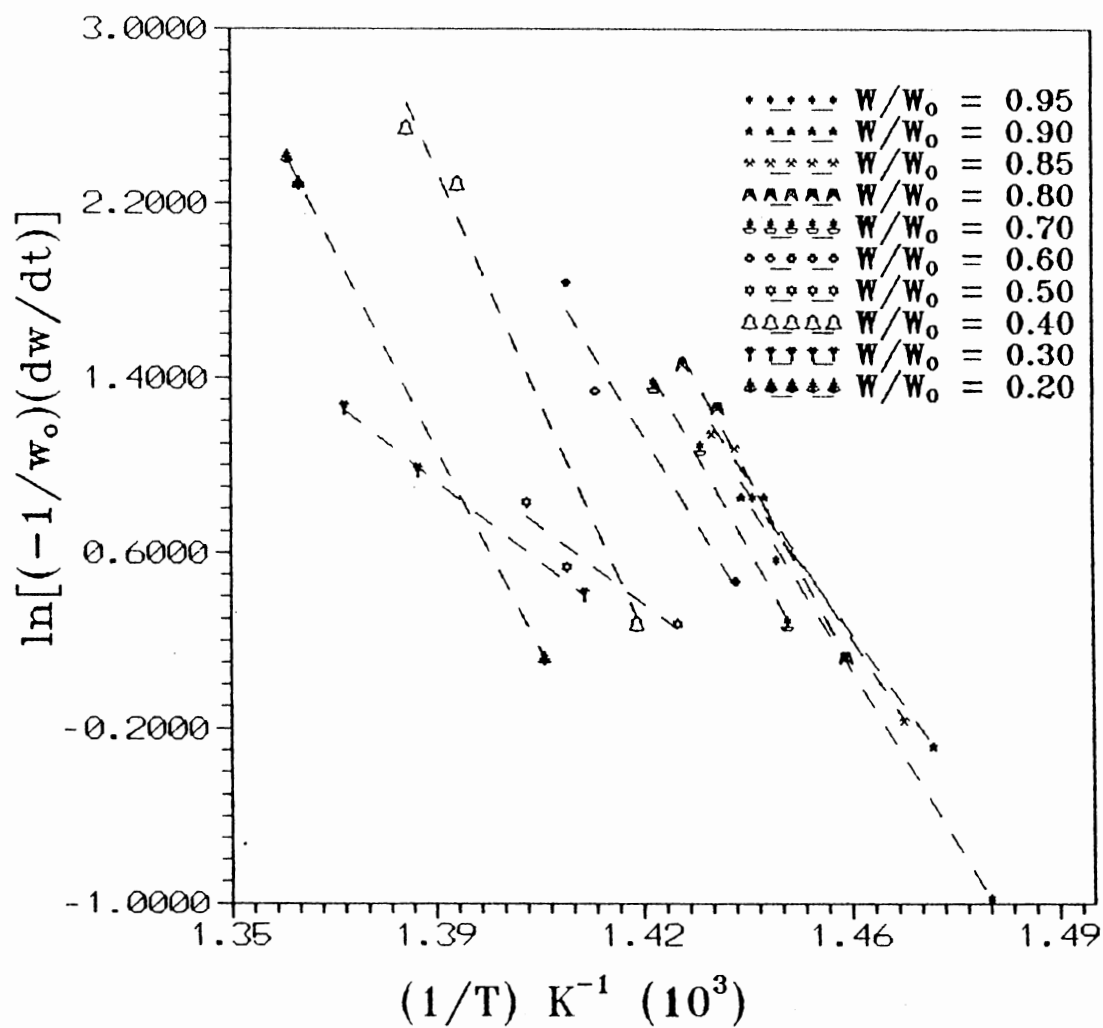
Figure 8. Plot for the determination of the activation energy E for the degradation reaction

The function, $f(W/W_O)$ was assumed to have the form

$$f(\frac{W}{W_O}) = [\frac{(W-W_f)}{W_O}]^n \qquad (3)$$

where W_f = final weight of the plastic

n = kinetic order of the reaction

Multiplying both sides of Equation (3) by A, and taking logarithm gives

$$\ln[A \, f(\frac{W}{W_O})] = \ln A + n \, \ln[\frac{(W-W_f)}{W_O}] \qquad (4)$$

The activation energy, E, and other experimental parameters were then fitted to Equation(4) to obtain values for $\ln[A \, f(W/W_O)]$. A plot of $\ln[A \, f(W/W_O)]$ vs $[\ln(W-W_f)/W_O]$ was then made as shown in Figure 9.

Summary of Results. The kinetic parameters obtained from this study are shown in Table I.

From Figure 9, we can observe that the reaction approximates a first order reaction.
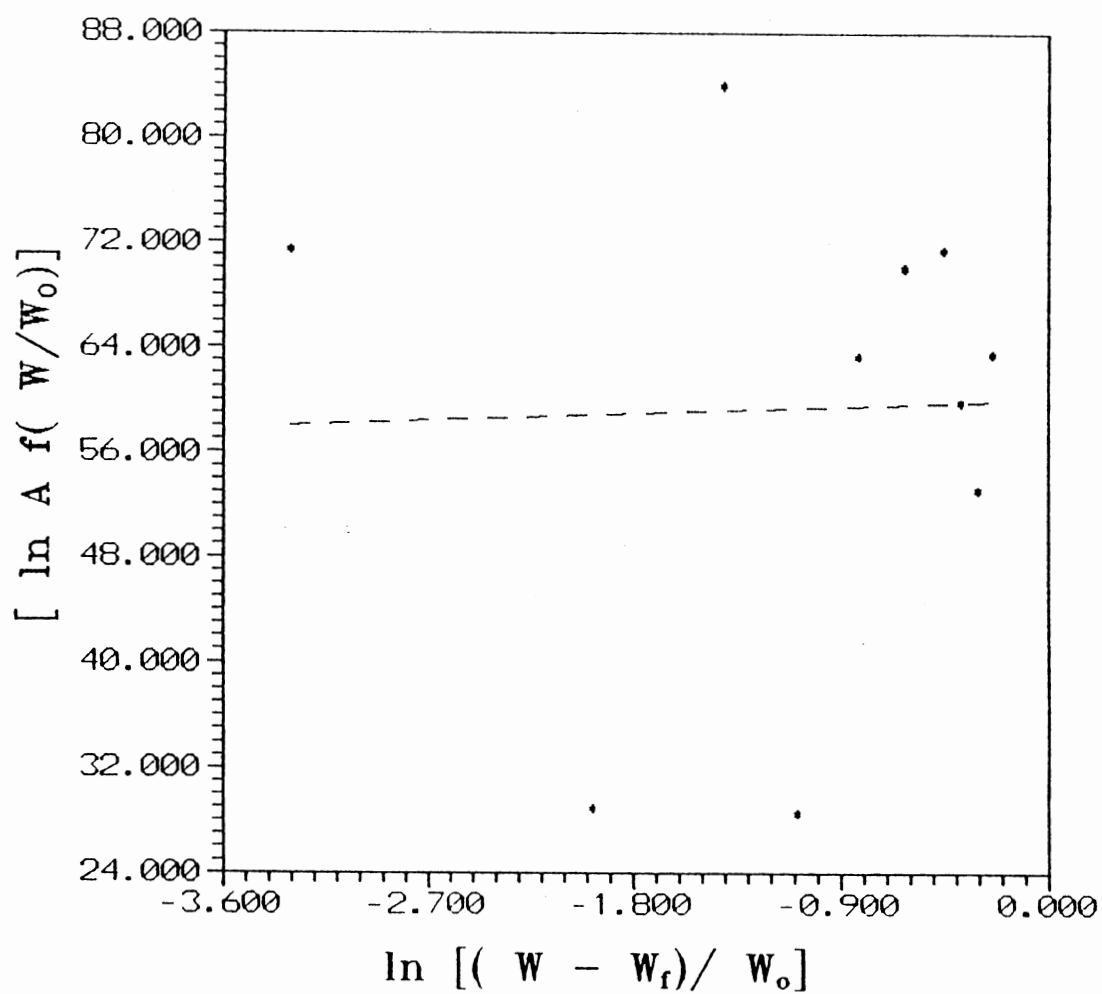
Figure 9.   Plot for the determination of the pre-
exponential factor A and the order n for
the degradation reaction

TABLE I

Results of the Kinetic Analysis

W/W_o	E	$\ln[A\ f(W/W_o)]$	$\ln[(W-W_f)/W_o]$
0.95	86.550	63.56	-0.243
0.90	72.208	53.22	-0.304
0.85	81.334	59.89	-0.379
0.80	97.293	71.47	-0.453
0.70	95.883	70.12	-0.623
0.60	86.947	63.37	-0.823
0.50	39.360	28.54	-1.088
0.40	116.960	83.95	-1.411
0.30	40.092	28.89	-1.976
0.20	100.782	71.39	-3.307

An average value of E = 81.74 kcal/mol and A = 1.27×10^{26} hr^{-1} was obtained.

A straight line was obtained using a least squares fit, confirming the assumed form. Therefore, the final form of the overall kinetic equation was

$$(-\frac{1}{W_o})(\frac{dW}{dt}) = k[\frac{(W-W_f)}{(W_o)}]^n \qquad (5)$$

where k = A $e^{-E/RT}$ hr^{-n}

The values of the kinetic parameters k, and A obtained in this study are similar to that of Anderson and Freeman's work (19). The overall reaction of the degradation approximated a first order reaction with a n = 0.63.

Advantages

The kinetic analysis technique that was employed in this study has several advantages:

(a)   By its use, it was possible to calculate an activation energy for each region of the degradation process, without any prior knowledge of the kinetic form of the equation.

(b)   It was also useful for determining the other parameters like the pre-exponential factor A, and the order of the reaction n and the rate constant k for each region.

(c)   Its application to the TGA data is very simple.

(d)   This method could also serve as a check for systems where the rate law seems to be so simple that TGA experiments would only be carried out at one rate of heating under normal circumstances.

CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

Equipment

The objectives of the equipment portion of the
experimental work were to interface both the
thermogravimetric analyzers to a computer and to perform
online data acquisition and control.

As a result of this research, one can now get digitized
weight and temperature data directly from both
thermogravimetric analyzers through the computer, without
having to calculate data from a strip chart recorder.

Conclusions

(1) The temperature readings fluctuate and this
     experimental setup provides an average of the
     values which helps in smoothing the data.

(2) Analysis of the data is now much easier than
     without data acquisition and can be extended to
     further studies and other applications.

(3) Both TGA's are capable of operating accurately and
     reliably under high vacuum conditions.

(4) An 80286 12 Mhz personnel computer with coprocessor is completely adequate for online data acquisition and control of the TGA's.

(5) In the high pressure prototype system, changing samples is not easily done, since three tube connections have to be dismantled. New commercial systems have solved this problem.

Recommendations

(1) Future enhancement of the standard Micristar temperature controller with a logger or computer interface module is recommended to avoid the distortion in the readings and to thereby get a good accurate output of the thermocouple.

(2) A small reactor tube could be used instead of the present bulky long one to facilitate easy opening to gain access to the sample pan or a lifting system could be added similar to current commercial units.

(3) The EXP-16 board needs a full, complete calibration using a voltage calibrator.

(4) Before attempting to carry out high pressure experiments with the high pressure TGA, a similar test run should be carried out under high pressure.

(5)   A new horizontal mountable furnace could provide a better heating of the sample, than the present vertical unit.

Kinetic Study

The objective of the kinetic study of the research was to evaluate the kinetic parameters which describe the thermal degradation reaction of polyethylene.

Conclusions.

(1)   The overall reaction approximates a first order reaction.

(2)   Kinetic parameters obtained were similar to that of an earlier work (19).

Recommendations.

(1)   Calculations based on this analysis, needs to be done for the whole integral range of weight values (W/W_o), ie., from the start to the end of the degradation.

(2)   More sets of data points have to be taken for the analysis, to get an integral average of the whole degradation mechanism.

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APPENDIXES

TABLE II

TGA DATA FOR THE POLYETHYLENE SAMPLE HEATED
AT 60°C/hr IN THE HIGH PRESSURE TGA

LABTECH NOTEBOOK		
data file		
The time is 15:12:04.68.		
The date is 12-23-1991		
temp	wt	time
deg c	mg	sec
393.625	74.6094	22425
394.785	74.3652	22450
395.945	74.2188	22475
397.105	74.1211	22500
395.945	73.8770	22525
397.105	73.6328	22550
398.265	73.5352	22575
395.945	73.3887	22600
397.105	73.0469	22625
398.265	72.9004	22650
399.424	72.6074	22675
398.265	72.4121	22700
400.583	72.1191	22725
400.583	71.9238	22750
399.424	71.7285	22775
399.424	71.4355	22800
401.741	71.2402	22825
401.741	70.8008	22850
401.741	70.6055	22875
402.900	70.2637	22900
402.900	69.9219	22925

TABLE II (Continued)

temp	wt	time
deg c	mg	sec
402.900	69.5801	22950
404.058	69.2871	22975
405.216	68.8965	23000
405.216	68.5059	23025
405.216	68.1641	23050
405.216	67.8711	23075
406.374	67.3340	23100
406.374	66.9434	23125
407.531	66.6016	23150
406.374	66.1133	23175
408.688	65.6250	23200
407.531	65.3178	23225
407.531	64.7949	23250
409.845	64.2578	23275
408.688	63.8184	23300
408.688	63.3301	23325
407.531	62.8906	23350
409.845	62.4023	23375
411.002	61.8652	23400
411.002	61.3281	23425
411.002	60.7910	23450
411.002	60.3027	23475
413.314	59.7168	23500
414.375	59.1309	23525
414.470	58.5449	23550

TABLE II (Continued)

temp	wt	time
deg c	mg	sec
414.470	58.0566	23575
414.470	57.5195	23600
414.470	56.6895	23625
415.626	55.9570	23650
415.626	55.3223	23675
415.626	54.6875	23700
414.470	54.1504	23725
416.781	53.4668	23750
416.781	52.9297	23775
417.936	52.2949	23800
417.936	51.6113	23825
417.936	51.1230	23850
420.246	50.4883	23875
419.091	49.9023	23900
417.936	49.2188	23925
420.246	48.7305	23950
420.246	48.1445	23975
421.401	47.5586	24000
422.555	46.8634	24025
421.401	46.2402	24050
422.555	45.6055	24075
422.555	45.0195	24100
422.555	44.1895	24125
422.555	42.5781	24150
423.709	41.9434	24175

TABLE II (Continued)

temp	wt	time
deg c	mg	sec
424.863	41.2109	24200
424.863	40.6250	24225
424.863	40.0391	24250
426.016	39.3066	24275
426.016	38.6230	24300
424.863	38.0371	24325
427.170	37.4023	24350
428.323	36.7188	24375
427.170	36.0352	24400
428.323	35.5607	24425
428.323	33.9355	24450
429.476	33.1543	24475
428.323	32.5195	24500
429.476	31.8848	24525
429.476	31.2012	24550
430.628	30.4688	24575
430.628	29.7852	24600
430.628	29.1992	24625
432.933	28.5156	24650
432.933	27.8809	24675
432.933	27.1484	24700
432.933	26.5625	24725
434.085	25.8301	24750
434.085	25.1953	24775
434.085	24.5117	24800

TABLE II (Continued)

temp	wt	time
deg c	mg	sec
434.085	23.0297	24825
435.237	22.6074	24850
435.237	21.8262	24875
435.237	21.1426	24900
436.389	20.3613	24925
437.540	19.5313	24950
437.540	18.8965	24975
435.237	18.2129	25000
436.389	17.5781	25025
438.691	16.9434	25050
437.540	16.3086	25075
438.691	15.6738	25100
438.691	15.0391	25125
442.144	14.4531	25150
439.842	13.8672	25175
440.993	12.8418	25200
441.088	12.2657	25225

TABLE III

TGA DATA FOR THE POLYETHYLENE SAMPLE HEATED
AT 180°C/hr IN THE LOW PRESSURE TGA

LABTECH NOTEBOOK		
data file		
The time is 20:12:54.41.		
The date is 12-24-1991.		
temp	wt	time
deg c	mg	sec
415.245	74.6094	8039.98
415.150	74.5117	8046.64
414.089	74.3164	8053.31
415.245	74.1699	8059.98
415.245	74.0723	8066.64
416.401	73.9258	8073.31
416.401	73.8681	8079.98
416.401	73.8281	8086.64
417.556	73.6328	8093.31
416.401	73.4863	8099.98
419.866	73.2422	8106.64
417.556	73.0957	8113.31
417.556	72.9980	8119.98
418.711	72.8027	8126.64
418.711	72.7539	8133.31
419.771	72.5098	8139.98
418.616	72.3633	8146.64
419.866	72.0703	8153.31
419.771	71.9238	8159.98
421.020	71.6797	8166.64
419.866	71.5332	8173.31

TABLE III (Continued)

temp	wt	time
deg c	mg	sec
420.675	71.3867	8179.98
420.789	71.1426	8186.64
420.815	70.8496	8193.31
420.829	70.5566	8199.98
421.075	70.3125	8206.64
421.229	70.1172	8213.31
421.280	69.9219	8219.98
421.388	69.5801	8226.64
421.434	69.3848	8233.31
421.483	68.9941	8239.97
421.483	68.7500	8246.64
421.529	68.4570	8253.31
421.636	68.1641	8259.97
421.683	67.8711	8266.64
421.690	67.5293	8273.31
421.695	67.1387	8279.97
421.695	66.8457	8286.64
421.943	66.4063	8293.31
422.790	66.0156	8299.97
422.790	65.7227	8306.64
422.796	65.2832	8313.31
422.894	64.9902	8319.97
423.348	64.5996	8326.64
423.796	64.2090	8333.31
423.996	63.7695	8339.97

TABLE III (Continued)

temp	wt	time
deg c	mg	sec
424.190	63.3789	8346.64
424.649	63.0859	8353.31
424.849	62.6465	8359.97
425.201	62.2070	8366.64
425.407	61.7676	8373.31
425.601	61.4258	8379.97
425.701	60.9863	8386.64
425.949	60.5469	8393.31
426.553	60.1074	8399.97
426.594	59.7168	8406.64
426.654	59.2773	8413.31
426.706	58.7402	8419.97
426.706	58.3008	8426.64
426.858	57.8613	8433.31
426.858	57.4219	8439.97
427.206	57.0313	8446.64
427.206	56.3965	8453.31
427.280	55.9570	8459.97
427.858	55.5176	8466.64
428.161	55.0781	8473.31
428.409	54.5410	8479.97
428.661	54.0039	8486.64
429.012	53.4668	8493.31
429.019	53.0762	8499.97
429.312	52.4902	8506.64

TABLE III (Continued)

temp	wt	time
deg c	mg	sec
430.112	52.0020	8513.31
430.312	51.4160	8519.97
430.868	50.9766	8526.64
430.717	50.4883	8533.31
431.612	49.9512	8539.97
432.312	49.4141	8546.64
433.314	48.8281	8553.31
434.463	48.2910	8559.97
434.614	47.8027	8566.64
434.619	47.1191	8573.31
435.670	47.0891	8579.97
435.765	46.7566	8586.64
435.915	46.7266	8593.31
436.220	46.2891	8599.97
436.765	43.3105	8606.64
437.265	42.5293	8613.31
437.515	41.7480	8619.97
437.915	41.0645	8626.64
438.065	40.4785	8633.31
438.170	39.6973	8639.97
438.665	38.9160	8646.64
438.971	38.2813	8653.31
439.216	37.9953	8659.97
439.216	37.8094	8666.64
439.365	37.6258	8673.31

TABLE III (Continued)

temp	wt	time
deg c	mg	sec
440.016	37.5887	8679.97
440.121	37.3027	8686.64
440.365	37.1191	8693.31
440.515	37.0332	8699.97
441.421	36.8961	8706.64
441.421	36.8590	8713.31
441.515	36.7730	8719.97
441.665	36.6871	8726.64
442.365	36.5500	8733.31
442.820	36.4613	8739.97
443.363	36.1270	8746.64
443.814	35.9434	8753.31
444.963	35.7551	8759.97
445.869	35.5156	8766.64
446.018	34.9297	8773.31
446.963	33.2949	8779.97
447.261	32.8555	8786.64
448.112	32.4160	8793.31
448.112	31.8789	8799.97
449.112	31.2930	8806.64
450.261	30.7559	8813.31
450.261	30.2676	8819.97
451.112	29.7305	8826.64
452.261	28.1445	8833.31
452.410	27.6563	8839.97

TABLE III (Continued)

temp	wt	time
deg c	mg	sec
453.261	27.2168	8846.64
455.558	26.6797	8853.31
456.707	26.1426	8859.97
455.558	25.6543	8866.64
456.707	25.6172	8873.31
456.927	25.5998	8879.97
455.464	24.2383	8886.64
457.855	23.7012	8893.31
456.707	22.2617	8899.97
456.707	21.8223	8906.64
457.855	21.3828	8913.31
456.707	20.8945	8919.97
459.003	19.4551	8926.64
457.855	18.0156	8933.31
459.003	17.6738	8939.97
459.003	16.1855	8946.64
459.003	15.7461	8953.31
461.298	14.3555	8959.97
460.150	14.0137	8966.64
460.150	13.5742	8973.31
460.150	13.0859	8979.97
461.298	12.7441	8986.64
462.445	12.4512	8993.31
461.298	12.1094	8999.97

TABLE IV

TGA DATA FOR THE POLYETHYLENE SAMPLE HEATED
AT 135°C/hr IN THE LOW PRESSURE TGA

LABTECH NOTEBOOK		
data file		
The time is 12:12:51.26.		
The date is 01-06-1992.		
temp	wt	time
deg c	mg	sec
417.485	74.6094	8119.99
417.485	74.3652	8127.99
417.485	74.1211	8135.99
417.794	73.7793	8143.99
418.240	73.5352	8151.99
418.394	73.1934	8159.99
418.594	72.9492	8167.99
418.549	72.6074	8175.99
418.649	72.2168	8183.99
418.899	71.8750	8191.99
418.902	71.6309	8199.99
418.902	71.2402	8207.99
418.949	70.8008	8215.99
418.967	70.5078	8223.99
419.986	70.1172	8231.99
420.000	69.6289	8239.99
419.008	69.2871	8247.99
419.410	68.8965	8255.99
419.563	68.5059	8263.99
419.663	68.0176	8271.99
419.816	67.6270	8279.99

TABLE IV (Continued)

temp	wt	time
deg c	mg	sec
419.993	66.2852	8287.99
420.000	65.1971	8295.99
420.516	65.1086	8303.99
420.869	65.0203	8311.99
420.869	65.0185	8319.99
421.068	65.0091	8327.99
421.322	64.4531	8335.99
422.322	64.0625	8343.99
422.522	63.6719	8351.99
422.721	63.1836	8359.99
422.974	62.6465	8367.99
423.022	62.1582	8375.99
423.274	61.7188	8383.99
423.574	61.2793	8391.99
423.726	60.6445	8399.99
423.926	60.1074	8407.99
424.078	59.7168	8415.99
424.178	59.1309	8423.99
424.278	58.5449	8431.99
424.126	58.0566	8439.99
424.23	57.5684	8447.99
424.27	56.9824	8455.99
424.281	56.3965	8463.99
424.35	55.8594	8471.99
424.581	55.2246	8479.99

TABLE IV (Continued)

temp	wt	time
deg c	mg	sec
424.781	54.7363	8487.99
424.830	54.1504	8495.99
424.984	53.4668	8503.99
424.984	52.8320	8511.99
425.081	52.3438	8519.99
425.084	51.6602	8527.99
425.235	51.0254	8535.99
425.735	50.4395	8543.99
425.835	49.8535	8551.99
426.386	49.2676	8559.99
426.386	48.5352	8567.99
427.536	47.9004	8575.99
428.536	47.3633	8583.99
428.536	46.5820	8591.99
429.386	46.5543	8599.99
430.536	46.4707	8607.99
431.592	46.2871	8615.99
431.837	46.1035	8623.99
432.837	46.0711	8631.99
432.837	45.9940	8639.99
433.714	45.9894	8647.99
433.987	45.8691	8655.99
434.136	44.2344	8663.99
434.537	43.5996	8671.99
434.636	43.3160	8679.99

TABLE IV (Continued)

temp	wt	time
deg c	mg	sec
434.786	43.2324	8687.99
434.786	42.5000	8695.99
435.286	41.8652	8703.99
435.536	40.2305	8711.99
435.635	39.4980	8719.99
435.836	38.9168	8727.99
436.286	38.8332	8735.99
436.435	38.4961	8743.99
436.585	37.7637	8751.99
436.734	37.5848	8759.99
436.785	37.0547	8767.99
436.834	36.7711	8775.99
436.883	36.4922	8783.99
437.031	36.2109	8791.99
437.683	35.9297	8799.99
437.731	35.7973	8807.99
437.934	35.5137	8815.99
438.744	35.3664	8823.99
439.18	35.0977	8831.99
440.031	34.9141	8839.99
441.180	34.7305	8847.99
442.180	34.6469	8855.99
442.328	34.5098	8863.99
443.423	33.7773	8871.99
443.476	33.0449	8879.99

TABLE IV (Continued)

temp	wt	time
deg c	mg	sec
443.476	32.9102	8887.99
444.476	32.7754	8895.99
444.624	32.1895	8903.99
445.624	31.8547	8911.99
445.624	31.8223	8919.99
446.624	30.1875	8927.99
446.624	29.6504	8935.99
446.772	28.0156	8943.99
447.624	27.3809	8951.99
447.920	26.7949	8959.99
448.014	26.2578	8967.99
448.920	25.6719	8975.99
449.068	25.0859	8983.99
449.068	24.5488	8991.99
449.543	24.4085	8999.99
449.920	23.4746	9007.99
450.215	22.9863	9015.99
450.362	21.4492	9023.99
450.362	21.0098	9031.99
451.362	20.5215	9039.99
451.362	19.0332	9047.99
452.509	18.6426	9055.99
453.215	18.3496	9063.99
454.803	17.9102	9071.99
455.656	17.5195	9079.99

TABLE IV (Continued)

temp	wt	time
deg c	mg	sec
455.751	17.2266	9087.99
456.897	16.8848	9095.99
457.803	16.6895	9103.99
458.949	16.2988	9111.99
459.190	16.0059	9119.99
460.949	15.7617	9127.99
460.949	15.6641	9135.99
461.096	15.4199	9143.99
461.096	15.2246	9151.99
461.242	15.0781	9159.99
462.096	14.9805	9167.99
462.383	13.3400	9175.99
462.389	12.6387	9183.99
462.483	12.5410	9191.99

VITA ⟩

Raghunathan Lakshmanan

Candidate for the Degree of

Master of Science

Thesis: COMPUTER CONTROL AND ON LINE DATA ACQUISITION FOR
           THERMOGRAVIMETRIC ANALYSIS

Major Field: Chemical Engineering

Biographical:

    Personal Data: Born in Kerala, India, July 9, 1967,
       the son of S. Lakshmanan and R. Saraswathi.

    Education: Graduated from Santhome High School,
       Madras, India, in June 1985; received Bachelor of
       Technology Degree in Chemical Engineering from
       Bharathiar University, India, in June 1989;
       completed requirements for the Master of Science
       degree in Chemical Engineering at Oklahoma State
       University in May, 1992.

    Professional Experience: Teaching Assistant, School
       of Chemical Engineering, Oklahoma State
       University, 8/90-12/91.