Propellants, Explosives, Pyrotechnics

SAND2016-12504J

Short Communication

DOI: 10.1002/prep.201500210

Small-Scale Thermal Studies of Volatile Homemade Explosives

Mary M. Sandstrom,[a] Geoffrey W. Brown,[a] Kirstin F. Warner,[b] Daniel N. Sorensen,[b] Jason J. Phillips,[c] Timothy J. Shelley,[d] Jose A. Reyes,[e] Peter C. Hsu,[f] and John G. Reynolds*[f]

Abstract: Several homemade or improvised explosive mixtures that either contained volatile components or produced volatile products were examined using standard small-scale safety and thermal (SSST) testing that employed differential scanning calorimetry (DSC) techniques (constant heating rate and standard sample holders). $KClO_3$ and $KClO_4$ mixtures with dodecane exhibited different enthalpy behavior when using a vented sample holder in contrast to a sealed sample holder. The standard configuration produced profiles that exhibited only endothermic transitions. The sealed system produced profiles that exhibited additional exothermic transitions absent in the standard configuration produced profiles. When H_2O_2/fuel mixtures were examined, the volatilization of the peroxide (endothermic) dominated the profiles. When a sealed sample holder was used, the energetic releases of the mixture could be clearly observed. For AN and AN mixtures, the high temperature decomposition appears as an intense endothermic event. Using a nominally sealed sample holder also did not adequately contain the system. Only when a high-pressure rated sample holder was used the high temperature decomposition of the AN could be detected as an exothermic release. The testing was conducted during a proficiency (or round-robin type) test that included three U.S. Department of Energy and two U.S. Department of Defense laboratories. In the course of this proficiency test, certain HMEs exhibited thermal behavior that was not adequately accounted for by standard techniques. Further examination of this atypical behavior highlighted issues that may have not been recognized previously because some of these materials are not routinely tested. More importantly, if not recognized, the SSST testing results could lead to inaccurate safety assessments. This study provides examples, where standard techniques can be applied, and results can be obtained, but these results may be misleading in establishing thermal properties.

Keywords: Small-scale safety testing · Thermal screening · Differential scanning calorimetry · Homemade explosives · HME · Round-robin test · Proficiency test

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1 Introduction

Testing energetic mixtures with volatile components or products can be problematic for a variety of reasons, such as evaporation of components during handling. This is particularly a problem for small-scale safety and thermal (SSST) testing, when very small amounts of material will necessarily be sampled and tested. Temporal changes could occur during the testing time scale that can skew results yielding inaccurate assessment of the sensitivity. The inaccurate assessment can lead to developing safe handling and storage procedures that do not adequately represent the material in the bulk.

Improvised or homemade explosives (HME) can have volatility in three areas, in the fuel, such as liquid hydrocarbons; the oxidizer, such as hydrogen peroxide; and in the products, such as the release of CO_2, H_2O, and H_2. These types of volatility causes testing problems, and if not adequately addressed, can lead minimally to inaccurate results to potentially damaging exothermic releases. Reported

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[a] *M. M. Sandstrom, G. W. Brown*
Los Alamos National Laboratory (LANL)
Los Alamos, New Mexico, USA

[b] *K. F. Warner, D. N. Sorensen*
Naval Surface Warfare Center
Indian Head Division (NSWC-IHD),
Indian Head, Maryland, USA

[c] *J. J. Phillips*
Sandia National Laboratories
Albuquerque, New Mexico, USA

[d] *T. J. Shelley*
Bureau of Alcohol, Tobacco, Firearms & Explosives
Redstone Arsenal, Alabama, USA

[e] *J. A. Reyes*
Jose A. Reyes
Applied Research Associates
Tyndall Air Force Base, Florida, USA

[f] *P. C. Hsu, J. G. Reynolds*
Lawrence Livermore National Laboratory,
Livermore, California, USA
**e-mail: reynolds3@llnl.gov*

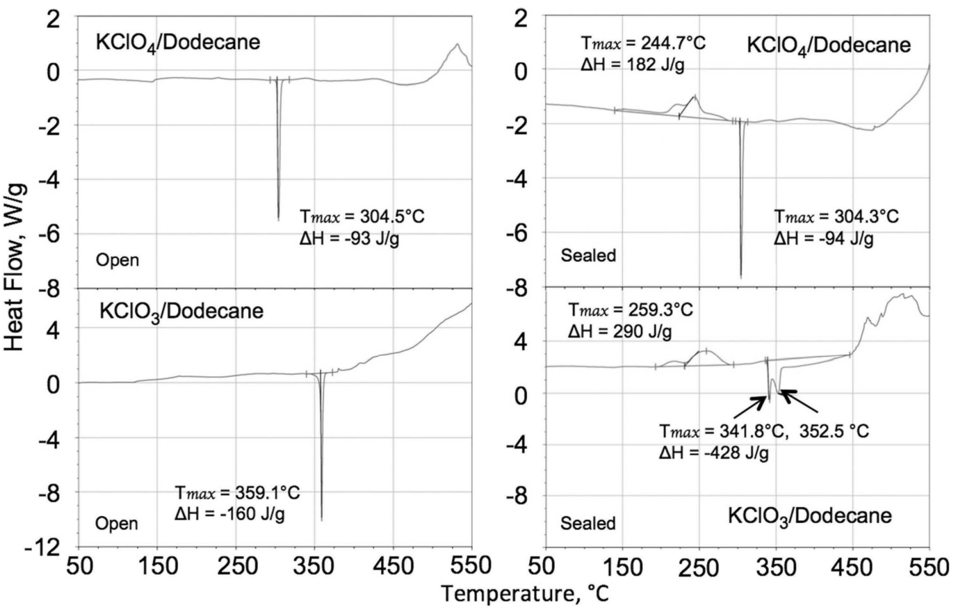

Figure 1. DSC profiles of $KClO_4$/dodecane and $KClO_3$/dodecane with TA Instruments vented sample holder and TA Instruments sealed sample holder (10 K min^{-1} heating rate).

herein are three examples of these issues and potential practical resolutions.

Recently, SSST testing data have been published by the Integrated Data Collection Analysis (IDCA) program on a variety of HMEs and selected military type explosives [1–3]. These data focused on the impact, friction, and spark sensitivity [1], the statistical aspects of SSST testing [4], comparison of two friction-testing methods [5], and selected thermal testing issues [6].

The IDCA program examined 19 different energetic materials by SSST testing, by five different laboratories – three U. S. Department of Energy and two U.S. Department of Defense – in a proficiency, or round-robin test.

The test performers were Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), Indian Head Division, Naval Surface Warfare Center, (IHD), Sandia National Laboratories (SNL), and Tyndall Air Force Division of the Air Force Research Laboratory (AFRL).

2 Experimental Section

The IDCA proficiency test methods have been discussed in detail previously [1,4]. In addition, the thermal testing methods and equipment are discussed in detail elsewhere [6]. Most examinations were conducted using the standard TA Instruments vented sample holders with a pinhole size of 75 μm. Samples were run in triplicate. Heating rates were 10 K min^{-1}. Also used in selected experiments were sealed sample holders – TA Instruments hermetically sealed, and the SWISSI high-pressure rated sample holder. The description and use of these sample holders has been detailed elsewhere [4,7].

The materials, sample preparation procedures, and mixing procedures have been described in detail previously [1,4,8,9]. Briefly, the solid materials were usually dried for 16 h at 60 °C and stored in a desiccator. The liquids were used as received. Mixing was performed at a 1 to 5 g scale, and mixtures were studied within 1 h of mixing, unless otherwise stated. All materials were from the same manufacturing lot and were distributed among the participants to eliminate batch-to-batch variations of starting materials.

3 Results

3.1 HME Mixtures with Volatile Fuels

In the proficiency test, the participants analyzed selected mixtures of a solid oxidizer and a liquid fuel. These types of mixtures were chosen to address the handling issues associated with testing materials that can change over time. In these particular cases, the change is not due to reactions occurring when the materials are mixed but physical evaporation of the volatile component. Figure 1 compares the effects of different DSC sample holders on two mixtures, $KClO_4$/dodecane and $KClO_3$/dodecane.

Examining the profiles on the left side of the figure shows prominent endothermic features for both the $KClO_4$ and $KClO_3$ mixtures. This corresponds to a phase transition and a melting of the oxidizer, respectively [10–13]. These endothermic features are representative of profiles obtained by all IDCA participants (Note: for some participants, but not all, a broad endothermic feature at low temperature due to the volatilization of dodecane). Closer inspection of these profiles reveals the low temperature endotherms are present in all the $KClO_4$/dodecane and $KClO_3$/dodecane mixture DSC profiles for all participants.

The profiles on the right side of the figure are with a hermetically sealed TA sample holder (though not the high pressure rated sample holder) and show a much more complicated thermal behavior. A series of very broad exothermic features are observed in the 200 °C to 300 °C temperature range. The origin of these exothermic features has not been resolved, but is probably due to the hermetically sealed sample holder preventing total evaporation of the dodecane and therefore providing some contact with the oxidizer at higher temperatures. Dodecane has a boiling point of 218 °C [14] so much of it is vaporized in the above temperature range, but if the system is closed, some vapor is still available for reaction. This same argument could be extended to the $KClO_4$/dodecane mixture. Further examinations of $KClO_3$/hydrocarbon fuel mixtures by DSC equipped with a high-pressure sample holder [15] show the prominent exothermic features around the 350 °C temperature range, suggesting the hermitically sealed TA sample holder ruptured probably by gas evolution.

3.2 HME Mixtures with Volatile Products

Ammonium nitrate (AN) and AN/gunpowder (GP) mixtures were examined in the proficiency test. The most notable part of the testing was that the results for the AN were inconsistent compared to other materials in the proficiency test. Although all aspects of the testing of AN – impact, friction, ESD and thermal – had issues, the DSC results were particularly difficult to interpret. The testing results were further examined to determine the cause of ambiguity in results among the testing participants.

The participants all had varied results for the thermal decomposition of AN. Table 1 shows the endothermic transitions (T^1–T^4) were in reasonable agreement for T_{min} and enthalpy values for all the participants. The temperature of transition for T^5 also is within reasonable agreement. However, whether the transition is a minimum or maximum, which affects the sign of the enthalpy, is the issue. The variation in the T^5 enthalpy is from highly endothermic to highly exothermic. The cause of this has been documented previously and is due to whether the sample holder captures the gases formed during the decomposition of the AN [16–20].

Table 1. DSC temperature and enthalpy of transitions observed for AN at 10 K min^{-1} heating rate.

Transition[a,b,c]	T [°C]	Enthalpy [J g^{-1}]
AN 1 (T^1 minimum)	53.6 ± 2.2	−19 ± 5
Range	46.6 to 57.5	−3 to −25
AN 2 (T^2 minimum)[d]	92.7 ± 2.3	−14 ± 13
Range	86.6 to 96.2	−57 to −3
AN 3 (T^3 minimum)	128.3 ± 1.0	−53 ± 6
Range	127.0 to 131.1	−60 to −38
AN 4 (T^4 minimum)	169.5 ± 0.6	−71 ± 9
Range	167.9 to 170.7	−82 to −32
AN 5 (T^5 minimum or maximum)	297.6 ± 17.4	−550 ± 1066
Range	263.4 to 325.9	−1703 to 1528

a) Temperature or enthalpy of event. b) min is endothermic, max is exothermic. c) Range of T or ΔH. d) T^2 observed in limited cases as a function of drying.

Experimentally, capturing the evolved gases in DSC is not a standard procedure. Figure 2 shows the DSC profiles using different types of sample holders. The top profile is from using the standard vented sample holder. T^5 profile

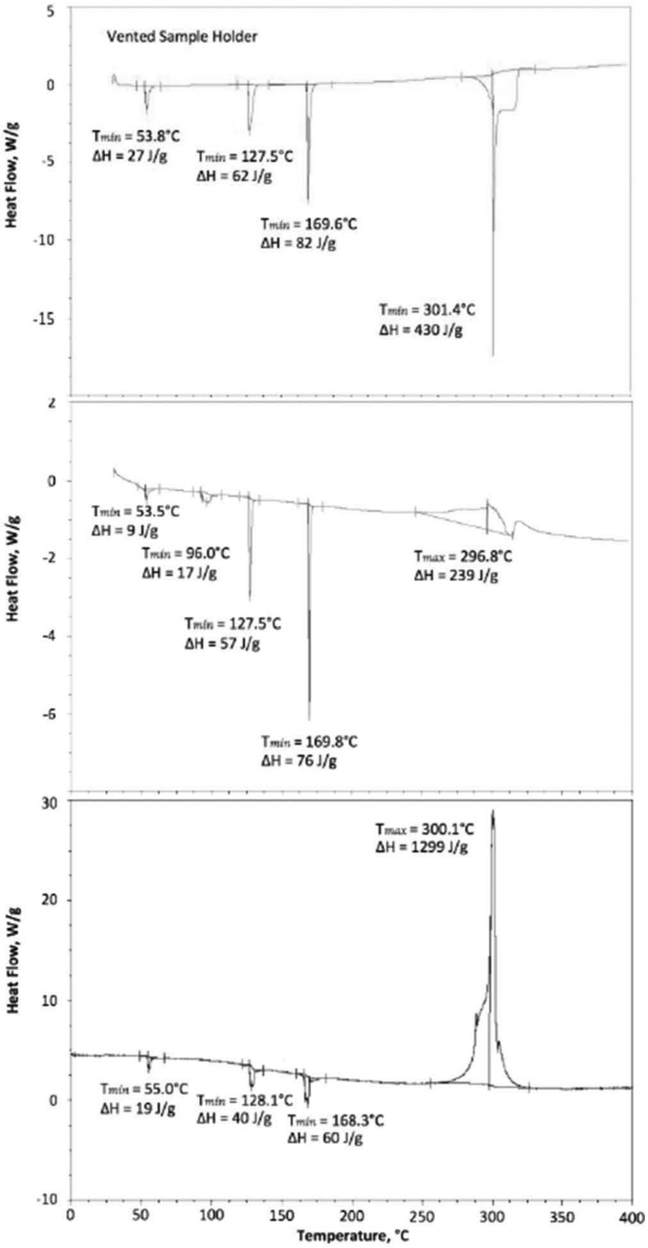

Figure 2. DSC profiles of AN with different sample holders; 10 K min^{-1} heating rate.

shows a highly endothermic release. The middle profile is from using the hermetically sealed sample holder. In this case, T^5 is a complex overlap of exothermic and endothermic behavior. The bottom profile is from using the high-pressure rated sample holder. T^5 profile shows a highly exothermic release, consistent with an energetic decomposition. This batch of AN was also examined by thermo gravimetric analysis coupled with mass spectrometry detection. The results verify gas evolution due to the decomposition of AN only occurred during the T^5 event, and had the composition of NH_3, H_2O, NO, N_2O, NO_2, consistent with the literature mechanism of decomposition

3.3 HME Mixtures with Volatile Oxidizers

In the proficiency test, some of the materials studied were H_2O_2/fuel mixtures [1]. These mixtures were chosen because of the high unpredictability of the physical form. Once the two components were mixed, the oxidizer began reacting with the reductant. In some cases, such as H_2O_2/cumin, the changes were fairly evident shortly after mixing. The H_2O_2 would start to bleach the material and form a gooey mixture, with the evolution of tiny gas bubbles. Obtaining representative samples was also difficult in these cases. In other cases, such as with H_2O_2/nitromethane mixtures, the mixture visibly looked stable with no apparent immediate reaction. Regardless of the material, the peroxide mixtures were handled with care (peroxide is extremely reactive towards most organic materials, including skin), and analyzed within 1 h of mixing. In all cases, except in aging studies, the mixtures were destroyed as soon as possible as there is evidence in the literature [21] that runaway reactions can occur over time.

Figure 3 shows the DSC behavior of an H_2O_2/glycerol mixture. This mixture is homogeneous as the H_2O_2 and glycerol are miscible, so obtaining a representative sample was not an issue. However, the volatility of the mixture is an issue. The mixture was examined using the standard vented sample holder. Clearly, volatilization of the H_2O_2 and water dominate the lower temperature region with $T_{min} = 99.7\,^{\circ}C$. The boiling point of H_2O_2 is 150 °C, but it has a high vapor pressure [22, 23]. There is enough peroxide remaining to eventually show an exothermic event with a $T_{max} = 139.1\,^{\circ}C$. A second broad endothermic event is also seen with $T_{min} = 206.8\,^{\circ}C$.

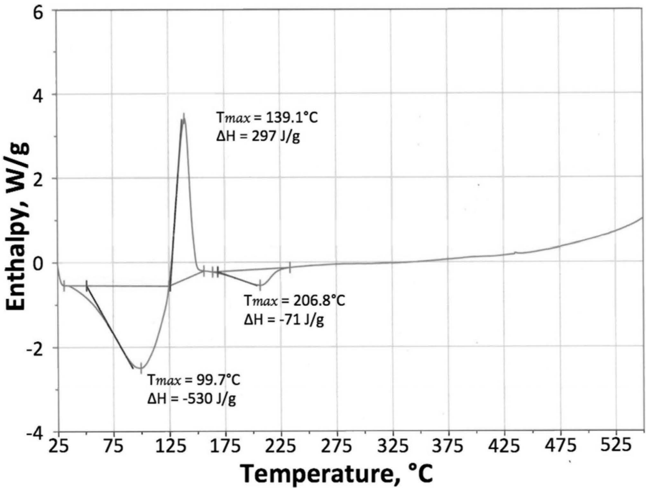

Figure 3. DSC profiles of H_2O_2/glycerol mixtures with vented sample holder; 10 $K\,min^{-1}$ heating rate.

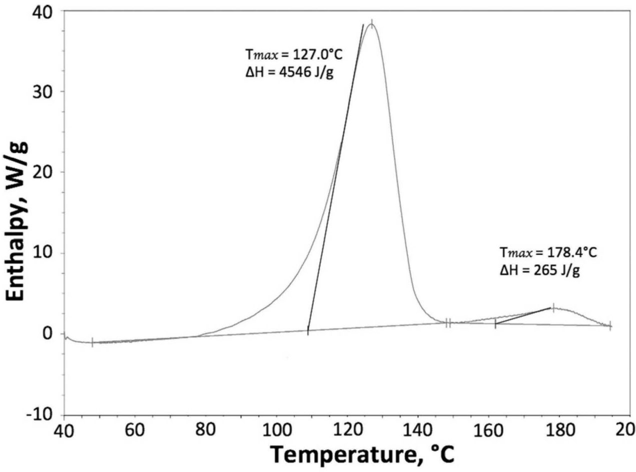

Figure 4. DSC profiles of H_2O_2/glycerol mixtures with hermetically sealed sample holder; 10 $K\,min^{-1}$ heating rate.

Figure 4 shows the low temperature range when using the hermetically sealed sample holder. The endothermic event at low temperature is not present because the H_2O_2 cannot escape from the sealed holder. The $T_{max} = 127\,^{\circ}C$ and the enthalpy is much higher than in the vented cell – 4546 vs. 296 $J\,g^{-1}$. The high temperature broad enthalpy event is also now exothermic instead of endothermic.

4 Discussion

DSC has been shown to be an excellent method for determining the thermal behavior of a single compound [24]. For potentially energetic materials, constant heating rate DSC is an inexpensive and fast method for screening, particularly when determining safe handling and storage properties. Most of the applications to energetic materials have been for military- and mining-type explosives and propellants. Recent work on HMEs in the proficiency test has shown the need to further scrutinize the testing conditions when dealing with non-standard materials.

Thermal volatility of components or reaction products plagues the accurate thermal assessment of many HMEs. The $KClO_3$/dodecane and $KClO_4$/dodecane mixtures, as shown in Figure 1, exhibit very important properties in this regard. Measuring the thermal properties in an open sample holder yields profiles, which are endothermic, and show only physical transitions of these materials. If thermal behaviors of these materials were to be assessed with this data, the mixtures would be deemed non-energetic. However, examining the same mixtures using the sealed sample holder shows exothermic releases at relatively low temperatures. Even these are not accurately portrayed because some of the volatile component is probably in the gas phase and is not completely in contact with the oxidizer, so the actual value of enthalpy is low. This change in apparent behavior (actually due to a change in experimental conditions) from harmless endothermic enthalpy to exothermic enthalpy is very important from a safety standpoint.

AN is another example that shows the importance of understanding the nature of the material before trying to assess thermal properties. The use of the vented, standard sample holder indicates that the AN is non-energetic. The use of a sealed but not pressure rated sample holder leads to essentially the same conclusion – AN is non-energetic. However, the use of the pressure rated sealed sample holder shows AN is an energetic material. This is incredibly important because the gases escaping change whether one measures an exothermic release or an endothermic release for the major event for AN. This also extends to be seen in mixtures, such as AN/GP where the mixture decomposition occurs in the same temperature range as for the exothermic release of the AN [25].

As a third, and very important example, H_2O_2/fuel mixtures were also tested with and without a sealed sample holder. Clearly, Figure 3 demonstrates the dominance of the evaporation of the H_2O_2 in the DSC profiles. Figure 4 shows with the hermetically sealed sample holder, the H_2O_2 volatility is contained in the holder and is available for reaction with the fuel. Without this containment, much less H_2O_2 is available for reaction, so the enthalpy is recorded to be much lower.

Hydrogen peroxide can energetically decompose without being mixed with any fuel, so measuring thermal properties can be tricky. It is used as a propellant at high temperatures (Hi Test Peroxide), so it can be stable to work with, but it can also decompose at lower temperatures (usually catalyzed by metals), so it still can be unpredictable. For the developments herein, some of the measurements with the vented and hermetically sealed sample holders lead to ruptured containers, probably linked to sample size. The high pressure rated sample holders would likely be the best selection for testing (they are gold plated), but care should be taken to minimize sample size and keep metal impurities under control.

5 Conclusions

From this study, volatility issues of HME mixtures were identified to cause measurement issues when employing DSC to establish thermal behavior. In all cases, a sealed sample holder is a solution to the problem. In mixtures, where the fuel is volatile, the escape of component tends to reduce the magnitude of the energetic release during the heating. The examples given were with a fairly non-volatile fuel. In mixtures, where the oxidizer is volatile, essentially the same behavior is observed, where contact of the two materials is reduced, because of evaporation, before and during the temperature range in which energetic release occurs. In some other cases, the oxidizer decomposes is such a way that the volatile gases, if not contained, can exhibit an overall cooling effect, causing the release to appear endothermic, when it is really exothermic.

Sample holder type is extremely important in obtaining the correct thermal profile of many of these mixtures also. In all cases, a high-pressure sample holder with very small headspace has advantages. The high-pressure rating will keep the holder from rupturing and the small headspace will assist in contact of the two materials.

The essential point of this study is to show how using standard small-scale thermal testing configurations, commonly used in safety evaluation of energetic materials, can be misleading for HMEs. This could ultimately lead to a dangerously inaccurate evaluation of the physical properties. The recourse is to have an intimate knowledge of the materials from a chemical and physical assessment. In addition, realize that standard testing methods may not adequately describe the thermal behavior and that additional tests, perhaps on a larger scale may need to be used to understand the thermal behavior.

Acknowledgments

The authors thank Doug Bauer, Laura J. Parker, and Greg Struba for their enthusiastic support. This work was performed by the Integrated Data Collection Analysis (IDCA) Program, a five-lab effort supported by Los Alamos National Laboratory, Lawrence Livermore National Laboratory, Sandia National Laboratories, the Air Force Research Laboratory, and Indian Head Division, Naval Surface Warfare under sponsorship of the U.S. Department of Homeland Security, Science and Technology Directorate, Explosives Division. Los Alamos National Laboratory is operated by Los Alamos National Security, LLC, for the U.S. Department of Energy under Contract DE-AC52-06NA25396. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. The Air Force Research Laboratory and Indian Head Division, Naval Surface Warfare also performed work in support of this effort under contract HSHQDC10X00414. LLNL-JRNL-669352 (791244).

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[25] Note added in proof. One reviewer observed that with the vapor pressure of the dodecane even at higher temperatures, there should be enough in contact with the KC materials for the DSC to show a strong exothermic release of enthalpy and not the endothermic features seen in Figure 1. This prompted further examination of $KClO_3$/hydrocarbon fuel mixtures using a high-pressure sample holder (rated 500 bar at 600 °C). The results showed strong exothermic releases starting around 340 °C, and no evidence of the endothermic features see in Figure 1. This indicates that the TA Instrument hermetically sealed sample holder ruptured at the onset of release of the product gases, something that has been seen in other samples (such as AN and even RDX [4]).

Received: August 12, 2015
Revised: October 13, 2015