HIGH PRESSURE/HIGH TEMPERATURE THERMOGRAVIMETRIC APPARATUS

RECEIVED
MAR 02 2000
OSTI

FINAL REPORT

Principal Investigators: J.M. Calo and E.M. Suuberg

Grant Number:DE-FG-02-95TE00059

Submitted by:

Brown University
Division of Engineering, Box D
Providence, RI 02912

December 1999

Prepared for:

U.S. DEPARTMENT OF ENERGY
University Research Instrumentation Program
Office of Science Education Programs
Washington, D.C. 20585

We have no objection from a patent standpoint to the publication or dissemination of this material.

2/10/00
Office of Intellectual Property Counsel
DOE Field Office, Chicago
Date

SUMMARY

The purpose of this instrumentation grant was to acquire a state-of-the-art, high pressure, high temperature thermogravimetric apparatus (HP/HT TGA) system for the study of the interactions between gases and carbonaceous solids for the purpose of solving problems related to coal utilization and applications of carbon materials.

The instrument that we identified for this purpose was manufactured by DMT (Deutsche Montan Technologie) - Institute of Cokemaking and Coal Chemistry of Essen, Germany. Particular features of note include:

- Two reactors: a standard TGA reactor, capable of 1100°C at 100 bar; and a high temperature (HT) reactor, capable of operation at 1600°C and 100 bar;
- A steam generator capable of generating steam to 100 bar;
- Flow controllers and gas mixing system for up to three reaction gases, plus a separate circuit for steam; and another for purge gas;
- An automated software system for data acquisition and control.

The HP/TP DMT- TGA apparatus was purchased in 1996 and installed and commissioned during the summer of 1996. The apparatus was located in Room 128 of the Prince Engineering Building at Brown University. A hydrogen alarm and vent system were added for safety considerations.

The system has been interfaced to an Ametek quadrupole mass spectrometer (MA 100), pumped by a Varian V250 turbomolecular pump, as provided for in the original proposal. With this capability, a number of gas phase species of interest can be monitored in a near-simultaneous fashion. The MS can be used in a few different modes. During high pressure, steady-state gasification experiments, it is used to sample, measure, and monitor the reactant/product gases. It can also be used to monitor gas phase species during nonisothermal temperature programmed reaction (TPR) or temperature programmed desorption (TPD) experiments.

Some examples of research applications to data are included.

The Office of the Dean of Research contributed $36,000 in cost-sharing for the requested apparatus, as per the original proposal.

TABLE OF CONTENTS

1.0. Background.

The purpose of this instrumentation grant was to acquire a state-of-the-art, high pressure, high temperature thermogravimetric apparatus system for the study of the interactions between gases and carbonaceous solids for the purpose of solving problems related to coal utilization and applications of carbon materials.

The instrument that we identified for this purpose was manufactured by DMT (Deutsche Montan Technologie) - Institute of Cokemaking and Coal Chemistry, Essen, Germany. The features of this instrument which make it well suited to augment, amplify, and extend our work to realistic operating conditions, are summarized below. Such an apparatus was not available anywhere else on the Brown campus, and, indeed, is not a typical instrument to be found on most college campuses in the U.S. A description of this system follows.

2.0. General Description of the HP/HT DMT-TGA System.

2.1 Overview.

The TGA system is designed for the determination of weight changes during gas-solid reactions under pressures up to 40 bar and temperatures up to 1100°C (standard reactor) or 1600°C (high temperature, HT, reactor). During experiments the temperature can be either held constant or increased linearly at heating rates of 1-100 °C/min. Even greater heating rates can be achieved by lowering the sample directly into the preheated reactor using the electrical winch system. Because of the sensitivity of the balance, a very constant flow of gas at controlled pressure must be maintained to allow for automatic correction of buoyancy and drag forces acting on the sample during an experiment.

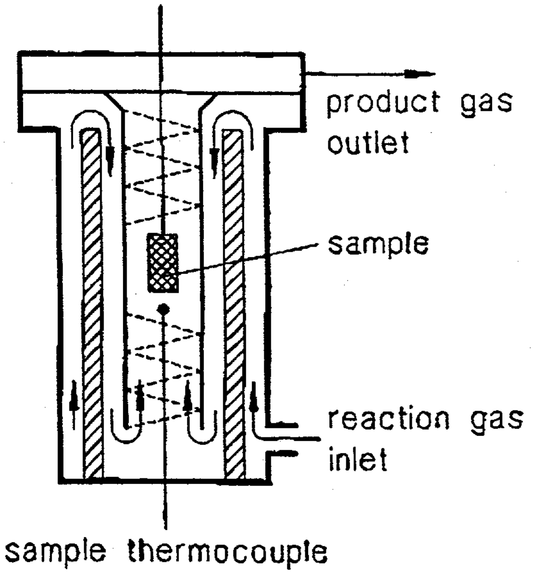
A computerized data acquisition and process control system allows for the recording of temperature, pressure, gas flow rates, and sample mass. The software also allows for automated pressurizing and depressurizing, control of total and partial pressures, flow rates, and internal and external temperatures.

2.2. Special Features.

A *Sartorius* microbalance (M 25 D-P) is used for measuring total weight changes of up to ±104 mg at 1 μg resolution, and +1040 to -104 mg at 10 μg resolution. The maximum absolute weight on each arm of the double quartz beam is 25 g. The digital balance electronics provides for adjustable damping of the signals, and variable sampling rates of up to 10 readings per second Both features are necessary to enable the accurate measurement of fast weight changes in flowing gases.

Since it is not possible to measure the sample temperature directly without disturbing the balance signal, a thermocouple is located a few millimeters below the sample holder, as shown in the accompanying figure. In order to insure that the sample temperature is the same as the gas temperature in this zone, the temperature profile must be very flat, and the heat of reaction/adsorption must be small. The former is achieved by gas preheating, and the latter requires the use of small samples.

The pressure vessels and auxiliary elements, such as filters, tubing fittings, etc. are all constructed of stainless steel, and designed for pressures up to 40 bar and temperatures of up to 400°C. The latter is necessary to allow operation with steam and other vapors without condensation.

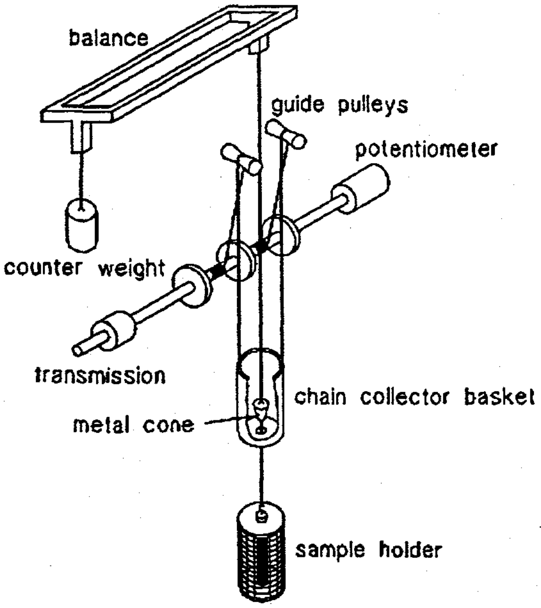


Reaction gas flow and temperature measurement (standard reactor).

In the standard reactor, an Incoloy 800 reaction tube is heating by a heating coil wound around it. This allows heating up to 1100°C. Underneath the heating coil A thermocouple is located underneath the heating coil for temperature control. The software allows for programmed heating rates from 1-100°C/min, variable isothermal dwell times, and pre-defined quenching regimens.

In order to avoid steam or vapor condensation inside the reactor, filters, valves and gas lines, are heated externally with heating tapes and jackets. These temperatures are also controlled by software PID controllers and can be set manually or automatically.

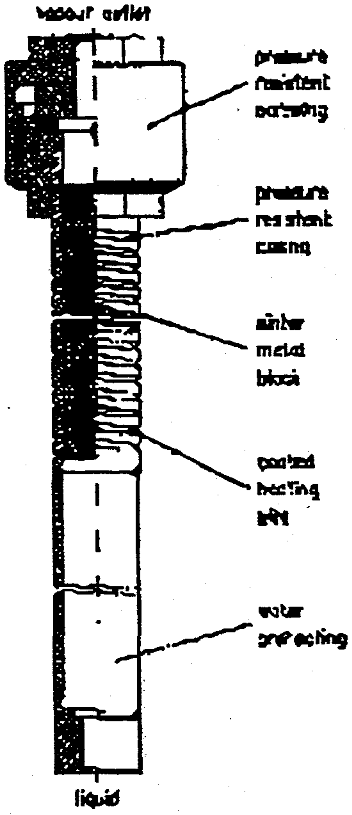
The sample holders are connected to the balance beam *via* a silver chain in the upper cold region, and an Incoloy 800 chain inside the reaction tube. Between the balance and the reactor, a cooled sample lock is located which is equipped with an electrically-driven winch system, shown here. This allows for quick and smooth lowering and lifting of the sample holder without disturbing the balance, even when the reactor is closed and operating at reaction conditions. All parts of this system are specially designed to prevent swinging of the sample basket. Also, the geometry of the winch system is designed to minimize the potential effects of thermal radiation on accurate weight measurement.



Sample winch system.

Since product gases, even. in low concentrations, can influence reaction rates, the reactor is designed as a differential type reactor. The sample holders have been designed with this characteristic in mind. The Incoloy 800 sample holder supplied with the instrument can accommodate 50 - 500 mg of sample, depending on the density of the material and the desired sample geometry.

Continuous and constant gas flow rates are achieved by a system of thermal mass flow controllers (FIC).



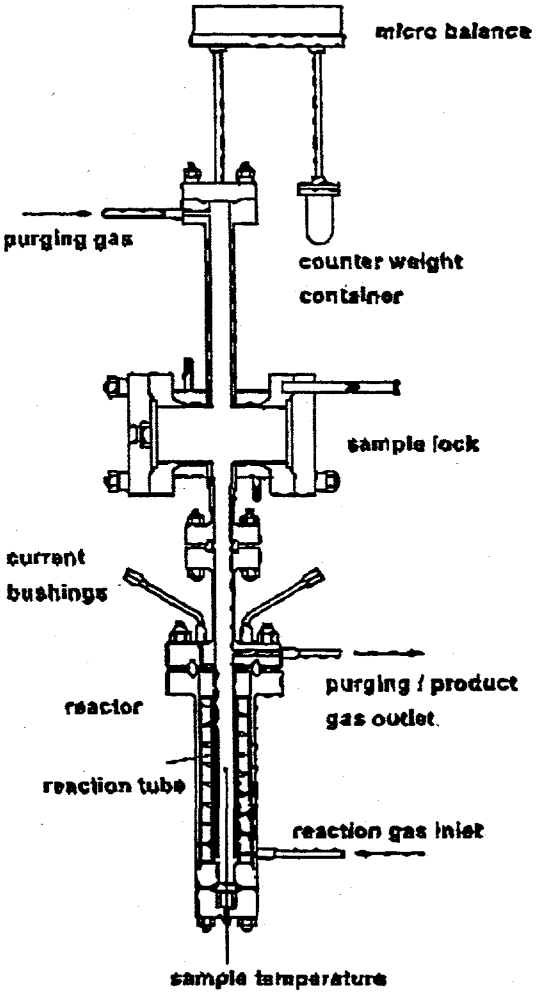
Steam generator.

A vaporizer is included for steam generation as part of the system. This device consists of a precision HPLC pump which can feed up to 10 ml/min of water directly into an externally heated vaporizer containing a sintered metal rod. The liquid water is preheated to a temperature slightly below saturation before entering the sintered rod. The large surface area of the rod ensures a very constant vaporization rate which is necessary to minimize disturbances to the balance as a result of varying drag forces. The steam generator is instrumented with several thermocouples used for control by the system software.

Controlled pressure expansion at the system outlet is carried out by a software control unit in combination with a pressure gauge and a motor-operated expansion valve.

Data acquisition and processing is accomplished with the system software running on a PC. Changes in sample weight are monitored by averaging multiple measurements. These data are recorded along with temperature, pressure, gas flow rates, etc. All relevant test parameters are presented on the monitor during the course of an experiment. Following a test, the raw data can be stored and plotted showing weight changes as a function of time pressure, or degree of conversion. Software is included which computes all necessary corrections for buoyancy and drag in nonisothermal experiments. The program can also be used to differentiate the data using a cubic spline fit. Different types of reaction rates can be calculated and displayed as a function of time, temperature, or degree of conversion.

2.3. Standard TGA. Reactor.



The standard TGA system consists of: (1) the entire TGA-reactor; (2) the gas supply for three reaction gases and the flushing or purge gas (e.g., He, N_2, H_2); (3) the expansion unit including the condenser; (4) the steam generator; (5) separate bypasses for the permanent reaction gases and the steam; and (6) computerized software control of the entire DMT-TGA system. Currently the pressure control range for the standard TGA reactor is restricted to <40 bar due to the use of only one pressure control valve (PCV-104). However, with the addition of a second pressure control valve, the maximum rated pressure of the standard reactor and the gas tubulation of 100 bar can be attained.

In order to provide rapid and smooth switching from one reaction gas (or mixture) to another without disturbing the balance signal, system of electromagnetic valves is provided which are operated by the computer software. This consists of three electro-pneumatic 3-way valves which are operated by compressed air at 5 bar and controlled by additional solenoid valves. The outlets of the 3-way valves are connected either to the reactor or to the bypass line. Both can be heated operation with condensable vapors and controlled independently. A fourth 3-way pneumatic valve for the steam line enables smooth for condensable vapors.

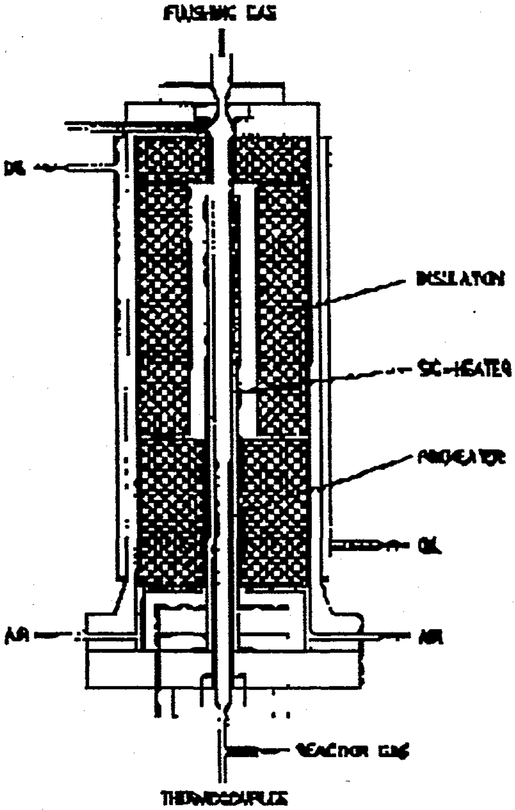
With this system the gas atmosphere can be pre-adjusted without exposing the sample to a reactive environment, while the sample is maintained under a separate inert flowing atmosphere. This guarantees a minimum of weight signal disturbance during switching from one atmosphere to the other.

2.4. High Temperature (HT) TGA Reactor.

The high temperature reactor vessel can be exchanged for the standard TGA. It is provided with a preheater similar to the reaction tube of the standard TGA, plus a SiC heating element surrounding the reaction tube which can be operated at temperatures up to 1600°C. The remainder of the TGA system is used in a similar fashion as with the standard TGA reactor.

At high temperatures, the SiC heating element must be operated under an oxidizing atmosphere. Thus, it must be constantly flushed with air or CO_2 to avoid any to avoid any contact with the reaction gases. This is accomplished by flowing the reaction gases through an alumina tube. The oxidizing purge gas flows through the space between the alumina tube and the SiC heating element. At the top of the alumina tube, the purge gas partially mixes with the reaction gas mixture. The necessary insulation and the Pt-PtRh thermocouple are placed inside the outer vessel of the reactor. To ensure that the reactor wall temperature remains below 400°C, the walls are externally cooled with an oil safety-stat. A metallic tube, similar to the reaction tube in the standard TGA, is mounted underneath the alumina tube to preheat the reaction gases, normally up to about 1000°C. The temperature controller for the standard TGA is used for this purpose. The gas temperatures in the preheater are measured with a NiCr-Ni thermocouple, and in the reaction zone with an alumina-shielded Pt-Pt-Rh thermocouple. The shielding is necessary since practically all metals will react with almost any gas at the high temperatures of interest. In order to minimize the effect of thermal radiation on operation of the balance, alumina apertures are mounted on the upper flange of the HT reactor. Because of the thickness of the required thermal insulation (70 mm), and the space required by the SiC heating element, the internal diameter of the HT reactor (230 mm) is greater than that of the standard TGA.

The use of stainless steel and a wall thickness of 7 mm, required by the 40 bar pressure rating of the reactor, results in a total weight of about 150 kg. In order to handle this weight during the exchange procedure with the standard TGA reactor, two devices were provided - one for transporting and mounting, and another for fixing and storage the HT reactor vessel.



High temperature (HT) TGA reactor.

2.5. Data Acquisition, Evaluation, and Control.

The computer software provides for logging and monitoring of all relevant test data, such as sample weight, temperature, etc., in time intervals (cycle time) ranging from 0.1 s to several hours. These time intervals may also be changed during a run. All graphics and listings that can be produced on the monitor, can be transferred to a printer or plotter.

The data analysis software can be used to calculate all the necessary corrections to the data, such as for buoyancy and drag force. The corrected data can then be fit with cubic splines, and differentiated to determine reaction rates as functions of time, temperature, and conversion. Arrhenius plots can then be formulated to determine the corresponding activation energies and frequency factors.

The TGA control software is used to operate the TGA, and provides for operating safety. It consists of several basic electronic hardware stations which work as interfaces between the software controllers and the TGA hardware. The link between the software controllers and stations is a high speed CAN-bus system, operating at 18 Hz. That is, all the measured data are transferred to the computer eighteen times per second.

The software provides up to 40 controllers which can be defined for controlling tasks either as a 2-point or 3-point PID controllers. All controllers are graphically displayed on the screen showing their current working status. By choosing a controller with the mouse, more detailed information is available; e.g., the actual and nominal parameter values, a graphical history over the last few minutes, hours, up to 7 days.

The TGA control software allows for free programming of the software controllers; e.g., linear and nonlinear ramps, set points, alarm settings, etc. In this manner it is possible to predefine entire experimental regimens, including the logical combination of subsequent actions. For example, an automated pressure increase, followed by a predefined temperature increase. The entire set of parameters for an experimental run can be stored so that the same experiment can be duplicated as many times as desired. In addition, these programs can be defined in a loop. The experimental data are stored in ASCII-code, so that data can be downloaded and used with other commercial software, such as EXCEL™.

3.0. Installation, Commissioning, and Modifications of the HP/HT DMT- TGA System.

The HP/TP DMT- TGA apparatus was purchased in 1996 and installed and commissioned during the summer of 1996. A diagram of the apparatus is presented in Figure 1, and a flow diagram in Figure 2.

The apparatus was located in Room 128 of the Prince Engineering Building at Brown University, as per the diagram presented in Figure 3. This room had been previously used for the storage of explosive materials, and was already equipped with explosion-proof electrical receptacles, lights, and switches. A hydrogen alarm and vent system were added for safety considerations. An image of the installed apparatus is included in Figure 4.

The system has been interfaced to an Ametek quadrupole mass spectrometer (MA 100), pumped by a Varian V250 turbomolecular pump, as provided for in the original proposal. With this capability, a number of gas phase species of interest can be monitored in a near-simultaneous fashion. The MS can be used in a few different modes. During high pressure, steady-state gasification experiments, it is used to sample, measure, and monitor the reactant/product gases. It can also be used to monitor gas phase species during nonisothermal temperature programmed reaction (TPR) or temperature programmed desorption (TPD) experiments.

Since the DMT-TGA is a piece of process equipment, rather than a conventional laboratory instrument, its proper and safe operation is somewhat complex. For this reason, a set of condensed operating instructions were formulated. These are included in Appendix A.

Two people who were most instrumental in commissioning and operating the apparatus are Dr. M.M. Antxustegi and Mr. W.D. Lilly, Senior Technical Assistant, Division of Engineering. Dr. Antxustegi was supported by the Spanish government for a two-year postdoctoral fellowship came to work with this apparatus. In addition, Mr. Miguel de la Casa Lillo, a Ph.D. student from the Department of Inorganic Chemistry of the University of Alicante, Spain, has visited our laboratory to utilize the apparatus as part of his studies concerning hydrogen storage in activated carbon fibers (ACF).

The Office of the Dean of Research of Brown University contributed $36,000 in cost-sharing for the apparatus and equipment for interfacing it to the mass spectrometer, in accordance with the original proposal.

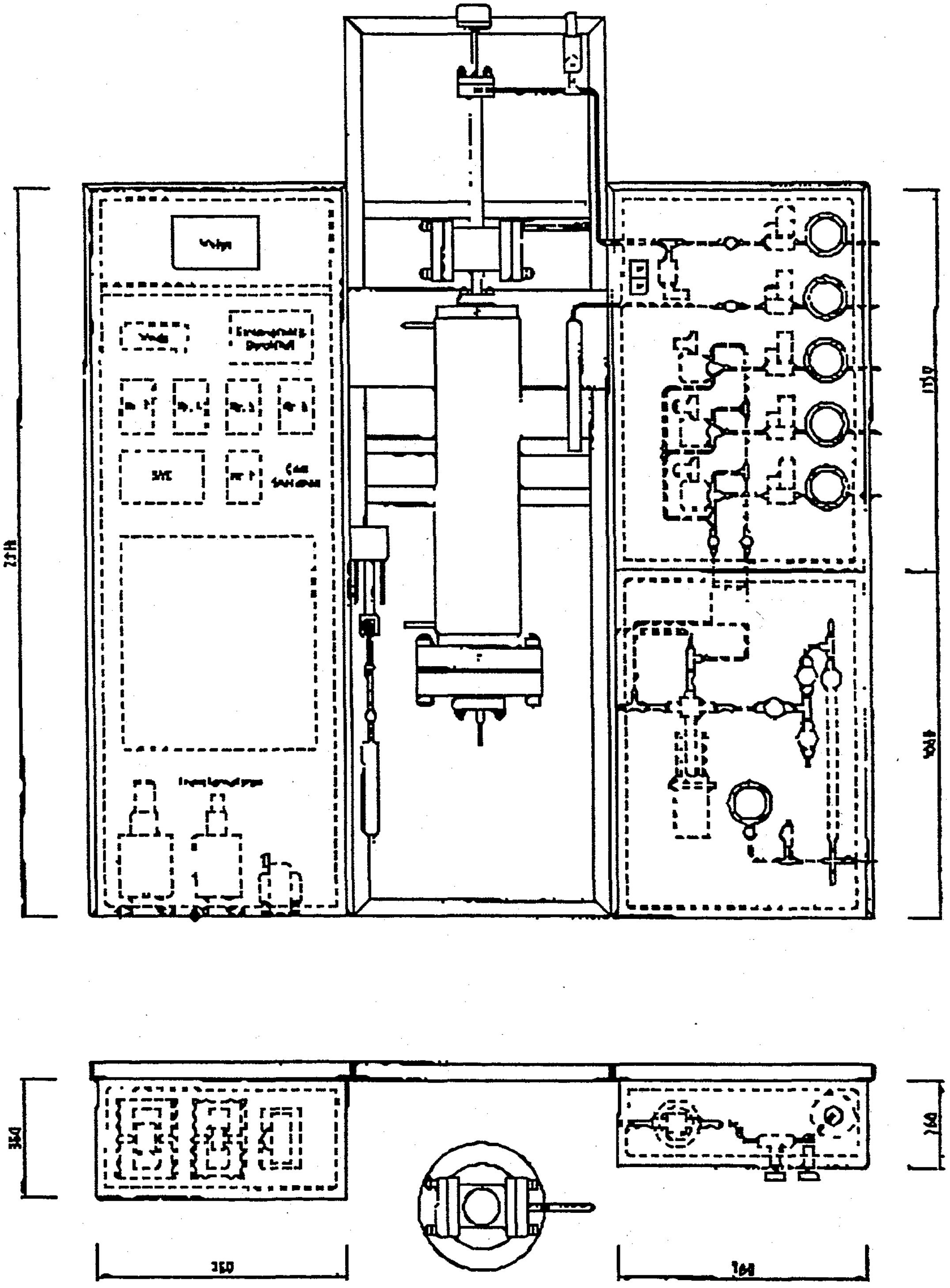


Figure 1. Schematic of the HP/HT DMT-TGA system.

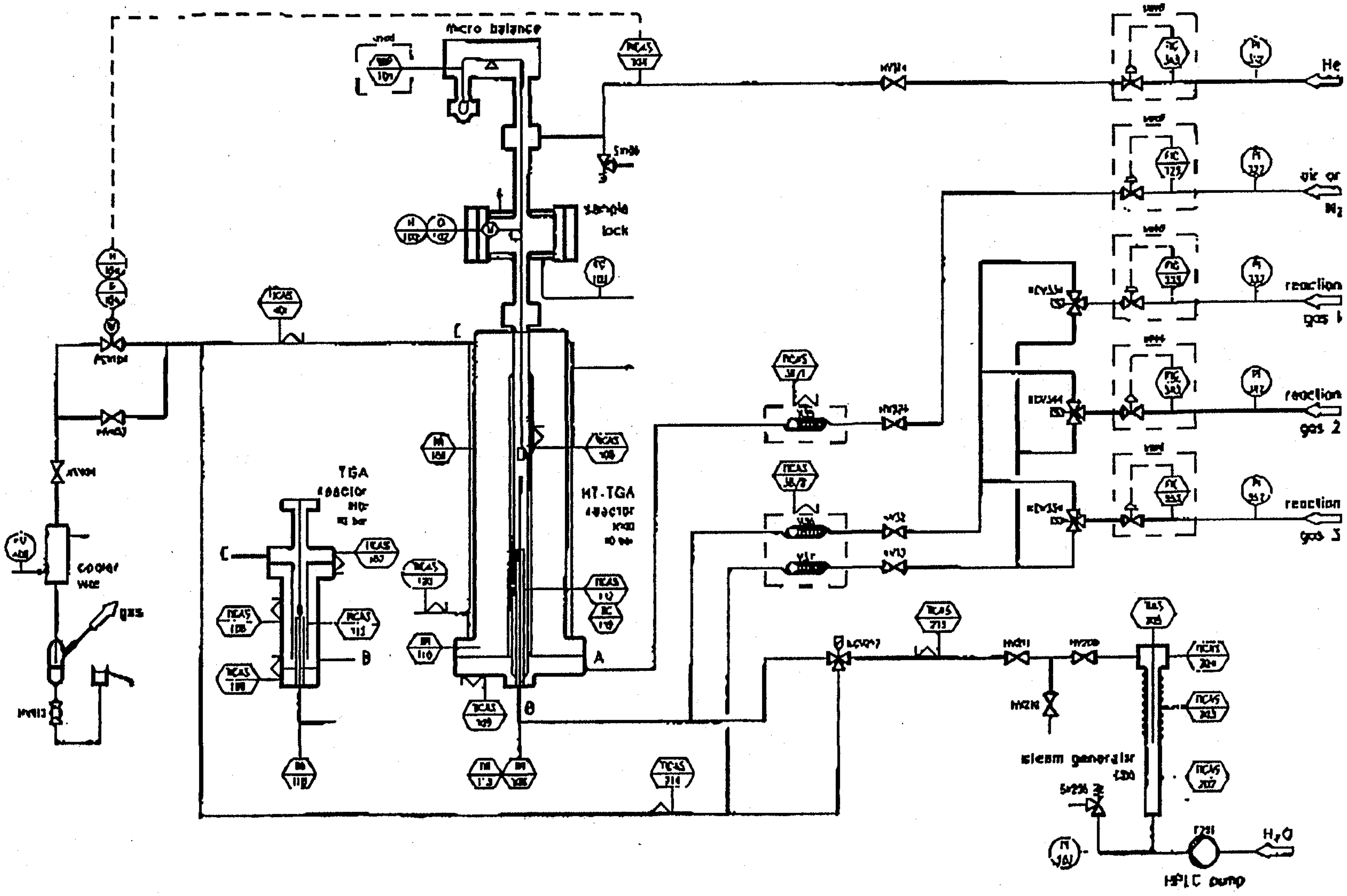


Figure 2. Flow schematic of the HP/HT DMT TGA.

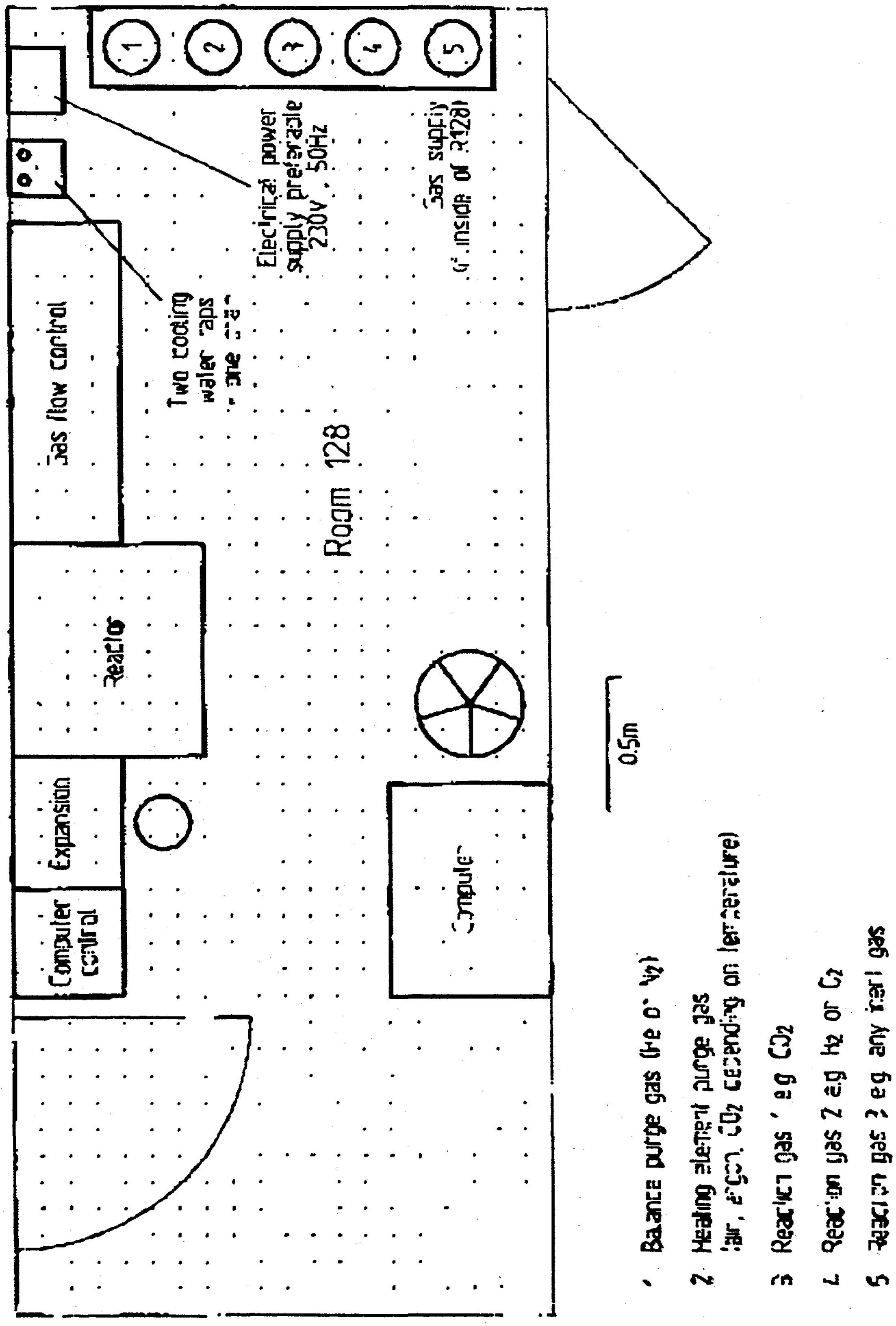


Figure 3. HP/HT DMT-TGA installation layout in Prince Engineering Room 128.

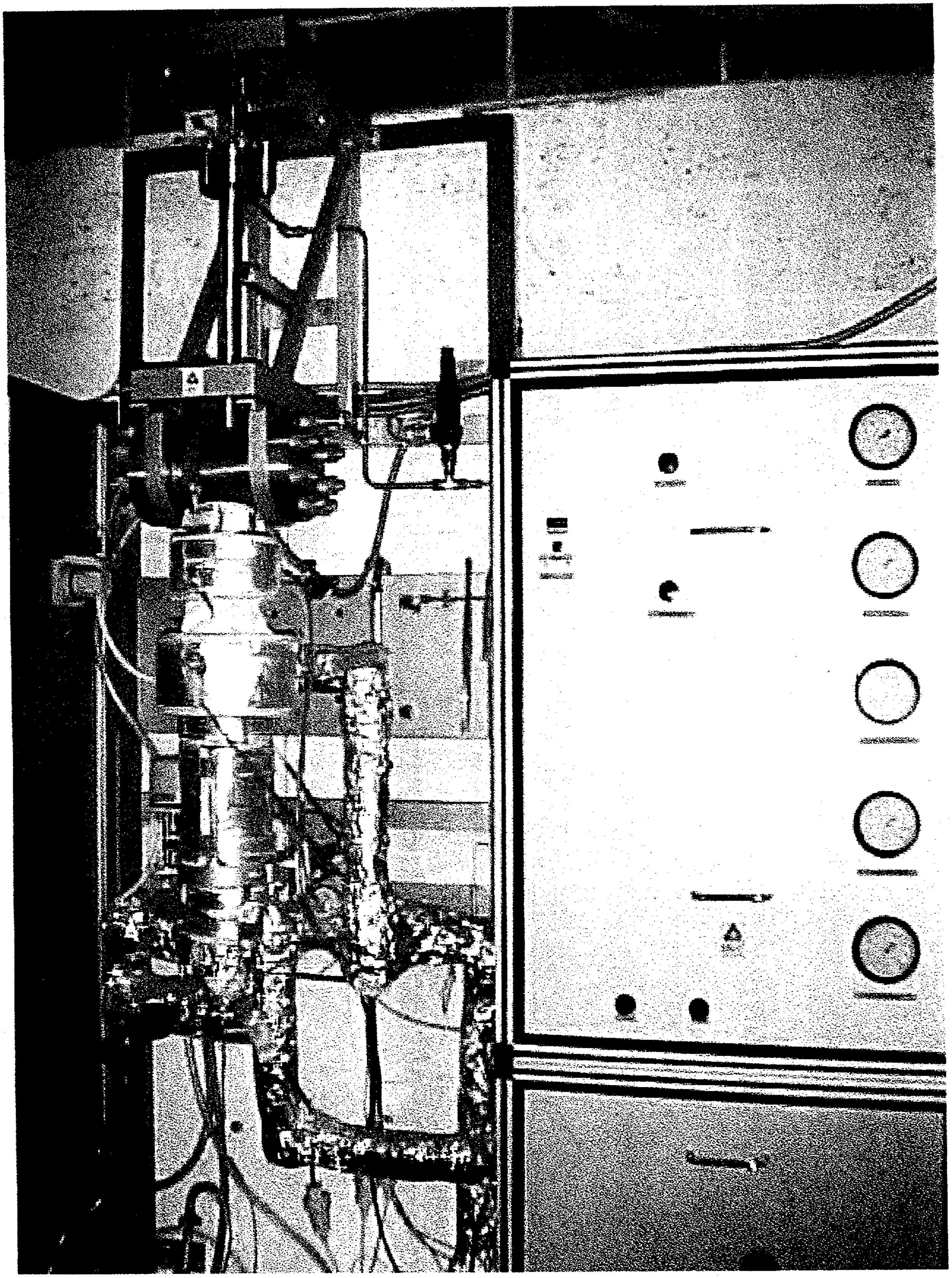


Figure 4. HP/HT DMT-TGA installed in Prince Engineering Room 128, Brown University.

3.1. Sample Test Data.

Results from test Run 110 are presented in Figures 5-9. This test was a *nonisothermal* CO_2 gasification run of a Wyodak coal char sample. The initial sample weight was 202.2 mg, and the final sample weight was 23.2 mg (~11.5% ash). The temperature in the TGA was increased as a linear ramp to 800°C at a rate of 10K/min. The CO_2 pressure was 26 bar and the flow rate was 3 slpm (standard liters/min).

In Figure 5 are presented the raw sample mass and temperature data. The buoyancy correction to the sample weight curve is shown in Figure 6. The lower curve is corrected for the decreasing density of the CO_2 gas in the reaction zone with increasing temperature. In Figure 6, the additional correction for drag on the sample holder is applied (i.e., increasing upward flow velocity with increasing temperature at constant pressure), yielding the final corrected sample weight-time history as the lower curve in this figure. The final sample weight has also been subtracted from this last curve. This curve is fit with cubic splines, and then differentiated to yield the reaction rates, r' and r'' (% weight loss/min), as shown in Figures 8 and 9.

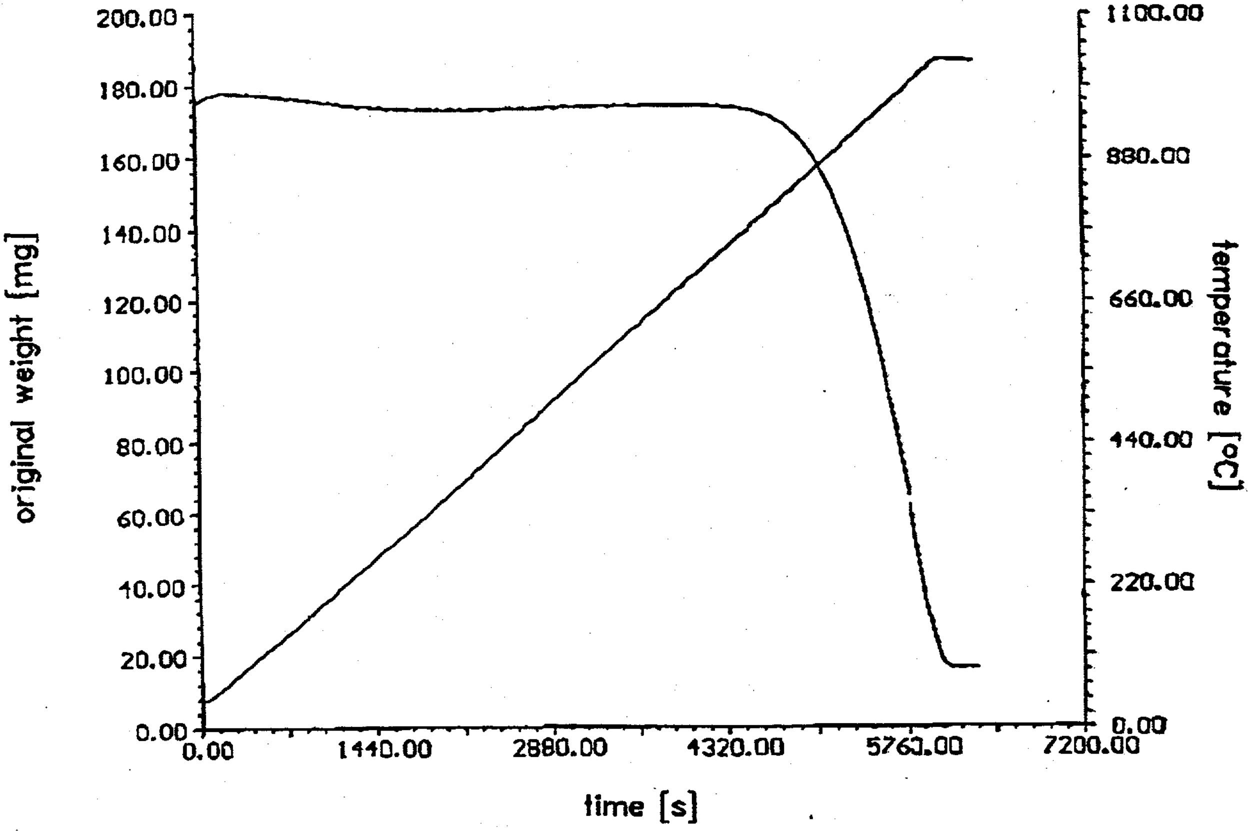


Figure 5. Raw sample weight and temperature data for Test Run 110 – nonisothermal gasification of Wyodak coal char in 26 bar of CO_2.

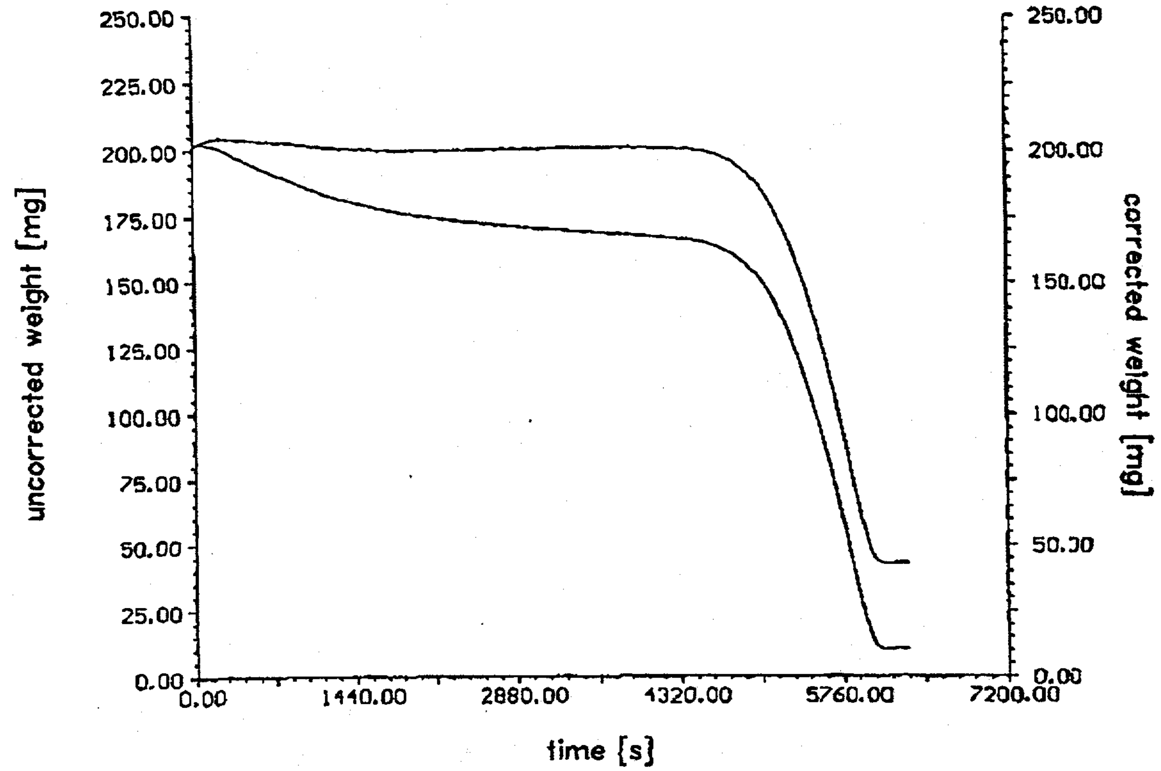


Figure 6. Sample weight data corrected for buoyancy (lower curve for Test Run 110 – nonisothermal gasification of Wyodak coal char in 26 bar of CO_2.

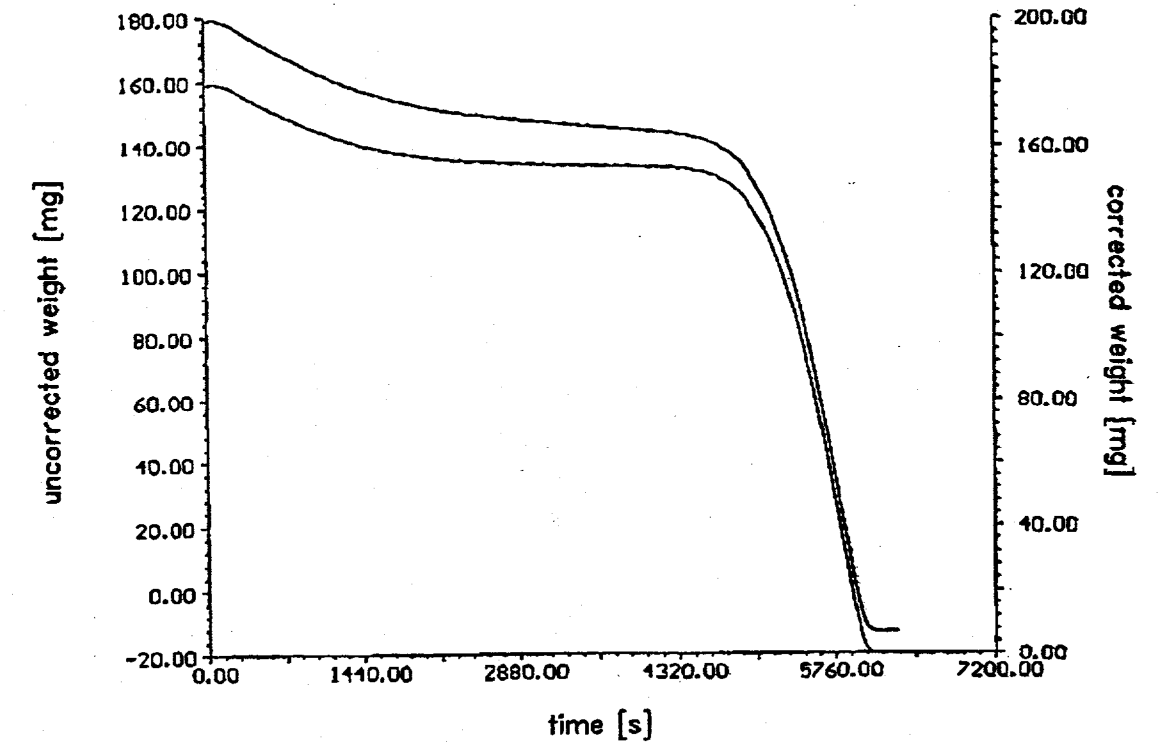


Figure 7. Sample weight data corrected for flow rate (lower curve) for Test Run 110 – nonisothermal gasification of Wyodak coal char in 26 bar of CO_2.

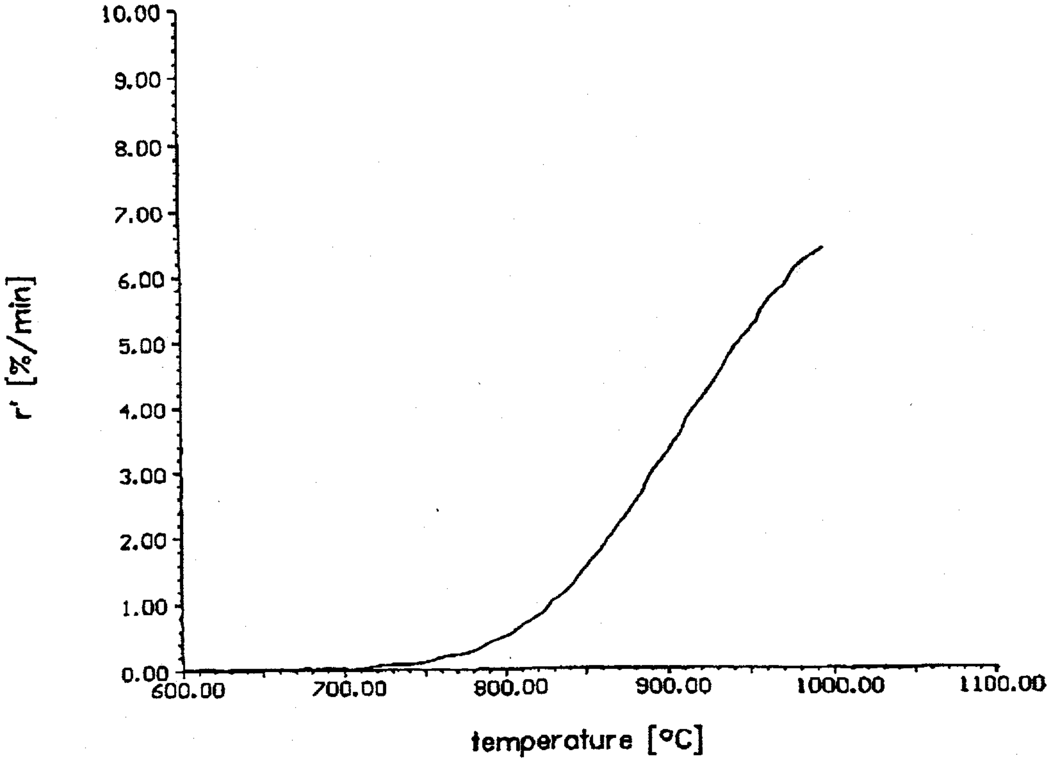


Figure 8. Sample reactivity as a function of temperature for Test Run 110 – nonisothermal gasification of Wyodak coal char in 26 bar of CO_2. r' is the % weight loss rate with respect to the initial sample weight.

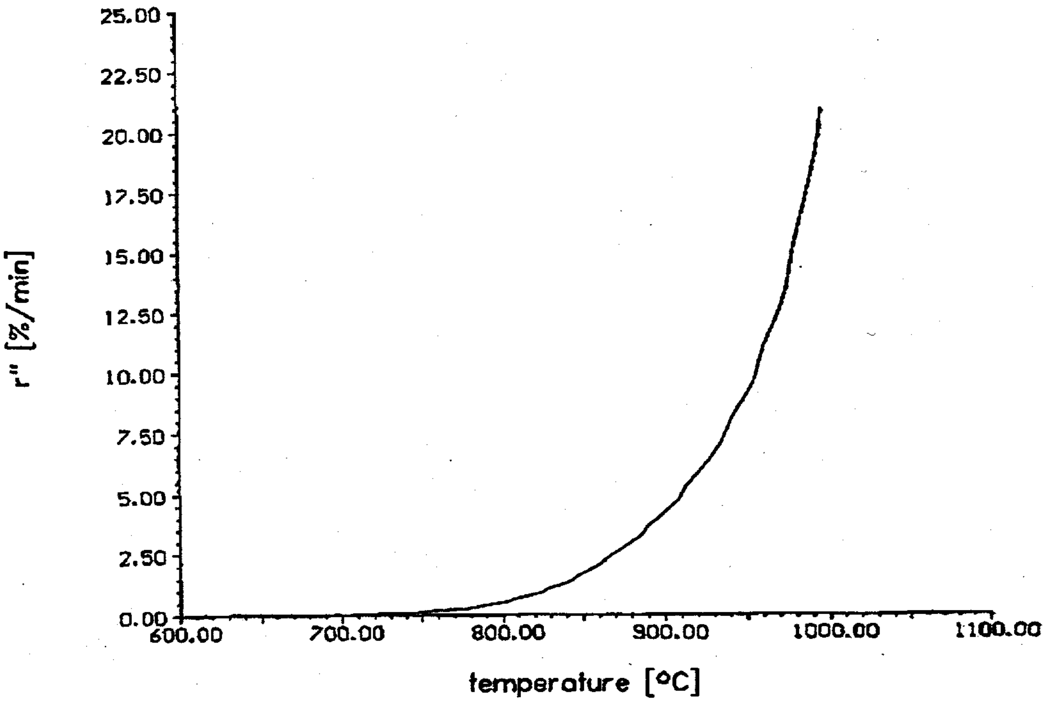


Figure 9. Sample reactivity as a function of temperature for Test Run 110 – nonisothermal gasification of Wyodak coal char in 26 bar of CO_2. r'' is the % weight loss rate with respect to the instantaneous sample weight.

Test Run 111 was an *isothermal* CO_2 gasification run for a Wyodak coal char sample (203.6 mg) at 900°C at 26 bar. The final sample weight was 25.8 mg (~12.7% ash). The initial raw sample weight and temperature history are presented in Figure 10 as a function of time, and the sample reactivity derived from this data, r'', in Figure 11.

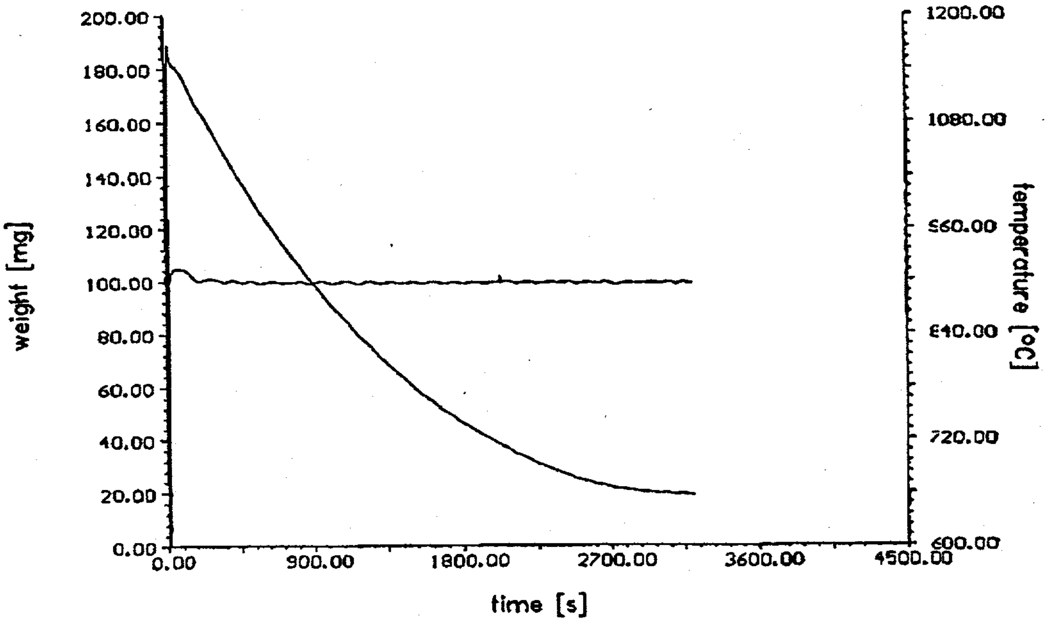


Figure 10. Raw sample weight and temperature data for Test Run 111 – isothermal gasification of Wyodak coal char at 900°C in 26 bar of CO_2.

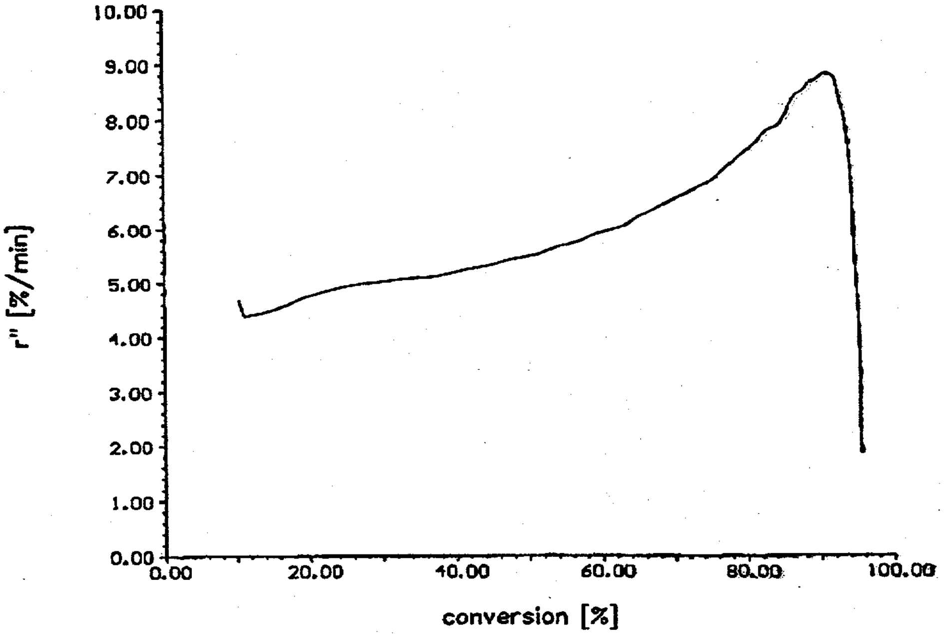


Figure 11. Sample reactivity as a function of % conversion for Test Run 111 – isothermal gasification of Wyodak coal char at 900°C in 26 bar of CO_2. r'' is the % weight loss rate divided by the instantaneous sample weight.

4.0. The HP/HT DMT-TGA and Current Research.

The DMT-TGA apparatus is well suited to our research requirements and for adaptation to our experimental techniques. Particular ongoing applications follow.

4.1. Gasification Kinetics at Elevated Pressure.

Almost any commercial coal gasification/combustion system for power generation or synthesis gas production must of necessity operate at elevated pressures in order to be economically viable. Unfortunately, the vast majority of gasification rate data and our knowledge of the surface chemistry and energetics that govern conversion rates under realistic operating conditions are available for the most part only at atmospheric pressure and below.

There is ample evidence to indicate that gasification mechanisms, and, consequently, the surface energetics of the oxygen surface complexes involved, are substantially different at elevated pressures than *ca.* atmospheric pressure and below. About forty years ago, Blackwood and co-workers concluded that a quadratic term in the partial pressure of the oxidant gas had to be included in the typical first-order, Langmuir-Hinshelwood/Hougen-Watson (LHHW)-type rate expressions (commonly used to describe gasification rates at lower pressures; e.g., see Laurendeau, 1978) in order to quantitatively describe the steady-state gasification rate of a coconut char in both pure steam (Blackwood and McGrory, 1958) and CO_2 (Blackwood and Ingeme, 1960) at elevated pressures (up to 50 atmospheres). This was contrary to the generally assumed behavior predicted by LHHW formulations that gasification rates become zeroth order at sufficiently high pressures (Laurendeau, 1978). Subsequently, a number of other workers have come to similar conclusions. For example, Kapteijn *et al.* (1991) concluded that a quadratic term was needed to explain their transient kinetic data on potassium catalyzed gasification of a Norit activated char in CO_2. In addition, van Heek and Mühlen (1991) in a summary of their work on fitting high pressure, steady-state gasification rate data obtained for a particular coal char, also concluded that quadratic terms are necessary in order to quantitatively describe the rate behavior with pressure for CO_2, H_2O, and H_2 gasification of coal chars. Unfortunately, these latter studies were not accompanied by thermal desorption experiments which would be necessary to investigate the nature of the surface complexes responsible for the observed rates, nor with transient experiments to probe the detailed nature of the kinetic mechanisms responsible. Thus this work contributed little in the way of improving the mechanistic understanding of the conversion behavior under these realistic operating conditions.

4.2. The Effects of Hydrogen.

During gasification, hydrogen is formed primarily *via* the recombination of hydrogen atoms on the carbon surface from the decomposition of steam. In addition to being surface intermediates for hydrogen gasification under the appropriate conditions, the relatively stable high-temperature C-H surface complexes effectively "poison" a fraction of the active carbon surface towards gasification by steam and other agents. For example, in a study of the effect of hydrogen on CO_2 gasification (Biederman *et al.,* 1976), it was clearly shown that hydrogen at very low partial pressures markedly inhibited the CO_2 gasification rate. It was concluded that inhibition occurred by dissociative chemisorption of hydrogen onto active sites.

In recent work, using TPR (temperature programmed reaction or reduction) techniques we have shown (Calo *et al.,* 1997) that hydrogen has a number of significant effects on intermediate carbon-oxygen surface complexes, and, consequently, also on gasification reactivity. It directly reduces certain types of complexes (CO-evolving semi-quinones), facilitates the thermal decomposition or desorption of others (carboxylic avid anhydrides), presumably by dissociative chemisorption at neighboring sites, but does not apparently interact with yet other types of complexes (e.g., high-temperature CO-evolving surface complexes).

Work at Brown (Lu, 1996) has also suggested that the energetically distributed nature of char surfaces allows hydrogen to inhibit steam gasification at high energy active sites *via* the exothermic oxygen exchange reaction:

$$C(O) + H_2 \rightarrow H_2O + C_f$$

(where C(O) is an oxygen surface complex, and C_f is an empty active site), whereas at low energy sites, the endothermic gasification reaction *via:*

$$C(O) \rightarrow CO + C_f,$$

still prevails. Such a mechanism can provide a mechanistic basis for reconciling a number of seemingly contradictory conclusions concerning hydrogen inhibition of gasification that may be found in the literature. In any case, it is clear that understanding the behavior of hydrogen in the gas milieux is an important key to establishing the mechanistic basis of gasification reactivity, especially at elevated pressures. This is one of the issues we propose to investigate.

4.3. Experimental Methods.

The mechanistic changes which occur at elevated pressures will be reflected in the evolution of the energetic distributions of the surface complexes resident on the char surfaces.

Here we provide some examples of the application of surface complex energetics to reactivity correlation/prediction.

4.3-1. Thermal Desorption, Surface Energetics, and Gasification Reactivity. Oxidizing gases, such as steam, CO_2 and oxygen, form intermediate oxygen surface complexes on carbonaceous surfaces, which subsequently decompose to CO, carrying off solid carbon in the actual gasification step. The oxygen surface complex intermediates that form on char surfaces in a reactive atmosphere can be thermally desorbed as CO and CO_2 by subjecting the char to a program of increasing temperature in an inert gas environment. This process is commonly known as temperature programmed desorption (TPD). The resultant peaks and their temperatures in the TPD spectra are related in a fundamental manner to the desorption processes, and, therefore, provide information regarding the energetics of the adsorbed species. The analysis and deconvolution of TPD spectra for energetically homogeneous surfaces is well known (e.g., see King, 1975). The corresponding situation for energetically heterogeneous surfaces, and for multiple surface species that are very close in energy, such as can occur in chars, is more complex. For continuous distributions of surface species, we have developed techniques to transform TPD spectra into probability density functions of desorption activation energies. This approach has been successfully applied to carbon-oxygen surface complexes produced by CO_2, H_2O, and O_2 to predict/correlate reactivity (Calo and Hall, 1991; Calo *et al.*, 1993; Zhang, 1996; Lu, 1996). The essence of this approach is briefly summarized below.

4.3-2. Reactivity and Distributions of Desorption Activation Energies. The specific gasification reactivity, r (e.g., g/g h), is given in general by:

$$r \equiv -(1/C)\, dC/dt = k_d\, C_t\, \theta, \qquad [1]$$

where C is the amount of carbon, k_d the desorption rate constant, C_t the total moles of active sites per mole of carbon, and θ is the fraction of the active carbon sites that are occupied by oxygen complex. For conditions where the char surface is saturated with oxygen complex, $\theta = 1$ and Eq. [1] becomes simply:

$$r = -(1/C)\, dC/dt = k_d\, C_t, \qquad [2]$$

and thus in this case the desorption rate constant becomes equivalent to the specific gasification rate, r. Eq. [2] applies specifically to a homogeneous surface; i.e., one discrete surface complex with a single desorption activation energy. Char surfaces, however, are known to be distinctly heterogeneous with a distribution of desorption energies. In this case, k_d must be the energyaveraged, such that the corresponding expression for r becomes:

$$r = \int_0^\infty \upsilon_o \exp(-E/RT)\, [C\text{-}O]_o\, S(E^*)\, dE^* \qquad [3]$$

where k_d has been written in its Arrhenius form with pre-exponential υ_o, and $[C\text{-}O]_oS(E^*)$ is the probability density function of desorption activation energies, which can be determined from temperature programmed desorption (TPD) data. For example, we have shown that the CO desorption rate from a heterogeneous char surface in response to a linear heating rate β, is related to the energetic distribution of oxygen surface complexes by the expression:

$$d[C\text{-}O]/dt = [C\text{-}O]_o\, S(E^*)\, R\beta\, [E^*/RT], \qquad [4]$$

where $d[C\text{-}O]/dt$ is the measured desorption rate at temperature T.

For situations intermediate between *single* energy and *continuum* descriptions of surface complexes, it is proposed to apply the relatively new technique of *intermittent temperature programmed desorption* (ITPD) (Joly *et al.,* 1994). This promises to be a very useful method for the current application, where various, energetically similar, surface species are to be identified. Briefly, the method is as follows. The rate of desorption from a *single* surface species, $d\omega/dt$, is typically well described by a first order process; i.e.,

$$d\omega/dt = \sigma\, \nu_0 \exp(-E/RT), \qquad [5]$$

where σ is the concentration of the species in the sample, ν_o is the pre-exponential factor, and E is the activation energy for the desorption of the particular species. The value of σ will be approximately constant for a sufficiently small degree of desorption, such that:

$$\ln[d\omega/dt] = \ln[\sigma\, \nu_0] - E/RT, \qquad [6]$$

and thus a semilogarithmic plot of gas evolution rate *vs.* 1/T will be linear with a negative slope of -E/R. A sample containing a number of distinct, but closely spaced (in desorption energy) species will yield a corresponding number of different activation energies, if the gas evolution process can be sufficiently well resolved so that the linear relationship in Eq. [6] is maintained. This can be accomplished by using a "sawtooth" heating program which repeatedly sweeps over a particular temperature "window", while progressively advancing the "window" in temperature at a lower rate. The effect of this type of program is to "slice-up" the desorption process into finely divided, overlapping "micro-TPD spectra," each of which is sufficiently short to maintain the concentrations of the locally active species approximately constant; i.e., approximating linear behavior as per Eq. [6]. It is noted that this result is not possible with a conventional linear TPD program which "interrogates" all the active species nearly simultaneously and under conditions of continually varying surface concentrations. The resultant semilogarithmic plots of all the "micro-TPD spectra" generated *via* this method yield "local" desorption activation energies which, when plotted *vs.* the fraction of total gas desorbed, reveal "plateaus" of constant activation energies corresponding to each of the chemically distinct species. We have demonstrated the resolution of three distinct species, very close in desorption activation energies (140, 150 and 160 kJ/mole), and relative abundances of 0.3:1.0:0.4, respectively, using a "sawtooth" heating program with a linear heating rate of 25K/min within each cycle, with a span of 120K per cycle, and a cycle-to-cycle displacement of 7K. These same species ***could not be*** *discerned from a conventional 25K/min, TPD spectrum.*

In addition to TPD/ITPD, temperature programmed reaction (TPR) will also be used to probe the nature of the intermediate surface complexes. This technique is similar to TPD, except that it is conducted in a reactive rather than an inert gas environment. For the reaction systems of interest here, the TPR data will be used in two ways. First, the comparison of TPR spectra can be used to provide a rapid, consistent method for the determination of relative reactivities of different samples, as well as the nature and behavior of the gaseous products as a function of temperature. This represents a "screening" function. However, the same TPR rate data can also be analyzed *quantitatively* to yield global activation energies, as was done in Illán-Gómez *et al.* (1993), for example, or to deconvolute the kinetics and energetics of the various mechanistic steps involved. An example of what can be done with this approach is provided in Calo *et al.*, 1997, where TPR with hydrogen and TPD data on the same oxidized samples were used to *quantitatively* analyze the energetics of the surface complexes and the kinetics of the interaction of hydrogen with oxygen surface complexes. It is proposed to apply a similar approach to the gasification TPR data.

All three methods – TPD, ITPD, and TPR – can be used to investigate the nature of the surface complex intermediates responsible for gasification at elevated pressures.

4.4. Activated Carbon Fibers for Hydrogen Storage.

Normally, the pressures required to effectively store hydrogen in various materials are quite high. This presents a significant problem for hydrogen fuel applications where hydrogen must be stored in a safe and reliable manner. A study was undertaken to investigate the efficacy of using activated carbons (actually activated carbon fibers, ACF) to store hydrogen at lower pressures.

Activated carbon fibers (ACF) produced from petroleum pitch were used to examine the hydrogen uptake using the high pressure TGA. These fibers have very narrow pore size distributions in the micropore size range <2nm.

In this study samples of the same ACF at different levels of activation (i.e., burn-off) were used in order to explore the porosity characteristics that would be most effective for hydrogen storage. Using adsorption measurements of nitrogen at 77K and CO_2 at 273K, it was determined that the degree of activation tended to increase the mean pore size. In a preliminary set of experiments conducted at ambient temperature and hydrogen pressures from 0 to 50 bar, it was found that it is possible to adsorb significant amounts of hydrogen over this range of pressures. It was also found that the fibers with the smallest mean pore sizes were the most effective for the same ACF materials.

Table 1. Activated carbon fiber samples used for hydrogen storage.

ACF Sample	CO_2 Surface Area (m^2/g)	N_2 Surface Area (m^2/g)
ACF 18	460	0
ACF 19	744	725
ACF 36	1199	1494
ACF 46	1420	1861
ACF 52	1453	2085
ACF 66	1549	2375
ACF 74	1497	2585

4.5. Oxygen Gasification of Automobile Tire-Derived Chars.

As part of an NSF-sponsored project concerning the production of activated carbons from non-traditional sources, the HP/HT DMT TGA was used to examine the kinetics of reaction of carbons as a function of oxygen partial pressure. In an earlier study in this laboratory, it had been concluded that the intrinsic order of the oxygen-carbon reaction (as represented in a single-step reaction process) is rarely unity. The present experiments were performed with a char prepared by pyrolysis of used automotive tires. The interest was in activation of this material to high enough surface areas so that it would be of commercial interest. As part of this study, the kinetics of the reaction of oxygen with this material needed to be explored.

The experiments involved placing a roughly 100 mg sample of previously prepared tire char in the TGA sample basket, and monitoring mass loss at different pressures of air in the TGA. A fresh sample was used for each pressure condition. The kinetics were followed until complete burnout to ash was achieved. Purified compressed air was used in these experiments. The TGA temperature was maintained at a constant value of 718K throughout the series of experiments. The results are shown below, in Figure 12.

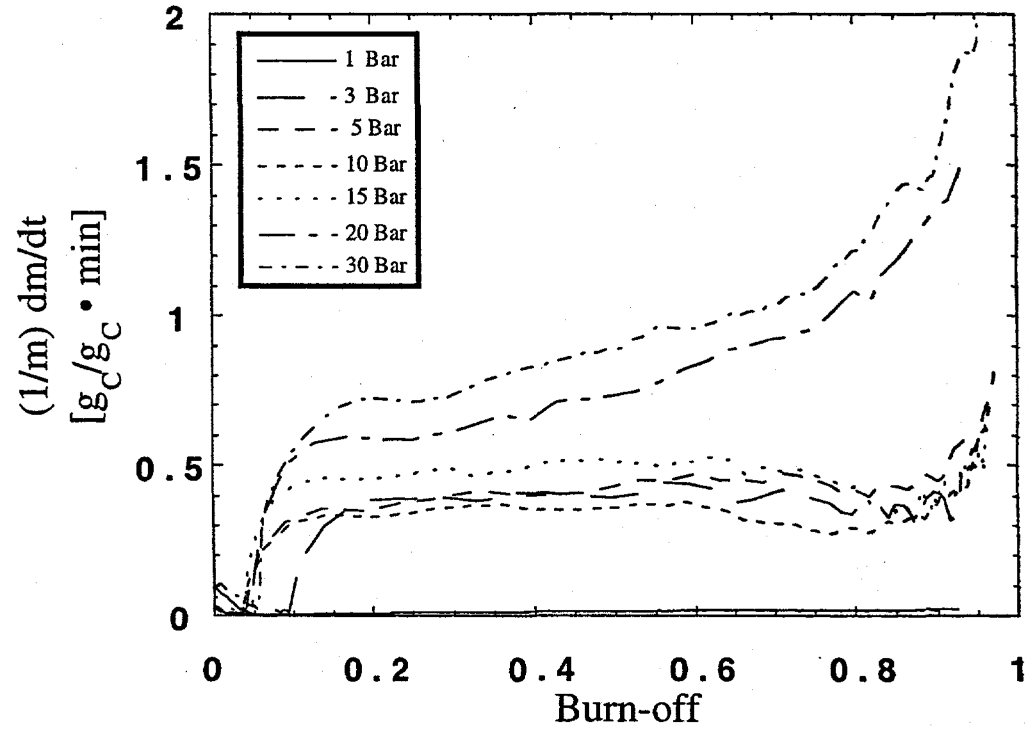


Figure 12. Reactivity of tire char samples as a function of burn-off. All experiments were performed at 718K in air at the indicated air pressure. The burn-off values have been corrected for the residual ash content of the samples.

With the exception of the experiment at 3 bar pressure, all of the results show an abrupt increase in rate near 5 % burn-off (the unexpected deviation in the latter result was not explored further). The reactivity is here expressed in terms of rate per unit mass of remaining sample. On this basis, many of the samples show a long period of relatively constant reactivity from about 10 to 90 % burn-off. Such a trend is quite common. The samples gasified at higher pressures deviated from this behavior somewhat.

With regard to the pressure dependence of rate, the high pressure data show the expected trend of increasing rate with increasing pressure. The pressure dependence of rate is much less distinct at lower pressures. It is not yet understood what determines this behavior. It is, however, possible to determine an apparent order of reaction from the data in hand. The result is shown in Figure 13. This figure shows that the apparent order is quite near the typically observed value of around 2/3, within the 10 to 90 % burn-off range. Clearly more work is required to better define the actual order in this case, but these results already confirm that the behavior observed at oxygen partial pressures well below 1 bar extends to oxygen partial pressures of over 6 bar. The very different burnout behavior of samples gasified at higher pressures also invites further examination.

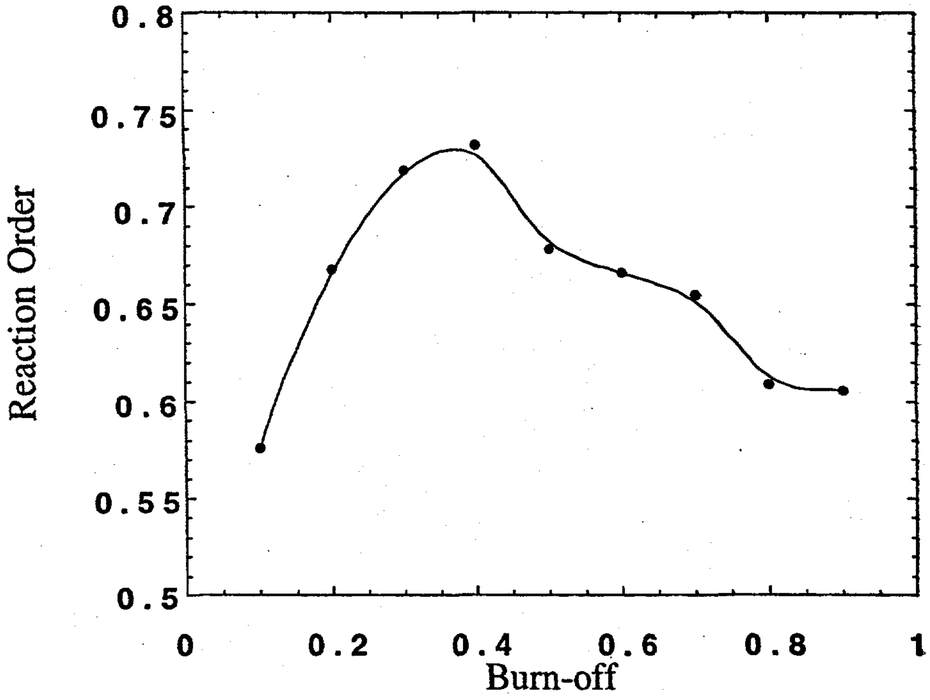


Figure 13. Apparent reaction order with respect to oxygen for the oxygen-tire char reaction at 718K.

REFERENCES

Biederman, L., A. J. Miles, F. J. Vastola, and P. L. Walker, Jr., *Carbon*, **14**, 351 (1976).

Blackwood, J.D.; McGrory, F; *Austr. J. Chem.* **11,** 16 (1958).

Blackwood, J.D.; Ingeme, A.J.; *Austr. J. Chem.* **13,** 134 (1960).

Calo, J.M.; Hall, P.J.; in *Fundamental Issues in the Control of Carbon Gasification Reactivity,* J. Lahaye and P. Ehrburger, eds, NATO ASI Series, Series E: Applied Sciences, Vol. 192, p. 329, Kluwer Academic Publishers, Dordrecht, 1991.

Calo, J.M., W. Lu, L-H Zhang, and J.A. MacKinnon, *Proc. Twenty First Biennial Conference on Carbon*, SUNY Buffalo, Buffalo, NY, 1993, p. 519.

Calo, J.M., D. Cazorla-Amorós, A. Linares-Solano, M.C. Román-Martínez, and C. Salinas-Martínez de Lecea, *Carbon* **35**, No. 4, 543, 1997.

Illán-Gómez, M.J., A Linares-Solano, L.R. Radovic, and C. Salinas-Martínez de Lecea, Energy & Fuels, 9, 97, 1995a; 9, 104 (1995b); 10, 158 (1996).

Kapteijn, F.;Meijer, R.;van Eck,S.C.;Moulijn,J.A.; *ACS Div. Fuel Chem. Prepr.***36(3)**, 990, (1991).

King, D.A. *Surf. Sci.* **47**, 384 (1975).

Joly, J.P., S. Haydar, A. Perrard, C.Moreno-Castilla, J. Rivera-Utrilla, and M.A. Ferro-Garcia, *Proc. Carbon '94,* Granada, Spain, July, 1994, p. 346.

Laurendeau, N.M., *Prog. Energy Combust. Sci.* **4**, 221 (1978).

Lu. W., Ph.D. Dissertation, Division of Engineering, Brown University, 1996.

van Heek, K.H.; Mühlen, H.J.; in *Fundamental Issues in the Control of Carbon Gasification Reactivity,* J. Lahaye and P. Ehrburger, eds, NATO ASI Series, Series E: Applied Sciences, Vol. 192, p. 1, Kluwer Academic Publishers, Dordrecht, 1991.

Zhang, L.-H., Ph.D. Dissertation, Division of Engineering, Brown University, 1996.

APPENDIX A.

DMT-TGA Condensed Operating Instructions

General Considerations:

1) System Software:

The detailed keystroke sequences included below should be helpful.

The software has a propensity to crash at the most inopportune moments; most often upon starting data acquisition if the keystroke sequence on the Process Control Page or some program parameter is not quite right, or if the computer has not been shut down and rebooted since the previous data acquisition run. A crash at this point in the procedure results in rapid depressurization of the reactor (also mentioned under "Things to Avoid"), which is a considerable waste of the time, effort, and gases spent to bring the apparatus to initial setpoint conditions. When hydrogen or other hazardous gases are in use, this becomes a serious safety issue as well. Certain precautions and actions can be taken to minimize pressure loss and associated hazards, should such a crash occur. These are noted in the procedures below, indicated by the symbol †.

The software allows only the 10 most recent data files to be stored on hard disk, with the oldest being overwritten by the newest run data. Consequently, it is advisable to transfer data files to a floppy disk at the end of each run, although this may also be done as a separate operation. There is some propensity of the software to crash during the Transfer operation, which has been supposedly fixed with a patch; but it probably still does not contain adequate traps for Disk Full, Duplicate Name, and other possible errors.

2) Things to Avoid:

Certain accidents or careless technique can result in lengthy apparatus downtime. The principal problems among these are:

2.0.dropping the sample holder into the reactor by its becoming unattached from the hangdown chain and falling;

3.0.having sample escape the holder; and

4.0.over-torquing the sample lock bolts.

Appropriate precautions are:

3.0.Always close the chain loop with pliers when attaching so that the holder cannot possibly fall off;

4.0.insure that the holder screen cylinder is fully seated in both top and bottom endcaps after filling with sample. Also: insure the screen mesh is small enough to retain the sample particle size used; inspect and replace the screen cylinder if it looks mechanically weak, too thin, or heavily corroded: do not allow the reactor to depressurize rapidly (the latter can be identified by the sound of gas flowing through the exhaust valves); and

5.0.use only the torque wrench in conjunction with proper flange tightening/loosening bolt sequence.

Resolution of problem (a) requires disassembling the bottom reactor flange to retrieve the holder, which will almost certainly ruin the alignment of the hangdown assembly. The realignment procedure has been known to take up to a week to accomplish successfully.

Inattention to problem (c) can cause the sample lock chamber to twist and gradually degrade the alignment. Adequate resolution requires proper alignment.

Problem (b) results in solid particles finding their way to every nook and cranny within the system, which quickly causes valves and flow controllers to leak internally and has potential to permanently damage valve seats and seals. Extensive disassembly will be required to clean the apparatus, and achieving leak-free seals upon reassembly is difficult. Realignment will also e necessary.

Pre-existing Conditions for Warm Start:

TGA Master & Power switches (lefthand side of power cabinet) remain on.

µBalance power remains on. If this (or TGA Master) is ever turned off:

The load arm (sample side) must be within ±10 mg of the counterweight arm before turning power on again, and balance electronics must warm up overnight before using.

Pneumatics air supply (tank) normally remains open, set to deliver 45 psig.

The empty sample holder should be installed on the balance chain, and the sample lock is closed.

If the computer is on, turn it off for two minutes before proceeding.

Apparatus Setup for the High Pressure Reactor:

1) Turn the computer on. This will boot to a DOS prompt.

Type [t g a][ENTER] to run the high pressure reactor software.

When the Home Page appears, the password is [d m t][ENTER].

Use [Arrow Keys] to highlight VISUALIZATION in the menu bar, then press [ENTER] to go to the Visualization Page.

Default values there should be: All flows = 0 (liter/min). All pressures = 1 (bar).

2) Go to the Apparatus. Open the manual Exhaust Bypass and Exhaust Shutoff valves.

Lower the sample holder (to 0.0 on position display)

Allow the MicroBalance display to stabilize, then tare.

Raise the sample holder into the sample lock chamber (to position ~ 72).

Open the sample lock chamber & remove the sample holder (when cool enough to handle).

3) Weigh the entire empty holder on a separate analytical balance, record mass as mHo.

Load the holder with ~ 100 mg sample and reweigh, record as mNeto.

The difference (mNeto - mHo) is the initial sample mass, mSo. Your will need to enter these data later, before starting the run, and for final mass calculations.

4) Go to the Apparatus. Install the loaded sample holder, leaving it suspended in the chamber (do not lower it into the reactor at this time). Close and bolt the flange.

Set cooling water flows to show about 2 revolutions per sec at water flow indicators.

Insure that gas cylinders to be used have sufficient contents to purge and stabilize the reactor at desired parameters, and to execute the intended experiment. If in doubt, use a full cylinder. There is no point in wasting time and gases.

Connect the purge gas and reaction gas cylinders to appropriate ports on the righthand side of the flow cabinet:

1) Top port, always used, for helium or hydrogen microbalance purge.

2) Next down, used with high temperature reactor only for air purge.

3) Reaction Gas 1: for helium or hydrogen.

4) Reaction Gas 2: for carbon dioxide.

5) Reaction Gas 3: for air, nitrogen, or oxygen.

All unused ports should be capped and sealed.

Open cylinder valves and set regulator delivery pressures to somewhat greater than the intended max reactor pressure, but not over 44 bar.

Gauges on the flow cabinet read in bar, which is the same unit as on the computer.

Leak check all connections just made. Leak check all external hydrogen fittings daily.

Open the manual Reactor Feed valve.

Close the manual Bypass Feed valve.

Close the manual Exhaust Bypass valve.

Open the manual Exhaust Shutoff valve (above heat exchanger). † Adjust this later.

Open the manual Exhaust Shutoff valve (below heat exchanger).

Close the manual Vacuum Line valve (below heat exchanger).

Set Parameters for Experiment Initial Conditions:

1) Start heating the reactor and insulating jackets to setpoint temperatures. Doing this first helps conserve gas consumption. However, if using hydrogen or other flammable gas, wait until after step (4) to do this.

- Go to Computer Visualization Page:

  Bring the mouse pointer onto the block labeled TICAS 112 (Main Reactor Heater).

  Press and hold the right mouse button briefly to access this controller's Parameters Page.

  Use [Dn Arrow] to move the cursor to "Setpoint", press [ENTER].

  Type the new setpoint value (eliminating old decimal point), press [ENTER].

  Set this value a few degrees above the desired initial target temperature.

  Press [F8] to store the new value, then [F9] to activate the controller.

  Press [ESC] twice to go to Home Page, press [ENTER] to go to Visualization.

  The actual internal reactor temperature is shown in the block labeled TIR 110.

- Repeat this procedure for blocks labeled TICAS 107, 108, 109 (Reactor Jackets). These values should be less than 2/3 the target reactor temperature.

- Repeat this procedure for the block labeled TICAS 38 (Feed Line Jacket).

  This value should be less than 2/3 the target reactor temperature.

- As needed to prevent condensation of reaction products or steam, repeat this procedure for blocks labeled TICAS 401 & TICAS 214 (Vent Line & Bypass Line Jackets). These values need only be sufficient to prevent condensation.

- The maximum temperature for the High Pressure Main Reactor Heater is 1200°C. The maximum temperature for all jackets is 400°C.

2) Set unused Reaction Gas switching valves to BYPASS, and valve to be used to REACTOR:

- Bring the mouse pointer onto the block labeled KCV 334 (Reaction Gas 1).
- Press the left mouse button briefly to access this valve's Indicator Page.
- Press [Ctrl-Page Up] or [Ctrl-Page Dn] to set to REACTOR or BYPASS.
- Press [ESC] twice to go to Home Page; press [ENTER] to go to the Visualization Page.
- Repeat this procedure for the block labeled KCV 344 (Reaction Gas 2).
- Repeat this procedure for the block labeled KCV 354 (Reaction Gas 3).

3) Enter the flowrate setpoint and start flow for each gas feed stream to be used:

- Bring the mouse pointer onto the block labeled FIC 313 (Balance He Purge).
- Press the right mouse button briefly to access this controller's Parameters Page.
- Use [Dn Arrow] to move the cursor to "Setpoint", press [ENTER].
- Type a new flow setpoint value (eliminating old decimal point), press [ENTER].
- Press [F8] to store the new value, then [F9] to activate the controller.
- Press [ESC] twice to goto Home Page, press [ENTER] to goto Visualization.
- Repeat this procedure for block FIC 333 (Reaction Gas 1), or other flows used.

† Hydrogen Use Note: Evacuate and then purge the system for a few minutes first with helium flow to remove most of the air before initiating hydrogen (Reaction Gas 1) flow.

4) Check to ensure the flow controllers are operating:

Visualization Page blocks FIC 313, 323, 333, 343, 353 report flows to the nearest integer value (liter/min). To view more precise numbers:

- Bring the mouse pointer onto the block labeled FIC 313 (Balance He Purge).
- Press the left mouse button briefly to access this Indicator Page.
- Indicator Page digital and graphical displays show the status.
- Scroll through Indicator Pages by pressing [F1]. [F2] scrolls backward.
- View pages for FIC 333 and/or other Reaction Gas used.
- Press [ESC] twice to go to Home Page; press [ENTER] to go to Visualization.

† Hydrogen Use Note: Begin heating the reactor now using procedure step (1), above.

- Important: The total of all feed flow rates must initially be 2.0 liter/min or better to get the pressure controller to engage properly. After the pressure setpoint is achieved (as per below), gas flows can be gradually reduced (as per above. The ratio of Balance He Purge flow to Reaction Gas flow should be maintained at 2:1 or greater.

5) Enter the reactor pressure setpoint:
   - Bring the mouse pointer onto the block labeled HG 104/1 (Pressure Controller).
   - Press the right mouse button briefly to access this controller's Parameters Page.
   - Use [Dn Arrow] to move the cursor to "Setpoint" and press [ENTER].
   - Type the setpoint value (eliminating old decimal point), press [ENTER].
   - Press [F8] to store the new value, then [F9] to put the value on-line to the controller.
   - Press [ESC] twice to goto Home Page, press [ENTER] to goto Visualization.

   Important: Repeat this procedure for the block labeled PIC (Pressure Indicator), whose setpoint must agree with that of HG 104/1.

6) Engage the pressure controller to build pressure:
   - Go to apparatus and fully close the manual Exhaust Bypass valve.
   - Bring mouse pointer onto block labeled HG 104/1 (Pressure Controller).
   - Press the left mouse button briefly to access its Indicator Page.

     The HG 104/1 Indicator Page contains immediate mode controls: [Ctrl-Page Up] or [Ctrl-Page Dn] for Manual Open or Close, [ENTER] to Stop at current % opening, [ENTER] again to engage Auto Control.

     Indicator Page digital and graph displays also show what is going on here.
   - Press [ESC] twice to go to Home Page, press [ENTER] to go to Visualization.

7) When all the above parameters are attain steady-state setpoint values (this may take a while), the apparatus is ready to run, but the computer still must be prepped before recording data:
   - From the Visualization Page, press [ESC] to go to the Home Page.
   - Use [Arrow Keys] to highlight V1 in the menu bar, press [ENTER] to go to the Experiment Data Entry Pages. You must go through the entire four page sequence under V1.

     The first item, "Run Number", will be used as part of the data file name, and is automatically incremented to avoid overwriting a previously recorded data file.

     Most other items are self-evident. Leave values for %Ash & %Water = 0 if unknown. Default values are those previously last entered. Arrow keys step through data items and retain current values. To change, type a new value for the item highlighted, then use [Dn

Arrow] to go to next item. Press [ENTER] when all items on the page have been changed, then press [Y] or [N] to answer the request at the bottom of each page.

The Home Page is returned when V1 is finished.

† Adjust the manual Exhaust Shutoff valve (above heat exchanger) to the minimum opening that will allow reactor pressure to be maintained at the setpoint. This will help prevent catastrophic pressure loss in the event of a software crash, but also, be prepared to manually close this valve ASAP (to hold pressure) following a crash. Upon crashing, flow controller setpoints should default to zero, but check these anyway (Visualization Page) after rebooting and restarting the software.

Instructions for Isothermal - Isobaric Experiments

The following instructions are only for experiments which are to be run isothermally and isobarically and with no changes to flowrates or valve settings during the run. At this point, all Apparatus Prep should be accomplished, and all actual process values should be at the desired steady-state setpoint values.

1) Start Run:

- Go to Home Page, highlight PROCESS CONTROL in menu bar, press [ENTER].
- Use [Up Arrow] [Dn Arrow] keys to highlight "Test Condition", press [ENTER].
- Press [F3] once to start data acquisition.
- Lower the sample holder into the reactor (to position 0.0).
- Check balance display. If there is more than 100 mg sample in the holder this will show "H", and you must change range to RI.

2) Display Data Diagram:

- Go to Home Page, highlight V2 in menu bar, press [ENTER]. (Function key operations are described at bottom of page.)
- There is no escape from the V2 Page until data acquisition is stopped *via* [F8] or Autostop occurs after the maximum 1000 data points have been acquired.
- After stopping, press [ESC] to go to Home Page, then go to Visualization Page.

Post-Run Instructions:

1) Raise Sample:

Raise sample holder into sample lock chamber (position ~ 72). This must cool for several minutes before it can be handled, and the reactor pressure must be released before the sample lock can be opened.

2) Stop Gas Flows:

- Bring mouse pointer onto block labeled FIC 313 (Purge Gas Controller).
- Press the right mouse button briefly to access this Parameters Page.
- Change the setpoint to 0.0; press [F8] & [F9] to save and to set new value on line.
- Use [F1] to step to Parameters Page of other flow controller(s) used.
- Change setpoint(s) to 0.0; press [F8] & [F9] to save and set new value(s) on line.
- Press [ESC] twice to go to Home Page, press [ENTER] to go to Visualization.

3) Release Pressure:

- Bring mouse pointer onto block labeled HG 104/1 (Pressure Controller).
- Press the left mouse button briefly to access this Indicator Page.
- If still active, press [ENTER] to disengage Auto Control.
- Using [Ctrl-Page Up], [ENTER], and [Ctrl-Page Dn] for Manual Open, Stop, and Close, slowly vent pressure from the reactor to a value of 1.0 bar.
- Press [ESC] twice to go to Home Page.

4) Remove Sample Holder:

- Open the Manual Exhaust Bypass valve to insure full pressure release.
- Open the sample lock chamber & remove the sample holder.
- Weigh the entire holder on a separate analytical balance, record the mass as mNetf.
- Disassemble and clean all residue from the holder, reweigh holder, record mass as mHf. Note that initial and final sample holder masses may differ due to oxidation / reduction.
- Calculate residue mass as mR = (mNetf - mHf). You will need to enter this and other mass data during the data file save.

  Note: Residue is defined as Ash only if the sample is completely consumed (converted); it defined as Residue.

  Note: Do not reload the sample holder with fresh sample for a subsequent run at this time.

5) Save Run Data to Hard Disk:

- From Home Page, highlight V3 in menu bar, press [ENTER].
- Entry dialog is more or less self-evident. Save diagram if you want to print it in future.
- The Home Page is returned when V3 is finished.

6) Transfer Data File to Floppy Disk:

- From Home Page, highlight TRANSFER in menu bar, press [ENTER].
- Be sure the floppy disk you insert has sufficient free space.
- Entry dialog is more or less self-evident. There are no options, all unsaved data files on hard disk will be copied.
- The Home Page is returned when TRANSFER is finished.

Other Menu Functions:

PROTOCOL:

Probably best to avoid this altogether. Unless you are fluent in German, and maybe not even then, nothing here is self-evident. If you get into this mode accidentally, the first item looks to be selection of the desired time unit for diagrams and/or data files, answer S. Answering 0 or N to all else will get you back to the Home Page safely.

EVALUATE:

This is the built-in data analysis subprogram, which seems difficult to get through without encountering a run time error during the slope calculation. It may, however, provide some potentially useful results up to that point. The entry dialog is usually self-evident. To continue from Diagrams, press [F8]. The error encounter returns a dialog page from which you can abort and go to the Home Page.

Data analysis will likely be much more streamlined using KaliedaGraph or Excel. Data files are spreadsheet readable (i.e., tab delimited text), albeit in a format where the sample and run information are included and written first. You will probably have to delete this before generating graphics and performing calculations. The data columns are formatted as:

A	B	C	D
Mass	Temperature	Pressure	Time

END:

This exits the TGA program, returning a DOS prompt. It is safe to turn the computer off here, or you can type [w][i][n][ENTER] to go to Windows. However, it is not safe to retype [t][g][a][ENTER] and expect the program to run again without crashing. If you do go to Windows, the machine will not shut down cleanly later by the usual means, even if you have not run the TGA program beforehand. Instead, it is recommended to select MS-DOS from Windows, then turn the computer off after the DOS prompt is displayed. Still running Windows in the background here, the TGA program will load and appear to run from DOS, but it will not control the apparatus.

Instructions for Temperature Programmed Experiments:

The following instructions are for experiments that will otherwise be run isobarically and with no changes in flowrates or valve settings during the run. At this point, all Apparatus Prep should be accomplished, and all actual initial process values should be at steady-state setpoint values.

1) Enter Temperature Program Parameters:
   - Go to Home Page, highlight PROCESS CONTROL in menu bar, press [ENTER].
   - Press [Page Down] once. BE CAREFUL, pressing twice will turn off all setpoint controllers.
2) Start Run:
   - Use [Up Arrow] [Dn Arrow] keys to highlight "Pgm 1.Pgm 2", press [ENTER].
   - Pgm 1.Pgm 2 is flashing. Press [F3] once to start data acquisition.
   - Go to the apparatus and lower the sample holder into the reactor (to position 0.0).
   - Check apparatus balance display. If there is more than 100 mg sample in the holder, the display will show "H". If so, you must change range to R1.
3) Display Data Diagram:
   - Go to Home Page, highlight V2 in menu bar, press [ENTER].
     (Function key operations are described at bottom of page.)
   - There is no escape from the V2 Page until data acquisition is stopped *via* [F8] or Autostop occurs after the maximum 1000 data points have been acquired.
   - After stopping, press [ESC] to go to Home Page, then go to Visualization Page.