First Technical Report

**United States Department of Energy
University Research Instrumentation Program
DOE Application Number 9202-097
Grant Number DE-FG05-92ER79119**

**A PRESSURIZED THERMOGRAVIMETRIC ANALYZER FOR USE IN STUDIES
OF GAS/SOLID SYSTEMS**

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September 22, 1993

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DOE University Research Instrumentation Program

Grantee: Prof. Reginald Mitchell, Mechanical Engineering Dept, Stanford University
Grant Number: DE-FG05-92ER79119
Project Period: August 8, 1992 to July 31, 1994
Description of Equipment: TG-151 Thermogravimetric Experimental Station
Date: September 22, 1993

1.0 Overview

We received a 1992 University Research Instrumentation Grant (URI) in the amount of \$122,335 to purchase a **TG-151 Thermogravimetric Experimental Station**, a pressurized thermogravimetric analyzer. The instrument allows typical thermogravimetric analyzer techniques to be performed over a wide range of pressures, from subatmospheric to 100 atm. The instrument is for use in advanced research in energy research areas concerned with coal conversion chemistry and other high temperature phenomena associated with coal use.

The instrument became fully operational in July 1993. At the present time, no significant experimental data or breakthroughs have resulted from using the instrument in our research efforts. We are still in the initial stages of gaining experience with using the instrument. We are exploring its capabilities and limitations. In this first technical report, we briefly describe the instrument purchased and its present status and use. New research projects that have been undertaken as a result of the instrument being available are described and the number of graduate students involved are discussed. Financial data on acquisition and installation costs are provided.

2.0 The Instrument Purchased and its Current Status of Operation

The instrument purchased and its modifications

A TG-151 Thermogravimetric Experimental Station, which measures and records weight changes of a solid material over a wide dynamic temperature range at a wide range of pressures in controlled environments, was purchased from Cahn Instruments, Inc. The TG-151 permits temperature to be programmed to follow a precise temperature profile of ramp and/or isothermal segments while monitoring the changes in weight of solid samples exposed to a gaseous environment of specified composition at a preset pressure. Weight and temperature measurements are made at user-specified time intervals and total time (up to 48

hours). Data are stored on the disk of a dedicated computer. The data can be processed by a data analysis program or exported to spreadsheet programs.

The pressure vessel is designed to operate in vacuum to 10^{-5} torr and over a wide range of pressures. At normal room temperature, the TG-151 can operate up to 100 atm and at 1273 K, it can operate up to 70 atm. The null balance has a sensitivity of 10 micrograms, capacity up to 100 grams, and a dynamic range of $10^6:1$. Both reducing and oxidizing environments can be established in the reaction chamber.

For our specific needs the instrument had to be slightly modified to allow for two reactant gas streams to enter the pressure vessel at prescribed times. This required the purchase and installation of a gas blending system. The gas blending system permits coal and char samples to be heated at a specified rate to a desired temperature in an inert environment before the sample is exposed to an oxidizing environment. This modification eliminates the need to quantify mass loss due to oxidation during the heating period; it permits isothermal combustion experiments to be performed. The system was also modified to include an effluent trap to prevent high-molecular weight compounds released during coal pyrolysis from condensing inside the pressure vessel exhaust tube. In addition, the exhaust tube was modified to permit a high-pressure slip stream to be directed to the chamber of a Fourier Transform Infrared Spectrometer for gas analysis. This arrangement permits the coal char offgas to be characterized.

Current Status of Operation

The TG-151 was delivered on October 26, 1992. A representative from Cahn arrived to unpackage the instrument and set it up in its initial configuration on January 4, 1993. The time between delivery of the instrument and installation was due to the fact that several components had to be purchased before installation could begin. Such purchases included high pressure test gases, high-pressure regulators, tubing, and miscellaneous fittings, connectors, and valves.

A graduate student was assigned the task of bringing the instrument to full operating status. Shakedown tests began in January 1993 shortly after the instrument was set up in its initial configuration. Full operating status was reached in July 1993, shortly after all modifications were completed. Presently, the TG-151 Thermogravimetric Experimental Station is ready for use in studies concerned with solid/gas reacting systems.

3.0 New Research Areas

During this first year, one new research program has been initiated that would not have been possible if the TG-151 were not available. This project is concerned with coal char

gasification. The TG-151 has also provided a means of extending an on-going research effort involving char combustion phenomena. This extension is concerned with the effects of fragmentation on coal char oxidation. In addition, a proposal for research aimed at characterizing the fundamental chemical and physical processes involved during the transformation of pyrite to hematite in coal combustor environments is just about complete. Aspects of the proposed work would not be possible without the TG-151. An overview of each of these research projects is given below.

Pressurized Coal Gasification Studies

A research effort concerned with determining the mechanisms and kinetics of coal char gasification in specified environments has been initiated. The TG-151 is used to obtain char weight loss rate data as a function of coal rank, char conversion, gas composition (CO , CO_2 , H_2 , H_2O , CH_4 , and inert), temperature, and pressure. The information obtained is used to formulate and validate chemical mechanisms and rates controlling coal char conversion. The results permit the prediction of offgas composition for specified reactor conditions and is useful in the development of gasification processes to produce syngas from coals for use in gas turbines in integrated coal gasification/combined cycle processes.

Char Fragmentation Studies

The TG-151 is being used to obtain chars at specified extents of mass loss in our study concerned with characterizing char fragmentation phenomena. Chars are produced under various conditions that influence char physical structure: slow versus fast heating rates during devolatilization and slow versus fast burning rates during oxidation. Such devolatilization and oxidation conditions are manifest in the TG-151 by controlling temperature ramp rates and by adjusting temperature, pressure, and oxygen concentration. The chars produced are characterized with respect to pore structure, surface area, and density and used in combustion tests designed to examine fragmentation phenomena. Information obtained is used to formulate and validate hypotheses put forth concerning the effects of fragmentation on char combustion. The data provides insight into the causes of unburned carbon in the ashes of coal-fired utility boilers and furnaces.

We use synthetic chars in our char fragmentation studies. Carbon black and the spores of lycopodium plants are used as additives in the synthesis process to produce porous chars having porosities ranging from 20% to over 70% and pore diameters that extend the micropore-to-macropore size range. The TG-151 is used in experiments designed to characterize the pyrolysis and combustion behaviors of the lycopodium spores and the synthetic chars.

Pyrite Transformation Studies

The fundamental chemical and mass transport processes that control the rate of conversion of pyrite to hematite are to be investigated. The proposed work aims to identify the mechanisms of pyrite combustion and to quantify their effects on the overall oxidation rate in order to formulate a rate expression for the combustion of pyrite that accounts for coal properties as well as furnace conditions. A key feature of the experimental approach taken is the sequential formulation of a reaction rate resistance network by isolating and quantifying the rate resistances induced by each of the following mechanisms: pyrite intraparticle kinetics, pyrite intraparticle mass transfer, gas-phase kinetics, and gas-phase mass transfer. The TG-151 permits the quantification of rates associated with chemical effects. Conditions can be established in the TG-151 in which mass transfer resistances both inside and outside pyrite particles are insignificant in limiting the overall pyrite combustion process. Results of the proposed research will be used to identify conditions that minimize the significance of those pyrite transformations responsible for the higher slagging propensity of staged, low- NO_x pulverized coal combustor retrofits.

4.0 Graduate Student Participation

To date, one Ph.D student has been involved in activities involving the TG-151. These activities have been primarily troubleshooting and testing the instrument. A Ph.D student will be associated with each of the research topics discussed above and hence, each will utilize the TG-151. It is estimated that over the next five years, the instrument will impact about 12 of the principal investigator's graduate students. Most of these are anticipated to be Master's students involved in directed research with the PI and his Ph.D. students.

5.0 Financial Data

Acquisition and Installation Costs

Costs associated with purchasing and installing the TG-151 Thermogravimetric Experimental Station are shown in Table 1. The table includes acquisition costs for all accessories needed to make the system ready for the anticipated combustion and gasification experiments. The costs of all materials needed to install the TG-151 and to modify it for our experimental needs are also included. On-site fabrication and installation charges levied by the university for purchases, fabrication, and machining done in campus stores and machine shops are indicated.

Table 1. Acquisition and Installation Costs

Acquisition Costs

• TG-151 and Flow Control Panel (plus tax)	\$104,415.00
• Shipping costs	\$1,423.30
• Miscellaneous accessories	
- Gas blending system	\$3,788.75
- Effluent trap system	\$1,623.75
- Quartz sample holders (2)	\$292.28
- Tube furnace for heated slip stream	\$1,039.00
- Thermocouple sensor for slip stream	\$259.80
Total Acquisition Costs (including shipping)	112,841.88

Installation Costs

• Ultrahigh-pressure brass regulators (3)	\$860.59
• Gas transfer lines	
- stainless steel flexible hoses	\$248.98
- stainless steel tubing	\$199.45
• Miscellaneous fittings, connectors, and valves	\$1,388.32
• Gases for leak and shakedown testing	
- high-pressure helium	\$237.69
- high-pressure nitrogen	\$237.69
• On-site machining/installation charges	\$5,234.35
Total Installation Costs	\$8,407.07

Total Costs 121,248.95

Operational and Maintenance Expenses

The primary operational expense is for high-pressure gases for experiments. These include O₂, CO₂, N₂, He, and Ar for combustion and pyrolysis experiments and CH₄, CO, CO₂, and H₂ for gasification experiments. Maintenance expenses are expected to be low. Operational and maintenance expenses are covered by research contracts. The university provides no support for such expenses.

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