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To cite this article: Quan Tran *et al* 2022 *Meas. Sci. Technol.* **33** 047002




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Technical Note

Direct demonstration of complete combustion of gas-suspended powder metal fuel using bomb calorimetry

Quan Tran¹ , Igor Altman² , Pascal Dube³, Mark Malkoun³, R Sadangi⁴, Robert Koch⁴ and Michelle L Pantoya^{1,*} 

¹ Department of Mechanical Engineering, Texas Tech University, Lubbock, TX 79424, United States of America

² Naval Air Warfare Center Weapons Division, China Lake, CA 93555, United States of America

³ Matsys, Inc, Sterling, VA 20164, United States of America

⁴ U. S. Army Combat Capabilities Development Command Armaments Center, Picatinny, NJ 07806, United States of America

E-mail: michelle.pantoya@ttu.edu

Received 4 August 2021, revised 15 November 2021

Accepted for publication 4 January 2022

Published 24 January 2022



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Abstract

Off-the-shelf calorimeters are typically used for hydrocarbon-based fuels and not designed for simulating metal powder oxidation in gaseous environments. We have developed a method allowing a typical bomb calorimeter to accurately measure heat released during combustion and achieve nearly 100% of the reference heat of combustion from powder fuels such as aluminum. The modification uses a combustible organic dispersant to suspend the fuel particles and promote more complete combustion. The dispersant is a highly porous organic starch-based material (i.e. packing peanut) and allows the powder to burn as discrete particles thereby simulating dust-type combustion environments. The demonstrated closeness of measured Al heat of combustion to its reference value is evidence of complete metal combustion achieved in our experiment. Beyond calorific output under conditions simulating real reactive systems, we demonstrate that the calorimeter also allows characterization of the temporal heat release from the reacting material and this data can be extracted from the instrument. The rate of heat release is an important additional parameter characterizing the combustion process. The experimental approach described will impact future measurements of heat released during combustion from solid fuel powders and enable scientists to quantify the energetic performance of metal fuel more accurately as well as the transient thermal behavior from combusting metal powders.

* Author to whom any correspondence should be addressed.



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Supplementary material for this article is available [online](#)

Keywords: energy of combustion, bomb calorimeter, powder fuels, dust combustion, metals, enthalpy

(Some figures may appear in colour only in the online journal)

1. Introduction

An important parameter characterizing calorific potential from a fuel is heat released during combustion (ΔH_c). Heat released during combustion is defined as the chemical energy liberated from a fuel and oxidizer reacted to its most oxidized state. The most common diagnostic to measure heat released during combustion is a bomb calorimeter that actually measures the temperature increase of a constant water volume from the exothermic oxidation reaction. In a bomb calorimeter, ΔH_c is determined in a chamber that is pressurized with oxygen to promote oxidation of the reactants.

One challenge when using metal powders in a bomb calorimeter is that they can coagulate during combustion and burn as a pool rather than as individual particles, as shown in figure 1, which leads to incomplete combustion and results in an underestimate of ΔH_c .

Pooling alters oxidation reactions and inherently affects the measured heat of combustion. Bulk powder combustion is complicated by the competing effects of oxygen diffusion and rapid heat transfer that are different in a molten metal pool compared to individually dispersed particles. Additives can help promote complete combustion of the metal powder but may not represent combustion of gas suspended particulates. Therefore, the choice of additive is conditioned by the purpose of the measurement, and an improper choice may potentially mask important features required for simulating an actual application. For example, liquid additives create a slurry that do not best represent the combustion process associated with discrete particle dust explosions. Liquids, such as ethylene glycol, may produce complete particle combustion that allow measurement of the calorific output, but a slurry will not represent the nuances associated with the combustion process specific to airborne particles that may also be a function of particle size. Colloids do not simulate completeness of combustion for airborne powder. Additionally, the quantity of additive should represent a reasonable fraction of the test specimen such that the contribution of energy from the metal simulates airborne particles.

Our goal is to present a technique that creates an environment within the bomb calorimeter simulating particles burning in dust explosion conditions [1] and assess particle heat output representative of these real conditions. Dust explosion environments are common in energetic material applications, such as enhanced blast [2], explosively dispersed [3–5], or high velocity impact [6] conditions that produce single particle or particle agglomerate burning in clouds. A method of measurement of the heat generated for powders is therefore useful.

The method introduces a highly porous starched-based medium (i.e. packing peanut (PP)) to contain and disperse the

metal powder in a way that simulates dust combustion processes inside a bomb calorimeter. The purpose of the medium is to suspend the powder such that particle sintering or pooling cannot impede combustion efficiency, and the medium itself also burns within the bomb to produce energy that can be subtracted from the measurement. Note that the energy produced by the porous medium should not exceed the energy produced by metal combustion in order to produce measurements that are representative of the dust combustion environment. Otherwise, the additive behaves more like a furnace that ensures complete combustion of the metal particles but is not representative of the airborne particle reaction environment.

Aluminum fuel particles are the most widely studied fuel particle in the literature today [7, 8] and their reactivity is a strong function of particle size [9]. Therefore, we establish the feasibility of this method with two particle size aluminum fuel powders. We also demonstrate that the temporal calorimeter output, which is rarely reported in literature, is sensitive to the rate of heat release. The latter finding allows for an extension of the standard bomb calorimeter apparatus capability such that the data generated can also be used to characterize the transient heat transfer behavior of reactive materials.

2. Experimental

The aluminum (Al) powders were supplied by Valimet, Inc. (Stockton, CA) [10] and two different Al particle sizes were analyzed: H5 has a 15 μm and H95 has a 160 μm characteristic particle diameter, respectively. The wide disparity in particle size selection was purposefully selected to show the method is applicable to wide ranging metal fuel combustion behaviors. From here forward the H5 sample will be identified as Al-015, and H95 will be identified as Al-160 for simplicity in connecting the material with particle size.

The porous medium was a starch-based biodegradable packaging filler identified as a PP [11]. It is noted that PPs can be polystyrene-based, but we have found the most effective dispersant is an organic, starch-based PP. The PP was procured locally from an office supply store (Item # 578-376, The Office Depot, Boca Raton, FL). The porous material was fabricated by extrusion of starches (i.e. wheat, corn and potato starches) in the presence of minor amounts of polyalkylene glycol and a particulate bubble-nucleating agent [11]. The Parr 6400 Automatic Isoperibol Calorimeter (Parr Instrument Co., Moline, IL) was used for all experiments [12].

Prior to experiments, standardization tests were conducted to determine the correct energy equivalent for the oxygen combustion vessel. The energy equivalent of the calorimeter is the

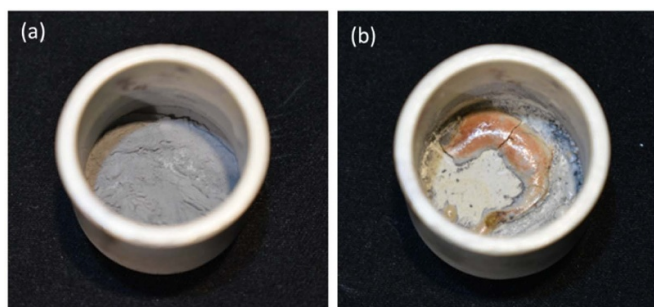


Figure 1. Photographs of pure aluminum powder (a) before and (b) after testing in a bomb calorimeter. Notice pooling and remaining unburned powder in crucible after testing in (b).

Table 1. Tabulated data for heat released during combustion (ΔH_c) from the standard one-gram benzoic acid (BzOH) pellet, and the packing peanut (PP) alone. The average and standard deviation are included.

| Test | BzOH (kJ g ⁻¹) | PP (kJ g ⁻¹) |
|------|---------------------------------|---------------------------------|
| 1 | 26.43 | 16.53 |
| 2 | 26.46 | 16.53 |
| 3 | 26.47 | 15.76 |
| 4 | 26.44 | 16.69 |
| 5 | 26.47 | 17.53 |
| Avg. | 26.46 ± 0.02 kJ g ⁻¹ | 16.61 ± 0.56 kJ g ⁻¹ |

amount of energy required for the oxygen combustion vessel to raise the temperature of the water bath by one degree. The energy equivalent essentially quantifies the energy capacity associated with the vessel. Standardization tests were performed using one-gram benzoic acid (BzOH) pellets (#3415, Parr Instrument, Moline, IL) in boron nitride (BN) crucibles (MTI Corp., Richmond, CA). The standardization tests resulted in an energy equivalent of 3.92 kJ C⁻¹.

After standardization tests, calibration-based deviation tests were conducted to ensure that the maximum permissible standard deviation in BzOH measurements was within a few percent of the accepted ΔH_c for BzOH, which is 26.43 kJ g⁻¹. The average ΔH_c of BzOH was 26.46 ± 0.02 kJ g⁻¹ (table 1) such that the relative instrument error was confirmed to not exceed 0.1%.

Following calibration, the ΔH_c of the PP was determined by averaging results from multiple bomb calorimetry experiments and abbreviated here in table 1. These experiments resulted in an average ΔH_c equal to 16.61 ± 0.56 kJ g⁻¹. The standard deviation did not exceed 3.5% and was higher than the instrument error of 0.1%. The higher standard deviation may be a consequence of the inherent inhomogeneity within the PP material. Therefore, a 3.5% standard deviation was also a reasonable upper limit on uncertainty for these measurements.

Powders were used in the range of 0.035–0.05 g but the PP was held constant at 0.10 g. The sample size was selected to align with the minimum ignition fuel concentration under ambient conditions. The overall heat of combustion of metal powder under this selection is comparable with the heat of

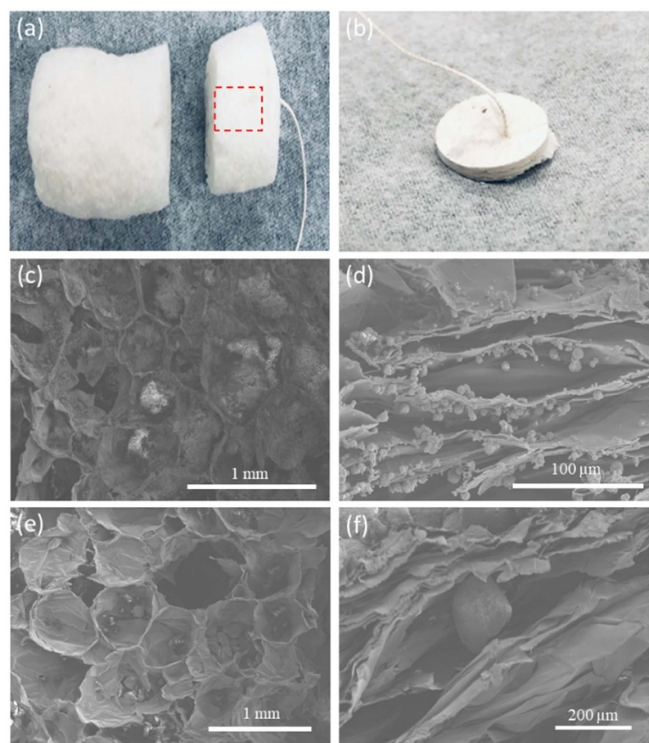


Figure 2. (a) Packing peanut (PP) sliced and Al powder is dispersed within the portion highlighted with a dashed red line. The two pieces are then pressed together to an approximately 2 mm thickness as shown in (b) PP and powder sample after pressed. Note the cotton ignition thread required for this bomb calorimeter is also included in the photograph. Micrographs of (c) uncompressed PP with Al-015, (d) compressed PP with Al-015, (e) uncompressed PP with Al-160 and (f) compressed PP with Al-160.

combustion of the PP. The latter makes the subtraction of the PP combustion heat required for the bare metal characterization (see equation (1)) possible. Figure 2 illustrates preparation of the powder within the PP. The PP was sliced into two sections as shown in figure 2 and a small cavity created using a detail knife (illustrated with dashed lines in figure 2(a)). The metal powder was poured into the cavity (figure 2(a)) of the smaller section, then the two PP sections were joined and with the cotton thread on top, the vertical PP was gently tapped to allow powder dispersion through the porous matrix. The sample was then pressed to 2 mm thickness using the Parr Pellet Press (Parr Instrument Co., Moline, IL) for consistency between experiments, as shown in figure 2(b). The cotton thread shown in figures 2(a) and (b) connects with an ignition wire that is heated by an electrical charge within the bomb calorimeter. The heated wire burns the cotton thread that then ignites the sample.

Figures 2(c)–(f) shows SEM micrographs of the powder filled PP before and after compression for both Al particle sizes. For the uncompressed PP, the effective pore diameter was 0.25 mm. After compression, the pore collapsed to about 40% of its original volume. The smaller Al-015 powder dispersed throughout the matrix and appeared to adhere to the surface of the pore structure (figure 2(d)). For the larger Al-160 powder a single particle can fill an entire pore (figure 2(f)).

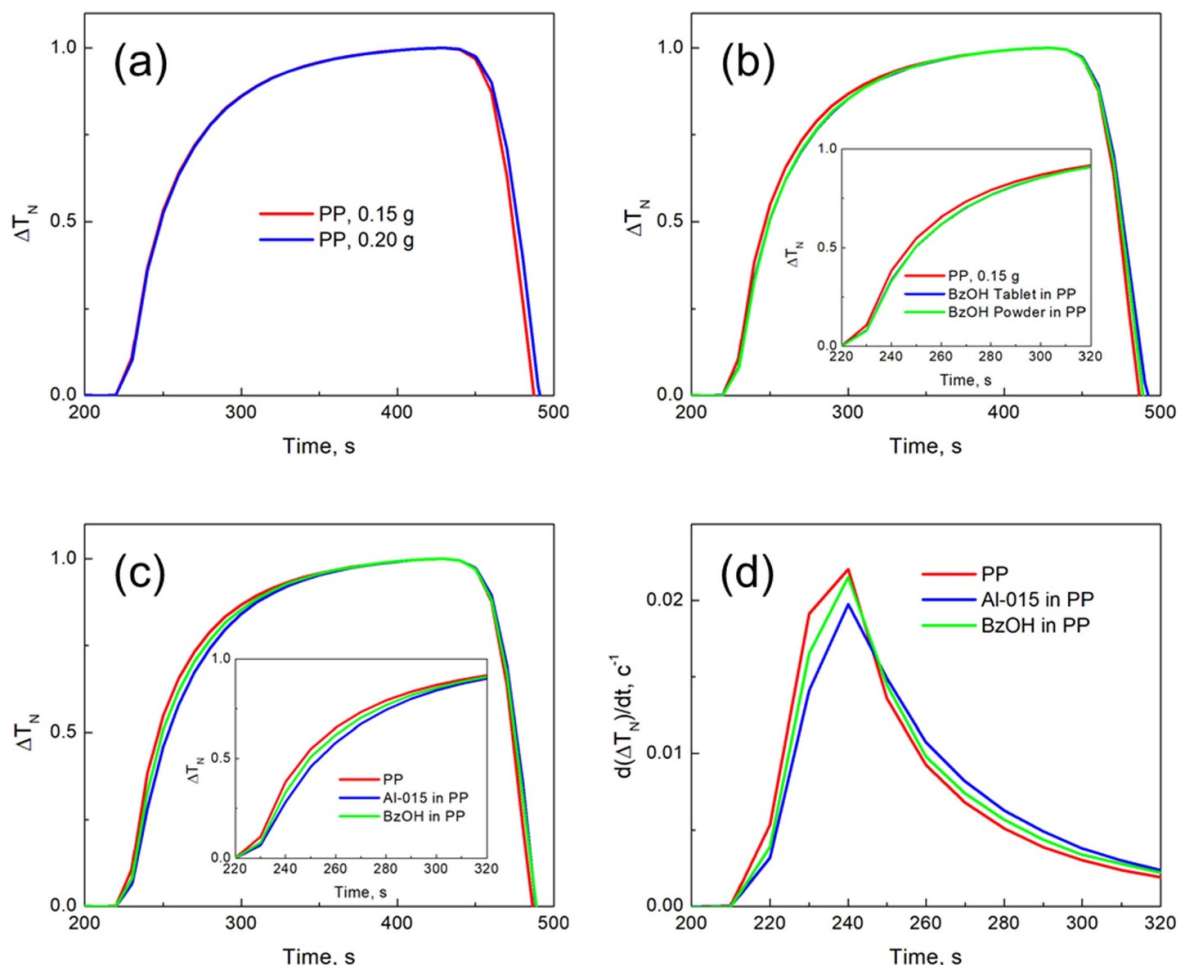


Figure 3. The normalized transient temperature of the water bath for experiments with different amounts and types of fuel materials. (a) Heating rate shows a low or no sensitivity to the amount of the PP sample. (b) Heating rates of two samples with the same weight and concentration of BzOH (0.05 g) and PP (0.1 g) compared with PP alone (0.15 g) demonstrates sensitivity to the sample composition (PP versus BzOH). One BzOH sample was in a consolidated pelletized form, the other BzOH sample was ball milled into a powder. (c) The normalized temperature of the water bath and (d) the time derivative of the normalized temperature of the water bath for a representative experiment with Al-015 powder contained in PP. The BzOH in the PP and bare PP curves are included to demonstrate the distinguishable difference in the heating rate region.

While the powder density appears well dispersed throughout the PP, a quantitative analysis of powder density gradient was difficult to assess.

The ΔH_c was determined by combusting the sample with standard excess oxygen at a pressure of 30 atm in the calorimeter. The ΔH_c was automatically calculated by the instrument using equation (1) [12] that considers the energy equivalent, the energy generated during combustion of the PP, sample mass, and instrument specific correction factors

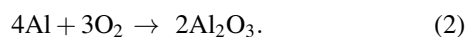
$$\Delta H_c = \frac{WT - e1 - e2 - e3 - (H_{cs})(M_s)}{m} \quad (1)$$

In equation (1), T is observed temperature rise, W is energy equivalent of the calorimeter, $e1$ is heat produced by burning the nitrogen portion of the air trapped in the bomb to form nitric acid, $e2$ is heat produced by the formation of sulfuric acid from the reaction of sulfur dioxide, water, and oxygen, $e3$

is heat produced by the heating wire and cotton ignition thread, m is the mass of the sample, H_{cs} is heat of combustion of the PP (cal g^{-1}), and M_s is the mass of PP [12]. Therefore, the previously measured ΔH_c for the PP (table 1) was input into the instrument software and the resulting Al ΔH_c was calculated using the built-in instrument procedure described by equation (1) that assumes the additive nature of reaction heat from the PP and Al combustion, correspondingly. Similar methods to calculate ΔH_c from calorimetric data could be applied using a procedure reported by previously [13, 14].

The experimentally measured ΔH_c for Al powders is $30.45 \pm 0.66 \text{ kJ g}^{-1}$ for Al-015 and $30.47 \pm 0.66 \text{ kJ g}^{-1}$ for Al-160. The results are an average of 20 measurements and standard deviation (see supplementary information for complete data available online at stacks.iop.org/MST/33/047002/mmedia). For both Al powders, the average values are 98% of the reference ΔH_c calculated by summing standard enthalpies of formation for product species using

JANNAF tables [15] assuming aluminum oxidation described by reaction (2)



The reference ΔH_c of Al for complete oxidation at standard pressure and temperature is 31.05 kJ g^{-1} . Considering the standard deviation is about 2% and within the experimental error, we were able to measure the complete heat of combustion of both aluminum powders.

Although the characterization of the rate of the heat release during material testing is not the standard feature of the bomb calorimeter, the recorded temperature history can be used for a qualitative comparison of the heat release rate. This additional bomb calorimeter capability is a new and useful tool for quick characterization and development of new reactive materials. Extracting rate data from the bomb calorimeter requires attention to the temporal behavior of the normalized temperature of the water bath, defined as ΔT_N in equation (3)

$$\Delta T_N(t) = \frac{T(t) - T_{\min}}{T_{\max} - T_{\min}}. \quad (3)$$

In equation (1) $T(t)$ is recorded time-dependent temperature and T_{\max} and T_{\min} are maximum and minimum temperatures of the water bath during the combustion experiment. Figures 3(a) and (b) show normalized curves for two different PP weights (figure 3(a)) and for a fixed amount of 0.1 g BzOH (figure 3(b)) in the PP. Figure 3(a) shows that the PP weight does not influence the heating rate because the two curves overlap up to about 450 s. Figure 3(b) shows the heating region of the normalized temperature is sensitive to the type of material tested, rather than to the sample form (i.e. powder versus pellet). In figure 3(b) the blue and green curves represent samples with BzOH overlapping throughout while the red curve represents only the PP and is slightly higher than the two curves with BzOH. This data indicates that the differences in heating rate, which are not described by the calorimeter manufacturer for characterizing material reactivity, expand the bomb calorimetry capabilities with a technique for monitoring transient thermal behavior of different materials.

Figure 3(c) shows the normalized temperature for three curves: (a) the bare PP, (b) Al-015 powder contained in the PP, and (c) the BzOH combined with the PP. It is noted that the BzOH combined with PP experiments were performed using a portion of the BzOH tablet combined with pressed PP in the BN crucible and included in figures 3(c) and (d) to show distinguishable features in the heating rate region of the transient temperature. Figure 3(d) shows the time derivative of the normalized temperature for the same three curves from the same experimental data. An interesting observation is highlighted in the inset below the curve in figure 3(b) that focuses on early times during heating. All three samples shown in figure 3 confirm measurable variations in heating rate further

demonstrating the temperature curve sensitivity within the initial heating region.

3. Conclusions

We demonstrated an experimental modification to a bomb calorimeter that enabled accurate measurements of heat of combustion from solid metal powders simulating dust combustion conditions. The technique used a porous starch-based packing peanut that dispersed the powder in the crucible to improve oxidation reactions by enabling more oxygen in the vicinity of the dispersed powder. The technique was demonstrated on two different particle sizes of Al powders with both sizes producing measured heat of combustion 98% of the reference value with a standard deviation of 2%. This closeness of the measured Al heat of combustion to its reference value is evidence of achieving complete metal combustion in our experiment. In addition, we introduced an extension to the instrument's data processing capability that enabled characterization of the temporal heat release, which is important for description of the transient combustion behavior of reactive materials. Expanding the capabilities of the bomb calorimeter beyond heat of combustion to observations of transient phenomena will provide a potentially new diagnostic metric for analyzing the heat release rates associated with reactive materials.

Author's contributions

All authors contributed equally to this work.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Acknowledgments

The authors M P, Q T are grateful for support from United States Army Research Office Grant No. W911NF-11-1-0439 as well as the Office of Naval Research (ONR) Grant Nos. N00014-19-2082 and N00014-21-1-2519. I A is thankful for funding from the NAVAIR ILIR program at ONR and administered by Dr Alan Van Nevel. P D and M M acknowledge support from the Army's Combat Capabilities Development Command Armaments Center under Contract W15QKN18-9-1008 for the development of novel analytical capabilities for reactive materials.

ORCID iDs

Quan Tran  <https://orcid.org/0000-0002-2878-835X>
 Igor Altman  <https://orcid.org/0000-0002-6273-1146>
 Michelle L Pantoya  <https://orcid.org/0000-0003-0299-1832>

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