

A New Technique for Thermal Analysis of Vapor-Producing Reactions*

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Synopsis

An apparatus was developed for measuring the rate at which vapors are evolved during the thermal degradation of materials and thereby deriving the kinetics of such reactions. Requisite to the operating scheme of the apparatus is the provision of a high-temperature zone to convert condensable or tarry vapors into noncondensable form. The apparatus yields a direct measure of reaction velocity, rather than the integrated indication obtained with thermogravimetric analysis. This simplifies the identification and calculation of kinetic parameters. Increases in sensitivity and operating range are also achieved. Flexibility in operation is obtained that permits the separate recording of reactions that tend to overlap. Although the apparatus principally has been operated using a combustible gas indicator to meter the evolved vapors, a number of options are available for the latter function, including flowmeters and various continuous gas analyzers. The applicability of the method appears promising.

INTRODUCTION

Numerous limitations are encountered in the application of conventional thermal analytical methods to the investigation of the pyrolysis and combustion behavior of materials. In the use of thermogravimetric analysis (TGA), various factors tend to degrade the accuracy of recordings,¹ particularly with samples of low thermal conductivity and/or as heating rates are increased above 10 to 20°C/min toward those encountered in the combustion of materials. Differential thermal analysis (DTA) involves compromises in signal quality arising from the conflicting needs that must be met in design of the equipment.² Combining or combined TGA and DTA measurements involve further problems. Even under favorable circumstances, as when dealing with a single well-defined reaction, results from these methods are often restricted in scope and certainty by unavoidable extraneous experimental effects. When samples undergo more than one reaction and these reactions are in part concurrent, the complications multiply. A clear interpretation of TGA results can then become impossibly difficult or inordinately laborious. Such limitations arise in part from the isothermal or linear temperature rise operation that is conventional to or required by the methods. The same appears to apply to other related systems that have been reported.³⁻¹⁰

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Differential gravimetric analysis (DGA) is an ancillary option of TGA consisting of a recording of the 1st differential of the primary TGA recording. Unfortunately, DGA recordings suffer an additional handicap to those imposed by the limitations of the primary recording—in that the electronic devices currently used to perform the differentiation have quite slow response times, in the order of minutes. Thus, these devices are the least effective when they are most needed, during intervals when change in the reaction velocity is appreciable. In turn, manual differentiation of TGA recordings is both laborious and difficult to perform accurately. Hence, the differentiation is commonly performed mathematically, which imposes constraints on the operating mode of the TGA and on the methods of treating the resulting data. An excellent critique of the methods of treating such data, and the problems involved, has been written by Flynn and Wall.¹¹

The system described in this report functions on a different and less restricted basis than conventional thermogravimetry. It is designed to derive the kinetics of pyrolysis reactions from measurements of the rate of vapor evolution, rather than from recordings of the weight loss of solids. The vapor evolution rate is representative of reaction velocity and is recorded directly. This record must then be integrated to derive the fraction of material reacted at any point. Thus the system is a reversal of the TGA case, with the primary and derived measurements interchanged and an integration step replacing the differentiation step. This is a favorable exchange as the integration may be easily and accurately performed, either manually, mechanically, or electronically. Additionally and importantly, the restrictions imposed on programming of the reaction temperature are avoided. Thus, the reaction temperature may be freely and usefully manipulated for purposes such as testing parameters and for segregating reactions that would normally overlap. The system also provides a second possibility for resolving concurrent reactions, through the use of meters that are responsive only to portions or components of the vapors evolved by reactions.

The apparatus includes an innovation found necessary to permit general use of the system. This consists of a high-temperature zone through which the pyrolysis vapors flow after their evolution. This zone is added, when necessary, to thermally reduce tarry or condensable vapors to volatile form and thereby avoid their deposition on equipment surfaces.

Data on reaction heat effects, corresponding to the information supplied by simultaneous DTA, may be obtained with the apparatus when it is appropriately operated.

PRINCIPLES OF OPERATION

The operating scheme of the apparatus is indicated in Figure 1. A flow of inert carrier gas is passed over the sample material centered within the tube furnace. The furnace is designed to afford a slight positive gradient

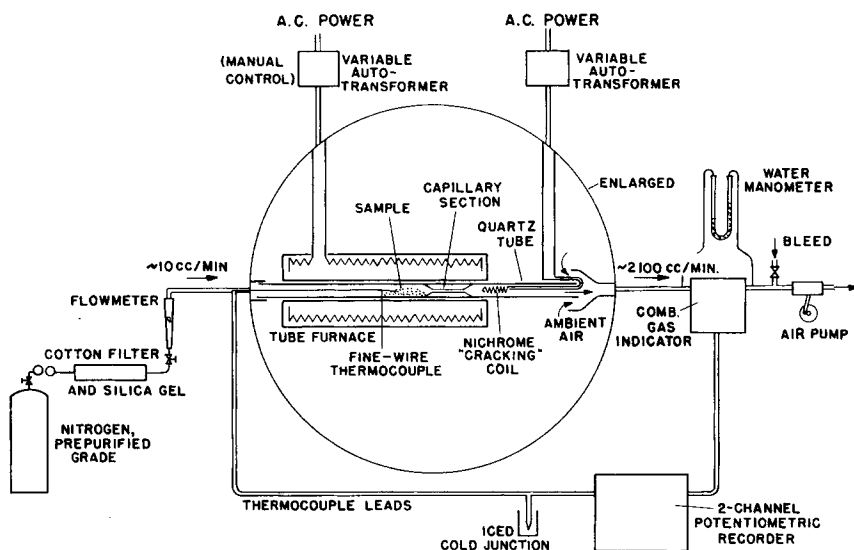


Fig. 1. Schematic diagram of apparatus.

in temperature toward its exit end. A single fine-wire thermocouple imbedded or immersed in the sample material serves for measurement of the pyrolysis temperature. As volatile materials are evolved from the sample with increasing temperature, they are swept from the furnace by the flow of carrier gas. When required, the "cracking coil" at the furnace outlet serves to reduce the heavier components of the pyrolysis vapors to volatile gases. The flow is then conducted to any suitable recording instrument that will serve to continuously meter the mass flow rate of the pyrolyzed vapors or a representative portion or a component thereof. Meters that have been used, other than the combustible gas indicator diagrammed in Figure 1 (a portable instrument sometimes termed a "sniffer," used by utilities and industry for the detection, down to a few ppm, of flammable or explosive vapors), include: (1) a linear mass flowmeter; (2) thermal conductivity cells, composition- and flow-sensitive types; (3) a thermopile-type CO analyzer; (4) infrared analyzers, H_2O , CO, and CO_2 types.

(As to thermal conductivity cells, it appears possible that other gas-chromatographic devices, such as electron capture and hydrogen flame detectors, could be useful with a smaller-scale apparatus, (such is exemplified in part by the apparatus described in references 9 and 10) or with appropriate splitting of a side-stream. Possibilities appear numerous for the use of meters in the system in parallel or sequential combinations.)

The combustible gas indicator, because of its superior response rate, has received the greater use and will be detailed. With use of this meter, the flow from the tube furnace, Figure 1, joins and is diluted by a considerably larger flow of ambient air being drawn through the meter. This dilution is normally over a hundredfold in volume. Therefore, the carrier gas and inert pyrolysis products are seldom of consequence to the meter response.

The combustible gas indicator¹² employs a hot platinum filament within a bridge circuit. As oxygen and combustibles of the throughput gases contact the platinum filament, they are catalyzed to react on the platinum surface. The heat from this surface oxidation reaction increases the temperature and the resistance of the filament. This causes an imbalance in the bridge circuit and a consequent proportionate increase in the output potential of the meter.

In measuring the kinetics of decomposition reactions, the linearity of the meter response to concentrations of the evolved vapors is of prime concern. In this system, as a pyrolyzing compound evolves combustible vapors, the response of the meter would be proportional to reaction velocity insofar as: (1) the transit time of the evolved vapors to and through the filament cell of the combustible gas indicator is appropriately brief; (2) adsorption and desorption of product vapors in the conduit tubes is not of significant magnitude; (3) oxidation of product vapors or secondary reactions of disproportioning effect do not occur in transit; (4) the decomposition performed by the "cracking coil" is uniform and does not introduce disproportioning effects in the product vapors in regard to meter response; (5) the response of the meter is linear to the concentration of combustibles in the filament cell.

The temperature record would represent the reaction temperature insofar as thermocouple registry is accurate and temperature gradients within the sample are minor. Tests and a variety of operating results indicate that these criteria have been met.

It was also found in operating the system that when the furnace temperature was uniformly increased, departures of the sample temperature from a corresponding increase could be clearly detected and serve to indicate reaction exotherms and endotherms.

DERIVATIONS

For typical simple reactions, the calculation of kinetic parameters from the recordings is straightforward. For example, the meter recording for a single first-order reaction with a linear reaction temperature increase would be of the nature indicated in Figure 2. The total vapor-evolving reaction is represented by the area under the meter curve. At temperature T ($^{\circ}\text{K}$) where the meter output is V (mV), the curve area to the right of the V ordinate, F (mV sec), represents the proportion or quantity of the sample material that has not yet decomposed. (A recorder with an integrator channel may be used to derive these curve areas F . Equivalent effort and accuracy were judged for use of an integrator versus manual integration by geometric equivalents. Integration by planimeter was found to be inferior in accuracy.) The specific reaction rate k (sec^{-1}) is then equal to V/F , or the ratio of reaction velocity to the amount of unreacted material. (The units of the meter output, as well as their mass calibration, are immaterial to this calculation as they are self-canceling.)

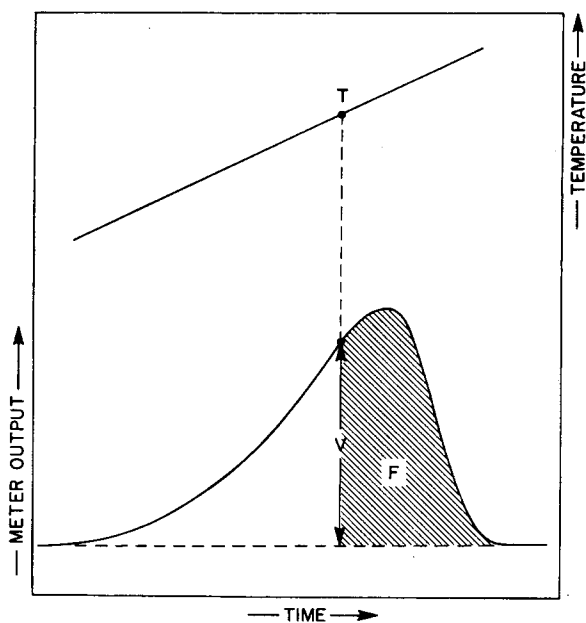


Fig. 2. First-order reaction curve.

Any convenient selection of points along the curve can be used to assess compliance to an Arrhenius equation by plotting $\ln k$ versus $1/T$. The excellence of agreement to such an equation serves to validate the derived reaction constants to the extent of the range of conditions explored. Various techniques can be used to confirm the order of reactions and their parameters. These could include isothermal operation or, conversely, conducting the reaction over a highly varied and irregular temperature history, e.g., Figure 6.

For information on the curve forms and the mathematics of other orders of reaction, reference may be made to an inclusive summary of the subject by Flynn and Wall.¹¹

DETAILS OF APPARATUS

The apparatus is diagrammed in Figure 1. The nitrogen (Matheson prepurified grade) was passed through silica gel and a cotton filter before entry to the flowmeter at a rate generally of about 10 cc/min. Helium was found to be less satisfactory as a carrier gas in use with the combustible gas indicator because it caused excessive baseline drift in this meter. Flow through the combustible gas indicator was maintained at 2.1 l./min by adjustment of a bleed valve before the diaphragm-type air pump. Recordings were taken with a two-channel potentiometric recorder.

Chromel-Alumel thermocouple leads of 28 B&S gauge wire were used, with a 2-cm extension of 40 B&S gauge wire to the hot junction. The "cracking coil," maintained at "orange" heat in use, was a 3.5-mm-o.d.,

3-cm-long helix of 24 B&S gauge nichrome wire of about 2 ohms resistance (cold) with a ceramic inner core. Various tube furnaces have been used. One furnace was 20 cm long, constructed with a 7.5-mm-i.d. copper tube bore which was wound with about 160 cm of asbestos-covered nichrome wire, with closer windings toward the tube ends to compensate for end heat losses, and enclosed with ceramic fiber insulation and a 3.2-cm-d. chrome-plated brass cover. Another furnace, without insulation and heated by a radiant source within a reflective shell, had less thermal inertia. This version was less stable in operation but permitted faster changes in temperature.

Tests of the response rates of the apparatus were: (1) imposition of a full-scale square wave input to the combustible gas indicator by connecting and disconnecting a premixed gas sample to the inlet, to which the meter indicated a 70% response in 2 sec; (2) measurements indicating a vapor transit time from sample to meter of 1 sec; (3) a perturbation in power to the radiant-type tube furnace was observed to effect a change in both the sample temperature and the meter recording in less than 3 sec.

The system's responsiveness and linearity is also indicated by the degree of correlation obtained in kinetic parameters; e.g., Figure 6. Temperature gradients within sample material are minimized by the convective heat transfer supplied by the inert carrier gas, and by adjustments in sample size and geometry when required.

PROCEDURES

Samples are weighed and loaded into a quartz tube for insertion into the furnace (Fig. 1). A small plug of glass wool inserted ahead of the capillary section of the tube can be used to help in the loading and retention of pulverized or powdered samples. Circuitry and flows are activated and run until baselines are stabilized and air is flushed from the upstream section. The "cracking coil" is then activated and, a minute or two later, power to the tube furnace is switched on and manually advanced. Predetermined voltage-time schedules are used when uniform advances in furnace temperature are desired. Such schedules can be useful in initial or exploratory pyrolysis runs. Meter outputs resulting from reactions then appear in a standard recognizable form, and departures of the sample temperature from the furnace temperature are apparent, indicating reaction heat effects. At completion of pyrolysis, the quartz tube is removed and cooled, and the sample residue is weighed.

Sample size requirements vary inversely to the pyrolysis rates to be used. Samples weighing 5 to 10 mg have yielded adequate meter outputs at heating rates in the order of 1°C/sec. Samples up to 200 mg weight have been used with lower heating rates. Samples in pulverized, sheet, fabric, and chunk forms have been used. Generally, the sample form has not been of consequence to the results. However, precautions are necessary with materials of low thermal conductivity to minimize temperature differences within samples by limiting their thickness.

Liquid samples and samples of materials that melt before pyrolysis have been pyrolyzed in the apparatus using quartz or metal boats for sample support. Some materials of this type have indicated excessive wetting or "creep" tendencies. Dispersion of such samples in a plug of glass wool has served in some cases to provide sufficient wettable surface to contain the material. The same technique can be useful in minimizing condensation reactions in melted or liquid samples, or in reducing "bumping" during pyrolysis of such samples by greatly reducing the film thickness of the materials.

EXPERIMENTAL EXAMPLES

An example of the system's capabilities is afforded in Figure 3 by the recordings for the pyrolysis of a cellulosic material. Thermogravimetric analysis had not been helpful in defining the pyrolytic reactions of this material. The thermogram for this material was judged undecipherable, as was its first derivative, recording A of Figure 3. However, the comparable output curve of the combustible gas indicator, recording C of Figure

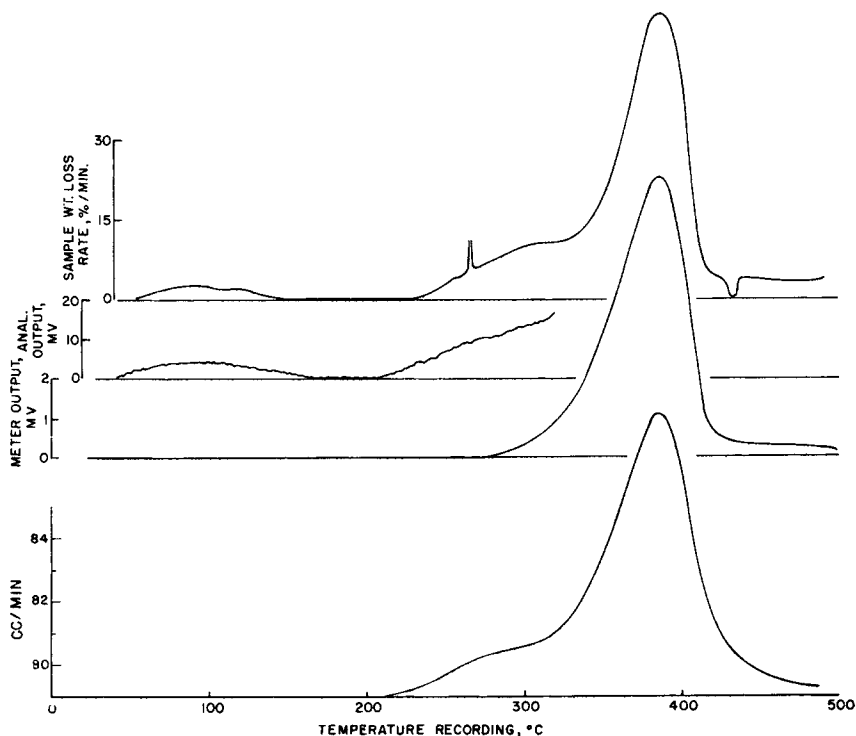


Fig. 3. Comparison of system recordings, pyrolysis of ashless cellulose powder with 1.5 wt-% KHCO_3 added. Heating rate, $60^\circ\text{C}/\text{min}$: (A) first derivative of thermogravimetric recording, 11.4-mg sample; (B) output of infrared water vapor analyzer, N_2 flow 280 cc/min, tube furnace outflow direct to analyzer w/o air dilution (analyzer responds to water and hydrocarbon vapors), 19.5-mg sample; (C) output of combustible gas indicator, 19.8-mg sample; (D) output of linear mass flowmeter, 13.8-mg sample.

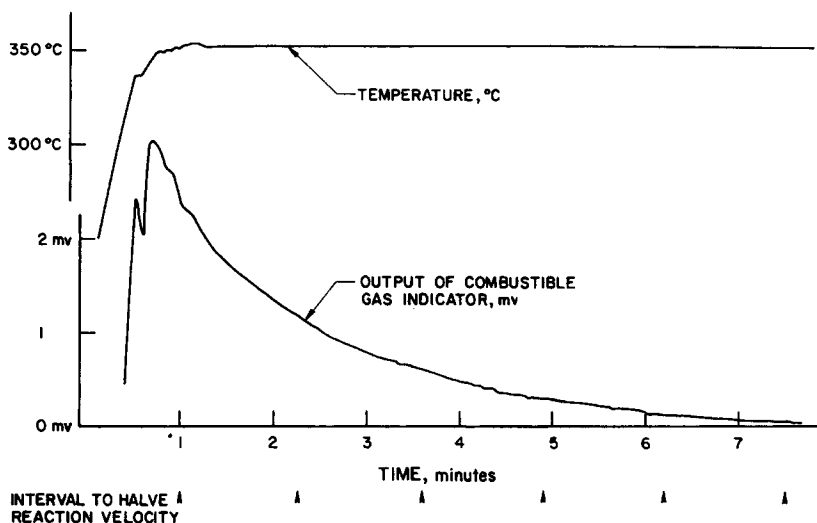


Fig. 4. Recordings of isothermal pyrolysis of treated cellulose. Interval for reaction velocity to half $t_{1/2}$, indicated as 78 sec at 352°C. Specific reaction rate k , calculated as 0.00888 sec^{-1} from $k = 0.693/t_{1/2}$, with $\ln k = -4.72$ at $1/T = 0.00160^\circ\text{K}^{-1}$.

3, clearly indicated a first-order reaction (the curve form of Fig. 2) for the principal decomposition. The recording was found on calculation to conform closely to first-order reaction kinetics, with an apparent activation energy of 40 kcal/mole (160 kJ/mole). (A minor area under the tail of the curve was subtracted as representing a secondary reaction and confirmed as such in other experiments.)

The differences between recordings A and C were resolved by various experiments, including the use of other meters in the apparatus. It was found that the initial pyrolysis reaction of the material (with precautions in sample desiccation) evolved essentially only noncombustible vapors, mainly water and secondarily carbon dioxide. The combustible gas indicator was not responsive to these vapors. Thus, this reaction had been conveniently "filtered" out of recording C. However, the reaction was recorded by the infrared H_2O analyzer (recording B of Fig. 3) and by the linear mass flowmeter (recording D of Fig. 3). The kinetics of the initial reaction could then be separated by various means. Most simply this could be done by appropriately limiting the reaction temperature and using the linear mass flowmeter to separately record the initial reaction. The reaction could also be deduced from the difference between recordings C and D, or from recording D alone by appropriate extrapolation of the later principal decomposition reaction and its subtraction from the total flowmeter recording.

The kinetics indicated by recording C of Figure 3 was confirmed, for other conditions, by a variety of other pyrolysis runs of the material. Examples of such runs yielding the same kinetic parameters are presented in Figures 4, 5, and 6, respectively, for (1) isothermal operation, (2) appreciably faster heating, and (3) irregularly cycled temperature. In the

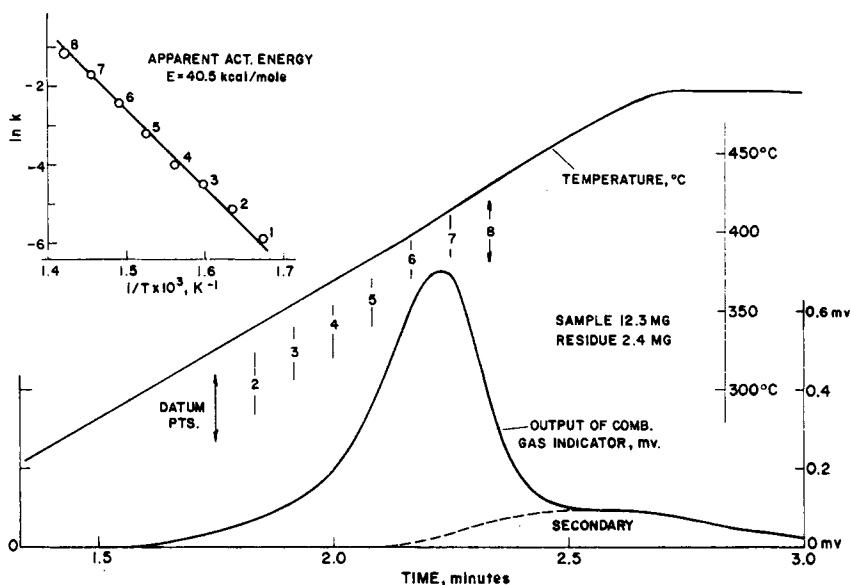


Fig. 5. Recordings and Arrhenius plot, faster pyrolysis of treated cellulose.

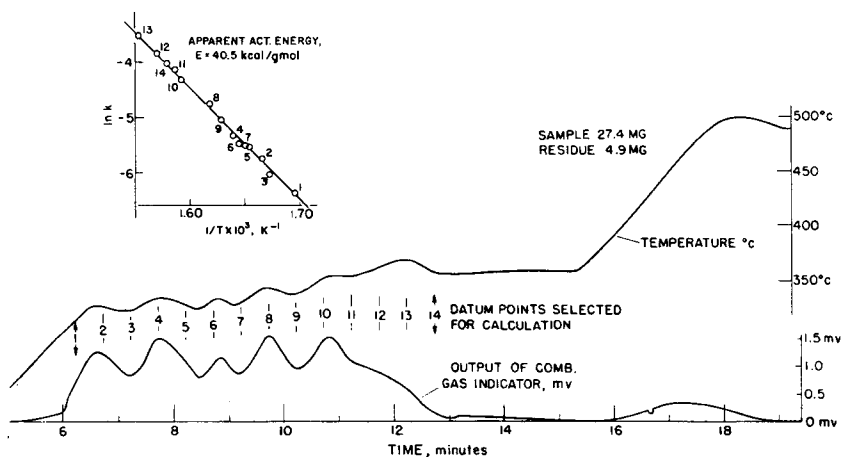


Fig. 6. Recordings and Arrhenius plot, pyrolysis of treated cellulose.

latter example, the pyrolysis temperature was purposely retained below 370°C to repress secondary decomposition during the principal reaction. The secondary reaction was subsequently recorded as the temperature was later increased to 500°C, an example of separating reactions by appropriate temperature control.

Another example is shown in Figure 7 of the system's capability to segregate reactions that normally would be overlapping and not identifiable by conventional thermal analysis. Three successive reaction stages have been isolated in recording A, Figure 7, of the total vapor flow from this

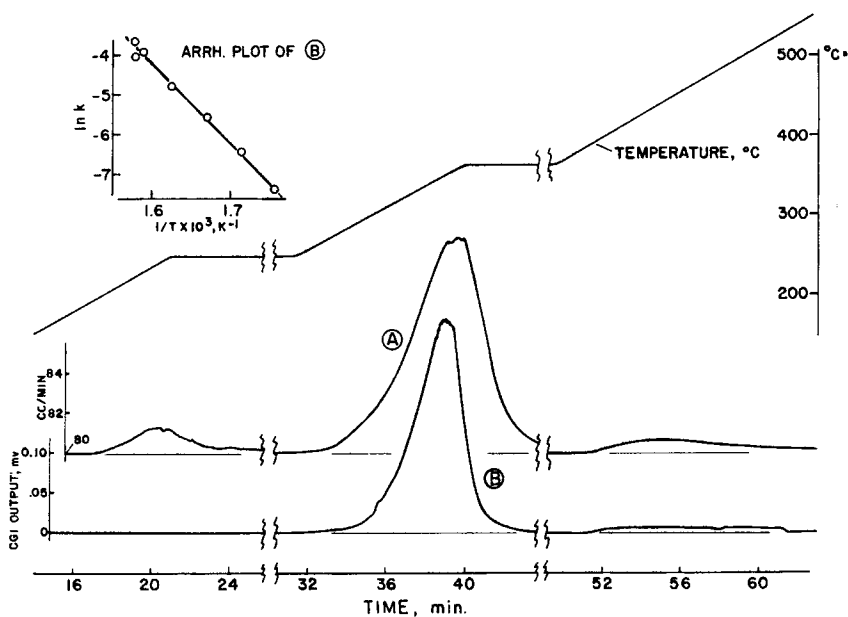


Fig. 7. Comparison of system recordings, pyrolysis of cellulose containing a fraction of barium oxycellulose (ashless filter paper, periodate-chlorite oxidized to 43 meq carboxylic acid/100 g cellulose and exchange reacted with barium acetate solution): (A) output of linear mass flowmeter, 84.6-mg sample; (B) output of combustible gas indicator, 41.7 mg sample.

pyrolysis by twice delaying the advance of the pyrolysis temperature at appropriate levels. Determination of these temperature levels was in part aided by the differences that were noted in the recordings of the pyrolysis by different metering instruments. The first reaction indicated in recording A was found to evolve about equal parts of water and carbon dioxide. Therefore, these vapors were not registered in recording B by the combustible gas indicator. Thus, this meter had been able to record the principal decomposition reaction in initial runs with only trivial "interference" from secondary reactions. In recording B, using this meter with its superior response speed, the separated main reaction yielded the Arrhenius plot included in Figure 7.

The above examples are indicative of how, in principle, the apparatus may permit even closely concurrent reactions to be resolved if an appropriate continuous analyzer is available which is specific to a vapor component evolved by only one of the reactions.

A quantitative measure of the performance of a method for kinetic measurements is difficult to specify, other than possibly by the degree of correlation to an Arrhenius relationship that is yielded by the method in certain cases. There is a lack of standard reference materials for such purposes. The performance of a method may involve many factors, including operator "art" and the nature of samples. The inaccuracies in

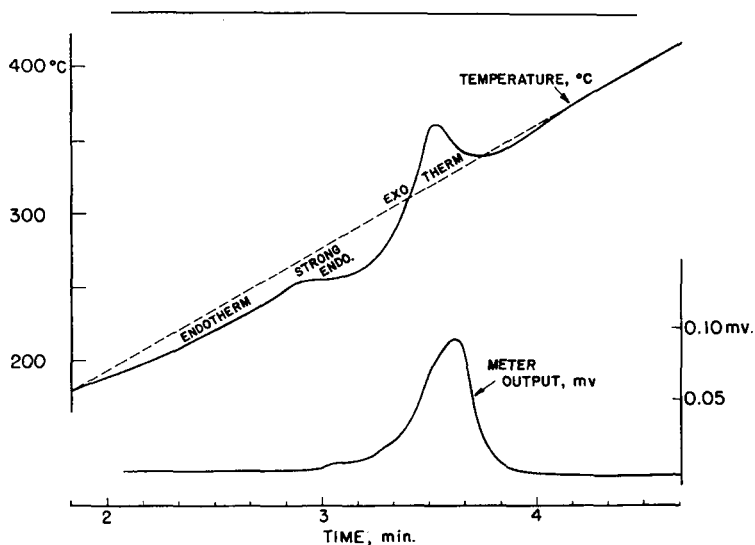


Fig. 8. Recordings, initial portion of pyrolysis of Verel fibers.

temperature measurements that may occur in thermogravimetry have been noted.¹ One such category of error results from reaction heat effects in samples. A temperature recording (Fig. 8) obtained with the system indicates the magnitude of errors possible in thermal methods where the temperature sensor is detached from the sample or has appreciable heat capacity. In this example, the indicated temperature of the sample has declined at one point to over 30°C below the immediate environment and then, within 20 sec, has risen to 40°C above the ambient furnace temperature. In some systems, these temperature excursions could remain undetected. Although this example may be somewhat extreme, such effects are not uncommon and tend to intensify and occur more frequently as pyrolysis rates are increased toward those of interest in studying combustion phenomena.

In context with the above, a limited number of direct comparisons of the system's performance to that of thermogravimetry were attempted. These were conducted under conditions adverse to vapor measurements and optimum for thermogravimetry, i.e., pyrolyses performed at low heating rates and with materials involving little if any reaction heat effects at these heating rates. The agreement in results between the respective methods was judged reasonable, and within the limits of uncertainty for thermogravimetry, in the pyrolysis of some common polymers. (Heating rates were 10°C/min. As derived respectively from recordings by the combustible gas indicator and by thermogravimetry,¹³ activation energies were estimated for polybutylene of 62 versus 62 kcal/mole, for polystyrene of 72 versus 75 kcal/mole, and for polyethylene of 78 versus 71 kcal/mole.) However, the decompositions were all in some respect less than ideal for the precise derivation of parameters.

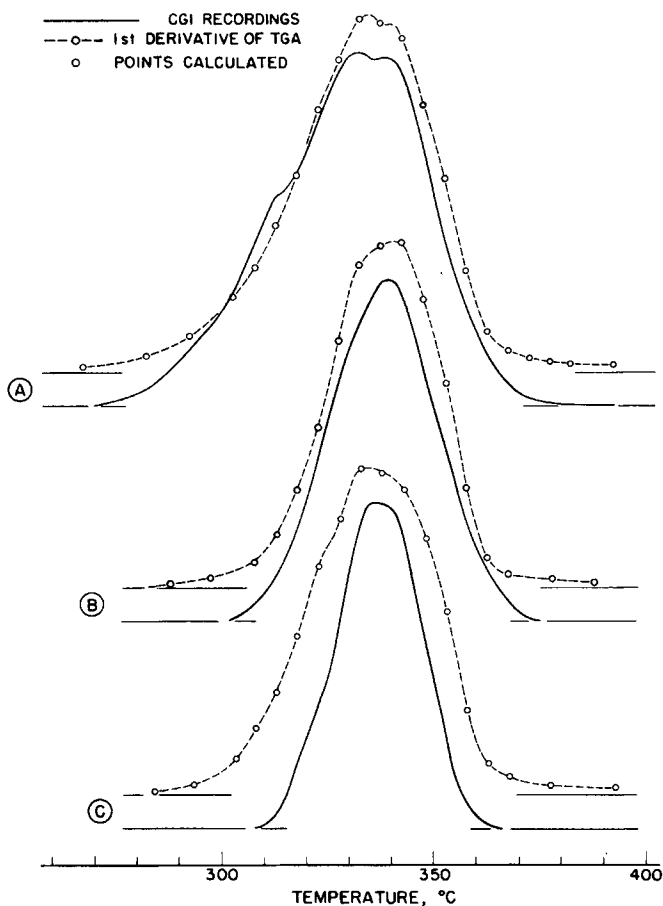


Fig. 9. Comparison of combustible gas indicator recordings to calculated thermogravimetric rates. TGA samples, 20 mg. CGI samples respectively 100, 41, and 50 mg. Cellulose containing traces of (A) aluminum, (B) magnesium, (C) copper.

Another set of performance comparisons are summarized in the diagrams of Figure 9 for nonideal reactions obtained in the pyrolysis of some cellulosic materials at heating rates of $8^{\circ}\text{C}/\text{min}$. In these diagrams, all of the thermogravimetric rates have been displaced 7°C downward on the temperature scale to correct for bias in the TGA temperature measurements. These rates were obtained by manually differentiating the thermograms with the utmost care. The relevant sections of the thermograms included only 10 cm or so length of pen recording. The resulting uncertainties in the estimated rates, as well as the variation in reproduced thermograms, appeared greater than the differences in results between the two methods.

The capability of the apparatus to detect reaction heat effects was tested in runs with samples of some standard reference materials certified for the calibration of DTA systems (NBS-ICTA Standard Reference Material 758, one of three sets of materials for calibration purposes available from

TABLE I
Transition Temperature Data Recorded for Reference Materials^a

Material	Temperature, °C			
	Transition noted on		Median of transition points	Quoted ^b "equilibrium" point
	heating	cooling		
Potassium nitrate	132	127	129	127.7
Indium	157	157	157	157
Tin	232	232	232	231.9
Potassium perchlorate	306	295	301	299.5
Silver sulfate	438	418	428	430

^a Sample size 50–100 mg, heating and cooling rates 10–100°C/min.

^b From certificate accompanying NBS-ICTA Standard Reference Material 758.

the National Bureau of Standards, U.S.). The transition points for these materials were clearly discernible in temperature recordings obtained at various conditions within the normal operating range of the apparatus and the indicated transition temperatures compared favorably with the reference temperatures and the standard deviation quoted for their derivation. Results are summarized in Table I.

DISCUSSION

Other advantages of the system may be noted. There is little "noise" in the recordings. Dynamic effects from evolved vapors, convection, etc., are not of consequence to the measurements. A wide range of pyrolysis rates may be accommodated by the apparatus. Heating rates up to 3°C/sec have been used without apparent impairment of the recordings. Sensitivity of up to two orders of magnitude greater than that of conventional thermal methods is obtained. Accuracy in temperature measurements is aided by the direct contact of a low-mass temperature sensor with the sample material. Uniformity of sample temperature is aided by the presence of an inert gas atmosphere serving as a medium for heat transfer.

Of particular merit is the simplicity of the system. The apparatus is simple and expeditious to operate. It does not involve the complications and delays of vacuum operation. The results are generally simple to interpret. The "visibility" of the recordings is such that effects can sometimes be recognized and explored by adjustments in temperature during the course of pyrolysis runs, in the manner of operating an analog computer. The data are simple to translate into kinetics terms. The equipment is relatively inexpensive.

CONCLUSIONS

The described apparatus is a sensitive and efficient means for measuring the kinetics of vapor-producing reactions. It permits measurements to be made at pyrolysis rates higher than practical with conventional methods

and comparable in magnitude to those occurring in combustion. The system has performed kinetic measurements of reactions that normally would be concurrent in part and not identifiable by conventional methods. It permits a variety of options in effluent sensing and mode of operation. The utility and applicability of the method appear promising.

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