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MEASUREMENT OF EVOLVED GAS RESULTING FROM CLOSED-SYSTEM PYROLYSIS OF FOUNDRY CORE BINDERS *

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ABSTRACT

The quantity of gas generated by pyrolysis of a foundry core binder during casting operations is of practical importance to the foundry industry. A method for measuring the gas volume was developed using a DuPont 951 TGA furnace system; this method eliminates many of the errors inherent in some of the traditional methods. The incorporation of an extrapolation technique eliminates the dependence of the final result on sample size. This method was found to be rapid, highly reproducible, and insensitive to the nature of the atmosphere in the pyrolysis chamber.

INTRODUCTION

In the production of metal castings, certain portions of the mold are constructed of a core made of sand held together by an adhesive binder. Cores are bodies placed into molds to form corresponding cavities in the casting, such as in the castings of a cylinder block for an automobile engine, where the cylinders and water jackets are cast around cores rather than the mold proper.

As the cores project into and are largely surrounded by molten metal, they must be rigid enough to withstand stresses generated by the static pressure of the liquid metal during pouring. Gases formed within the core due to thermal decomposition of the binder must have ample means of escape without "blowing" into the metal; indeed the common foundry practice is to provide ample venting of the core to exhaust an amount of gas above that expected. Finally, as the cores must be removed by the shake-out operation, the core binder must be such that it is readily destroyed by the heat liberated from the liquid metal as it solidifies. Thus, the amount of gas liberated due to decomposition of the core binder is of great interest to the foundry.

Different core binders have been used in the past to meet the many and varied requirements of the foundry industry. Types of materials utilized as core binders include water-soluble materials such as molasses and sodium

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silicates, cereal pastes such as flours and dextrins, colloidal binders and clays, oils, wood rosins, coal tars, and even concrete [1]. More recently, hot melt adhesives, consisting of blends of thermoplastic polymers, wax diluents, and resin modifiers, have been gaining increasing popularity, and have been formulated to meet a variety of foundry requirements.

APPARATUS AND PROCEDURE

Figure 1 shows one arrangement of apparatus recommended by the American Foundrymen's Society [2]. The obvious advantage of this apparatus is that it can be readily, inexpensively, and quickly constructed from materials found in most laboratories. The gas buret is filled with water by inversion, and a sample of the core or core binder is weighed into a porcelain combustion boat and inserted into the test tube in the position shown. The system is sealed and a Bunsen burner flame applied. When the level of water in the gas buret becomes constant, a reading is taken. A blank determination must be made to compensate for the thermal expansion of the gas originally in the combustion tube. Results are reported as volume of gas evolved per weight of core or binder.

The main disadvantage of this apparatus is that the total heat transfer, and especially the heat flux, bear only a remote resemblance to those encountered in industrial casting operations, and are, at best, only marginally con-

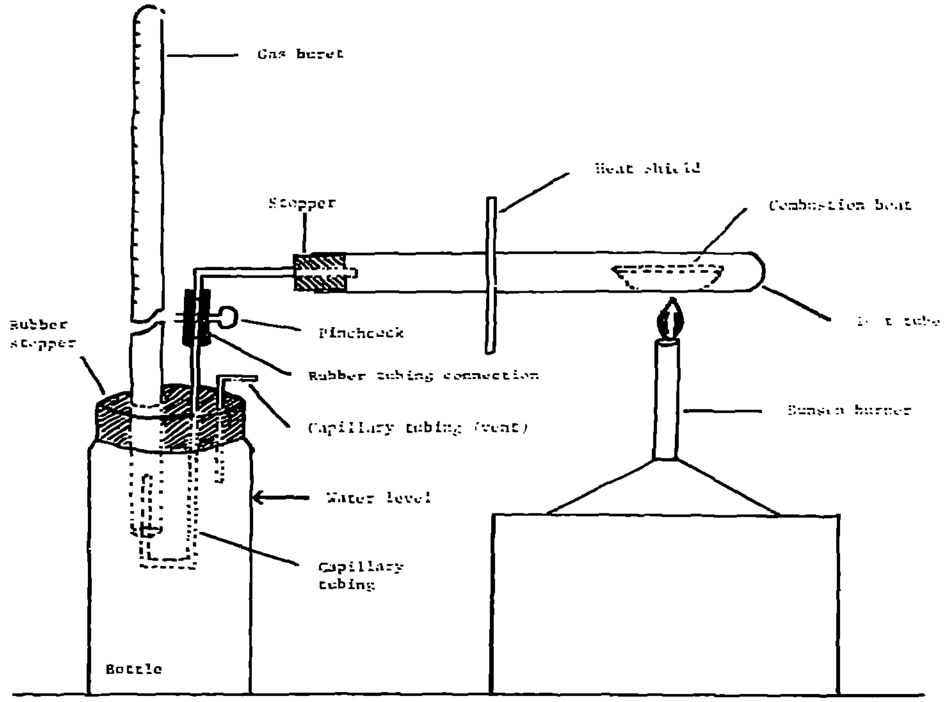


Fig. 1. Apparatus recommended by American Foundrymen's Society for determining gas evolution of cereal core binders.

trollable by the operator. Although this does not present any great handicap in the testing of cereal binders, the pyrolysis of a hot melt binder proceeds at too low a temperature, forming significant and varying amounts of condensable material. These by-products condense on the tube walls downstream from the heat shield, and give rise to low results and long analysis times. The time needed to achieve constant volume in the buret may be so long that a glass or even a Pyrex pyrolysis tube is subject to sag and eventual rupture at the point of flame application. In the event of rupture, contact of the hot, gaseous decomposition products in the tube with air generally results in an explosion.

Figure 2 shows an improved apparatus used at H.B. Fuller Company to determine the gas evolved during pyrolysis of a hot melt core binder. The pyrolysis portion of the apparatus consists of a quartz pyrolysis tube and a furance equipped with a temperature controller. We have found that the combination of a DuPont 990 thermal analyzer and the furnace portion of the 951 TGA module is excellent for this purpose, providing a suitable geometry, accurate temperature control, and rapid thermal equilibration. The quartz tube has the same outside diameter and wall thickness as the furnace tube supplied with the TGA, and is allowed to extend about 3 in. beyond the furnace on the open end, providing a relatively cool zone to facilitate sample loading. The pyrolysis tube is connected to the gas buret via a rubber stopper. The "cool" end of the tube does become sufficiently warm to harden the stopper through vulcanization and/or loss of plasticizer, but the effect on the experiment is not measurable.

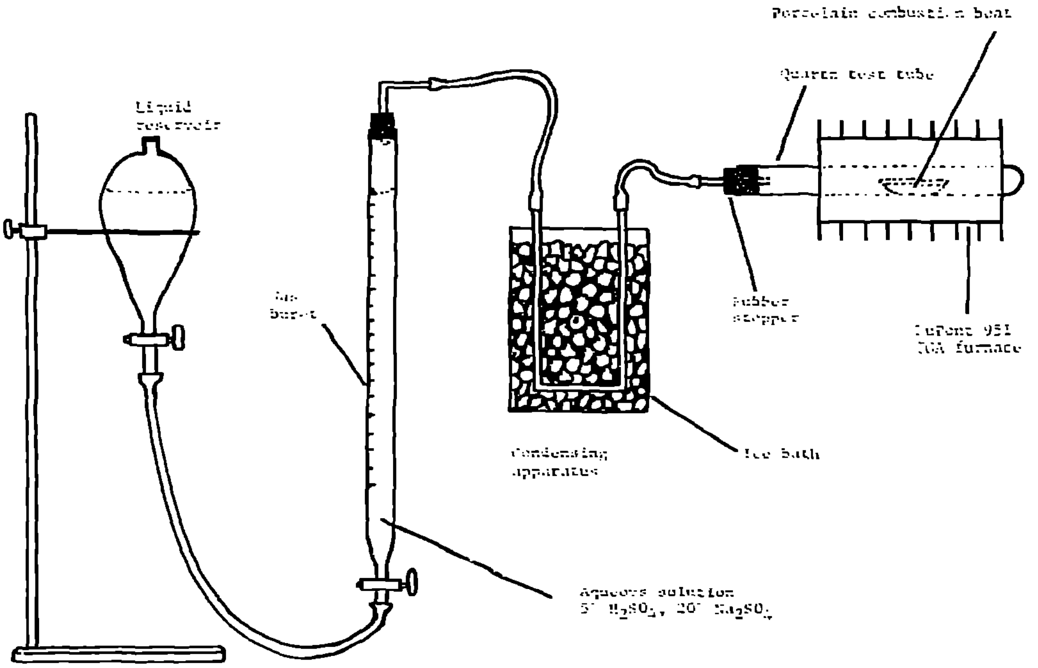


Fig. 2. Apparatus used in this work for determining gas evolution of hot melt core binders.

A condensing apparatus is connected between the gas buret and the pyrolysis tube to minimize errors due to the production of water vapor from oxidation of the pyrolyzate. The lower end of the buret is connected to a leveling reservoir filled with an aqueous solution of 5% sulfuric acid and 20% sodium sulfate, since it has been found that the solubility of carbon monoxide and carbon dioxide is low in such a solution [2]. A small amount of cationic surfactant may be added to this solution to enhance wetting of the buret wall.

The furnace is operated isothermally at a temperature of 982° C (1800° F), as specified in foundry industry standards [2]. An amount of hot melt binder between 0.02 and 0.07 g is weighed into a porcelain combustion boat. The height of the reservoir is adjusted to give a zero buret reading with the system open to the atmosphere.

From this point, the experiment requires two operators. Operator A places the sample into the cool portion of the pyrolysis tube. Operator B pushes the sample into the hot zone at the furnace center with a metal rod, and starts a stop-watch. Operator A connects the buret to the tube, and holds the connection in place during the initial period of rapid gas evolution, while Operator B lowers the liquid reservoir. If the liquid levels in the buret and reservoir are kept nearly equal, excessive pressure cannot build up in the system. After 7.5 min the height of the liquid levels in the reservoir and buret are matched and the buret read.

A blank determination must be performed and the volume determined substracted. The results are expressed as cm^3 gas evolved per weight of binder, corrected to 1 atm pressure and 25° C.

RESULTS

Figure 3 shows a plot of the volume of gas evolved as a function of time. Note that essentially no gas is given off during the first 10 sec or so, and that gas evolution is complete in 7.5 min. Nearly all the gas is evolved between 15 and 75 sec after insertion of the sample. A few seconds are required to load the sample and connect the buret, but a finite time is also required for the

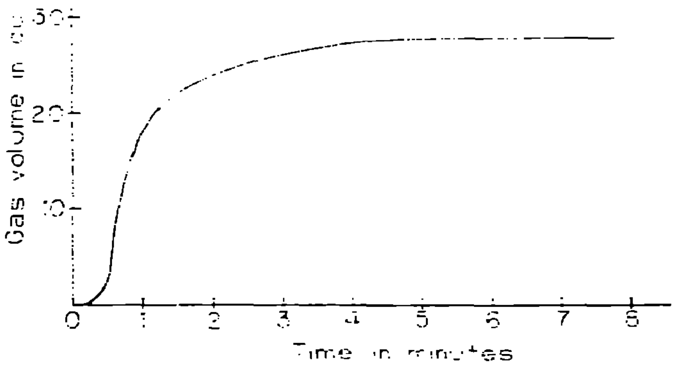


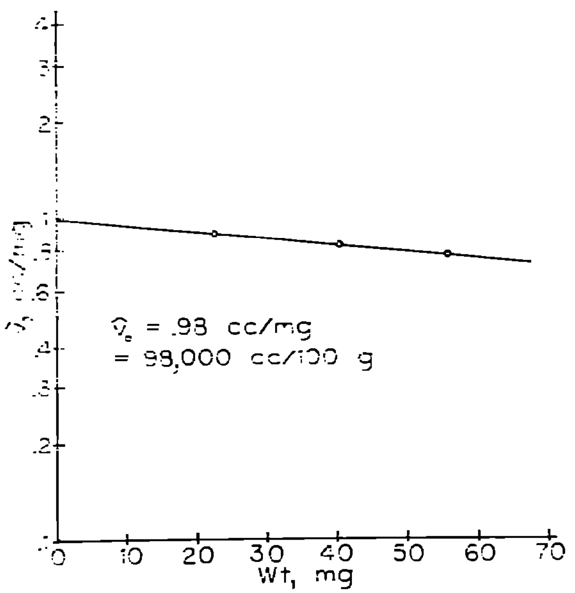
Fig. 3. Plot of volume of gas given off vs. time for a typical core binder.

sample to reach its decomposition temperature. Ten seconds was found to be ample time for a pair of moderately coordinated operators to load the sample and seal the system.

Initial results, expressed as gas volume per unit sample weight, $\hat{V}$, were found to be dependent on sample size. Empirically it was found that plots of log $\hat{V}$ against sample size were linear, as shown in Fig. 4. This relationship was found to hold for all materials examined to date. This led us to define an "extrapolated" gas evolution parameter, $\hat{V}_0$, as the zero sample size limit of $\hat{V}$. This parameter may be read directly from a plot of the type shown in Fig. 4, or may be calculated using a non-linear regression technique and a programmable calculator, as was done in this work.

A comparison of results obtained on 18 lots of a single commercial hot melt core binder gave a mean value of 967 cm^3 gas g^{-1} binder, with a relative standard deviation of 0.6%. This degree of reproducibility has been routinely achievable.

To determine the affect of air vs. an inert atmosphere in the pyrolysis chamber, we tested two samples in air, and repeated the tests in a nitrogen atmosphere. The nitrogen atmosphere was achieved by purging the combustion tube with nitrogen for 10 min at a flow rate of 0.5 l min^{-1} immediately before inserting the sample. As is seen in Fig. 5, the data all fell on the same lines. We conclude, therefore, that as long as the system is kept sealed, the air originally in the combustion tube is swept out into the cooler region before oxidation can proceed to a measurable extent, or that oxygen uptake is negligible under the conditions of the experiment.



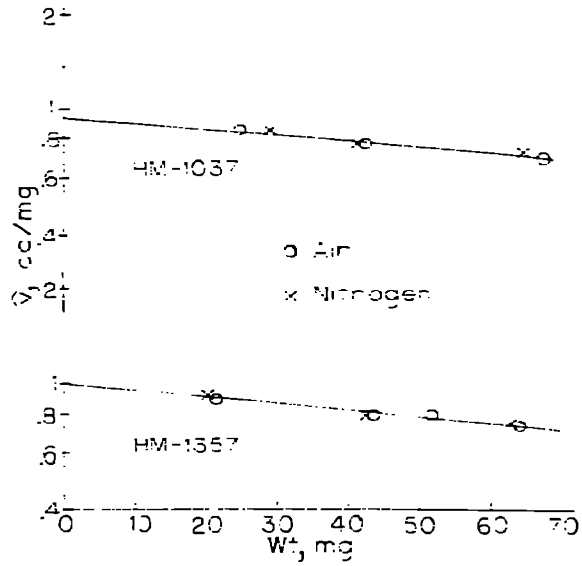


Fig. 4. Plot for determining extrapolated value of gas evolution. The sample is an experimental hot melt binder.

Fig. 5. Plots showing equivalency of air and nitrogen atmospheres in the pyrolysis chamber. The samples are commercially available hot melt binders.

TABLE 1

Contribution to evolved gas for different pyrolysis products

Gas	M	$\hat{V}$ ($cm^3\ g^{-1}$)
Carbon dioxide	44	559
Carbon monoxide	28	879
Water	18	1367
Methane	16	1538
Ethane	30	820
Ethylene	28	879
Acetylene	26	946
Propane	44	559
Propylene	42	586
Benzene	78	315

CONCLUSIONS

For a given pyrolysis product, the contribution to $\hat{V}$ can be calculated from the ideal gas law. The relationship is, for 25°C and 1 atm

$$\hat{V} = \frac{24\,600}{M}\ cm^3\ g^{-1} \qquad (1)$$

where M is the molecular weight of the pyrolysis product. Table 1 shows calculated values of $\hat{V}$ for gases which could conceivably be produced from pyrolysis of a hot melt core binder.

Since V_0 is typically 900—1100 $cm^3\ g^{-1}$ for these systems, it would appear that the pyrolyzate produced under these conditions is predominantly simple hydrocarbons, with smaller amounts of carbon dioxide, carbon monoxide and water vapor, the amounts of the latter being dependent on the oxygen content of the raw materials used in making the sample tested. Since values of $\hat{V}$ decrease with increasing sample size, becoming as low as 650 $cm^3\ g^{-1}$ for samples between 0.06 and 0.07 g, it is apparent that the degradation is enhanced as smaller samples are pyrolyzed. In any case, the data obtained appear quite reasonable for the products tested.

It must be remembered, however, that moisture and soil organic material present in the core sand itself may contribute different pyrolysis products, and that the air in the core will undergo expansion by a factor of up to 5.5 near the mold—metal interface [3], thus contributing not only additional gaseous products, but also enhancing oxidation. The method discussed here is intended only for laboratory screening or quality control of the binder alone.

Thus, the method outlined here is shown to be simple (although two operators are required for a portion of the test) and reproducible in the limit of vanishingly small sample size, and to give results in agreement with those expected. The procedure outlined here may be a useful tool for studying the pyrolysis of complex organic materials, although such studies were beyond the scope of this work.

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