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The Design and Development of a High-Heating-Rate Thermogravimetric Analyzer Suitable for Use With Ablative Plastics

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SUMMARY

The development of a high-heating-rate thermogravimetric analyzer for use with ablative plastics is described. Data are presented for the decomposition of a nylon-phenolic ablator.

INTRODUCTION

Certain contemporary problems in applied chemistry dealing with ablative plastics require the scientist to have at his disposal detailed information regarding the decomposition phenomena of a wide variety of polymers. It is, of course, well known that, in general, the method of decomposition depends critically upon the heating rate employed in the "unzipping" process. Furthermore, it is interesting to note that the heating rates of practical interest to the designer of space vehicles have increased orders of magnitude from those which were encountered during the early part of the present decade. For example, during experiments conducted in hypersonic wind tunnels, it was not unusual to encounter heating rates in the material of less than $10^{\circ}\text{C}/\text{sec}$, whereas currently values of more than 10 times that rate are common.

The wide divergence between contemporary heating rates experienced by polymers during hypersonic experiments and the heating rates encountered by polymers undergoing similar tests during the latter part of the 1950s has imposed a substantial burden upon the scientist and engineer who must reduce and interpret these experiments kinetically for putative design application. The nature of this difficulty resides in the attempt to extrapolate the results of classical thermogravimetry to the high-heating-rate environments which are far in excess of the capability of current equipment.

It is to be noted that the classical technique of thermogravimetry involves the use of very small samples (i.e., approximately 1 mg or smaller). Employing the assumption of a negligible temperature gradient through the sample and imposing modest heating rates (less than $10^{\circ}\text{C}/\text{min}$), one then computes appropriate kinetics parameters based upon the well-known Arrhenius expression. The activation energy, E , and the order of the reaction, n , are then obtained by the best straight-line fit of the experimental data plotted on a semilogarithmic scale.

However, when the heating rate is increased to levels comparable to those experienced at some points on a re-entering space vehicle, it is found that this experimental technique and method of data reduction must be altered. Very small samples having a weight range of 1 mg or smaller literally explode when exposed to these inordinately high rates of heating.

EXPERIMENTAL METHOD

As a consequence of the above difficulty, a new experimental method has been designed to skirt this problem. The new technique has the following features.

Balance System

The balance portion of the apparatus consists of four active strain gauges [1] arranged in a Wheatstone bridge configuration. The gauges are cemented to a strip of 10-mil-thick stainless-steel shim stock from which the sample hangs. Two gauges on top measure the contraction forces, and the two located on the bottom measure the expansion of the shim stock as the sample is heated. The balance is designed to be independent of sample sizes. Weights up to 10 g can be accommodated with a detectable weight loss of ± 1 mg.

Since the bottom strain gauges are subject to thermal gradients during a

heating cycle, a 2000- Ω thermistor is made part of a separate Wheatstone bridge to obtain a signal proportional to the temperature of the gauges. A fraction of this signal is selected by a pair of potentiometers and is fed into a stable dc microvolt amplifier. The amplifier output is electronically subtracted from the strain gauge weight-loss signal which is read out on the Y axis of a high-speed X-Y recorder or an oscillograph. Figure 1 is a photograph of the system showing the sensor head, the radiant heater, and associated equipment.

Furnace

The source of thermal energy is a vertically mounted infrared radiant heater with elliptical reflectors. Lamps used in this heater peak at a wavelength of 5000-5800 \AA . Heating rates are changed by transformer control of the 440-V ac line. Heat fluxes at heating rates of 100°C/sec have been shown to be in excess of 17 Btu/ft²-sec as measured by a copper calorimeter placed at the location of the sample in the system.

Vacuum System

An oil diffusion pump and roughing forepump combination is used to provide pressures of less than 1 μ . To eliminate spurious effects due to rapid outgassing of the sample as it is heated, two "dump" tanks are placed in parallel with the system. These serve as expansion chambers for the large amounts of gases liberated.

RESULTS

It is now necessary to discuss the method of analysis appropriate to this new technique. The semiempirical analytical model described below has been utilized for some time to predict the response of ablators which char during thermal decomposition.

In the design applications using this model, one investigates mainly the interaction between the decomposition products of the material and the hypersonic environment. As is noted later, the extension of this application to the present experiment involves the proper use of the experimental boundary conditions rather than those appropriate to flight, since the experimental procedure cannot be conducted in hypersonic flow. With an a priori knowledge of the variables involved, however, this approach does not invalidate the data reduction.

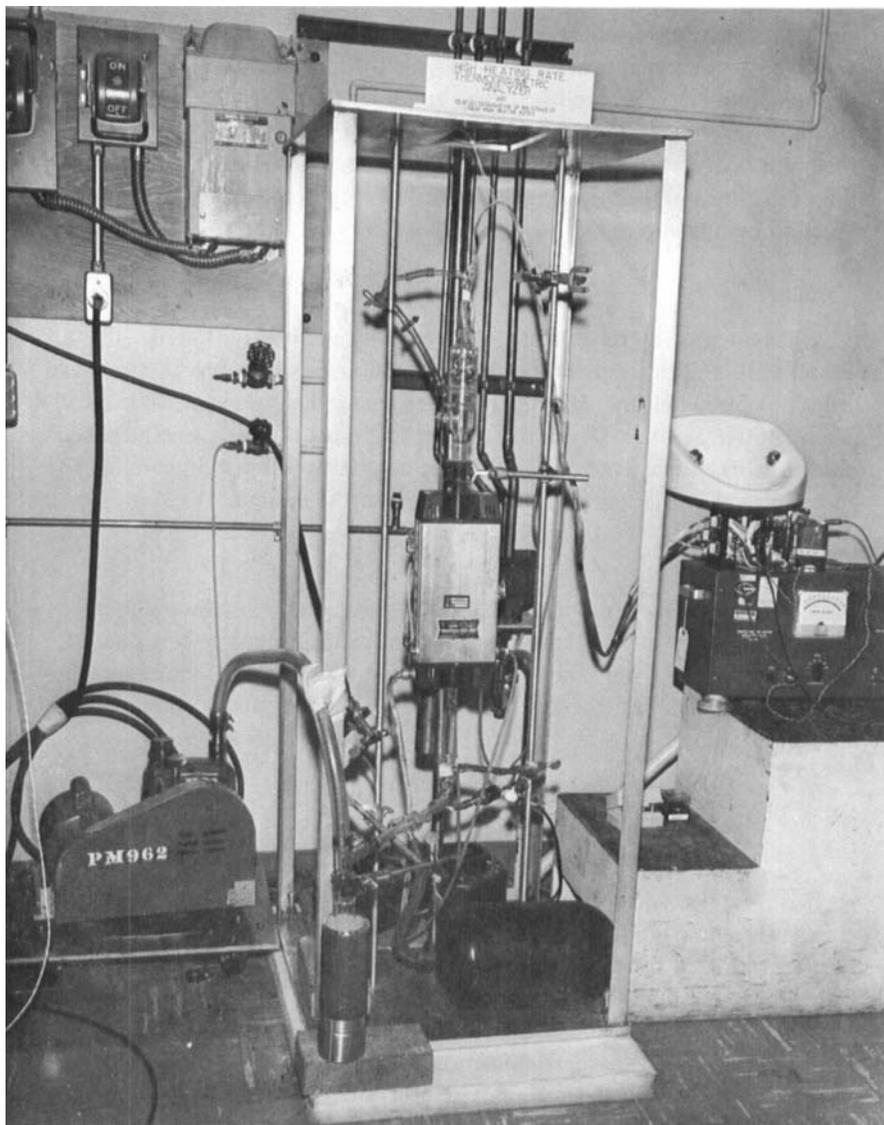


Fig. 1. Balance system: the sensor head, the radiant heater, and associated equipment.

The following set of equations, which are used in the data reduction scheme, were deduced from appropriate conservation laws, details of which are given in Ref. [2].

Because of the nature of the experiment, the equation relating the behavior of the condensed phase during decomposition is considered first.

Condensed Phase (Radial Dimension Only)

$$\rho c_p \frac{\partial T}{\partial t} + \Delta H(\rho - \rho_c) A \exp\left(-\frac{\Delta E}{RT}\right) = \frac{1}{r} \frac{\partial}{\partial r} \left(kr \frac{\partial T}{\partial r} \right)$$

In this equation, the right-hand side represents the heat conducted into any element of the condensed phase. The first term on the left-hand side, $\rho c_p (\partial T / \partial t)$, denotes the heat stored in the condensed phase; the term $\Delta H(\rho - \rho_c) A \exp(-\Delta E / RT)$ represents the heat absorbed during the decomposition reaction, and it is the value of the parameters occurring in this term, A , ΔE , etc., in addition to the order of the reaction, which comprises the main area of this investigation. The conditions of the experiment can obviously be closely controlled; hence, we have neglected the term which denotes the energy stored in the evolved gases and the term reflecting the change in energy occurring during gas cracking, since these will then be adjusted to a second-order effect.

In the foregoing formulation, the gas evolved at a given location during decomposition is presumed to have been generated at all points interior to this location during the same time, that is

$$\dot{m}_r = \int_r^{r_0} (\rho - \rho_c) A \exp\left(-\frac{\Delta E}{RT}\right) dr$$

where r_0 is the center of the cylinder.

Note that the transport properties may be considered as temperature dependent, if desired; and the enthalpy, specific heat, and molecular weight of the evolved gaseous products are included as functions of pressure and temperature.

Boundary Conditions

The following "word" equation states the energy conservation condition at the surface of the cylindrical sample in one space dimension with negligible surface recession.

$$k \frac{\partial T}{\partial r} = \dot{q}_c + \dot{q}_{\text{net gas radiation}} + \dot{q}_{\text{gas combustion}} - \dot{q}_{\text{surface radiation}} - \dot{q}_{\text{mass transfer}}$$

One observes that all the terms on the right-hand side must be considered in the case of thermal transport in an ablating space vehicle.

However, in the absence of a hypersonic environment, not all of these terms are of first order. For example, the last or "blowing" term is not large in the experiments described herein. In a like manner, the gas combustion term would vanish because of the absence of oxygen in the experiment. Although very likely not large, the net gas radiation term should be included, but its magnitude will be checked before final experiments are attempted.

It may be seen, therefore, that the terms which remain on the right-hand side are the first and fourth, i.e., \dot{q}_c and the surface radiation contribution. The latter may be computed because the surface temperature is measured as a function of time. The first term, which is the contribution of convective heating due to aerodynamic forces, must be replaced by the equivalent heat source for the experiment, namely, the surface radiation of the heater. The value of this heat flux is measured by calibration by solving the transient heat conduction equation using the results of several "in depth" thermocouple responses as boundary conditions.

For ease in computation, use is made of an instrumented copper calorimeter for the purpose of measuring the heat flux during calibration. In order to eliminate end effects, the calorimeter is made with a length sufficient to minimize the contribution of the term $\partial^2 T / \partial Z^2$ to

$$\rho c_p \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(k r \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial Z} \left(k \frac{\partial T}{\partial Z} \right)$$

Measurements are made within an area approximately confined to the center of the axis for further insurance that this problem be kept minimized.

APPLICATION OF EXPERIMENTAL TECHNIQUE

As an example of the use of the foregoing experimental technique and subsequent data reduction, data have been obtained on the decomposition of nylon-phenolic.

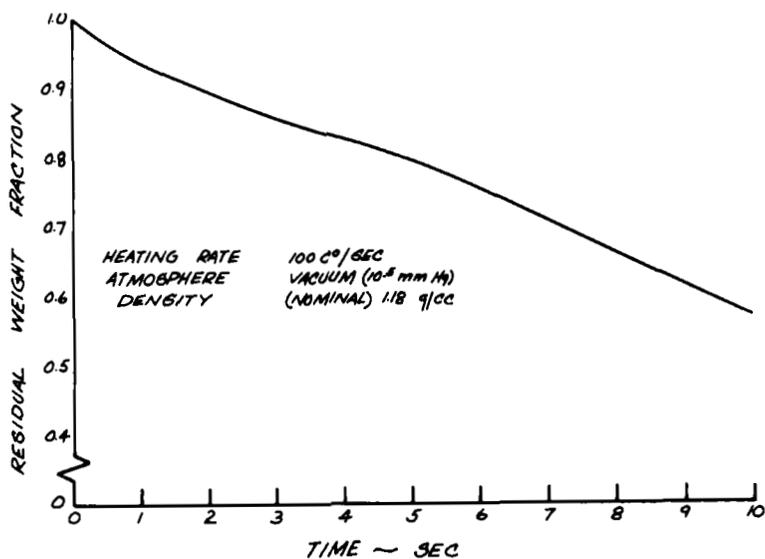


Fig. 2. Thermogram representing the decomposition of nylon-phenolic heated at a rate of 100°C/sec.

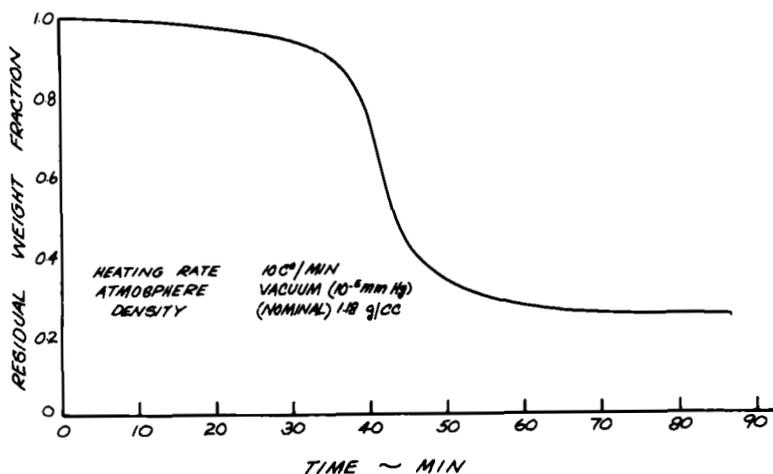


Fig. 3. Thermogram representing the decomposition of nylon-phenolic heated at a rate of 10°C/min.

Figure 2 is a thermogram which represents the decomposition of nylon-phenolic heated at a rate of $100^{\circ}\text{C}/\text{sec}$.

For comparison, in Fig. 3 a thermogram is shown of the same material heated at a rate of $10^{\circ}\text{C}/\text{min}$.

It is significant to note the different Arrhenius parameters which result. For example, in the case of the higher heating rate, the activation energy ΔE is 1.34×10^3 cal/g-mole and the collision frequency A is 0.16 sec^{-1} , while in the case of the lower heating rate, ΔE is 0.85×10^3 cal/g-mole and the collision frequency is $2.69 \times 10^{-4} \text{ sec}^{-1}$ for a reaction order of unity.

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