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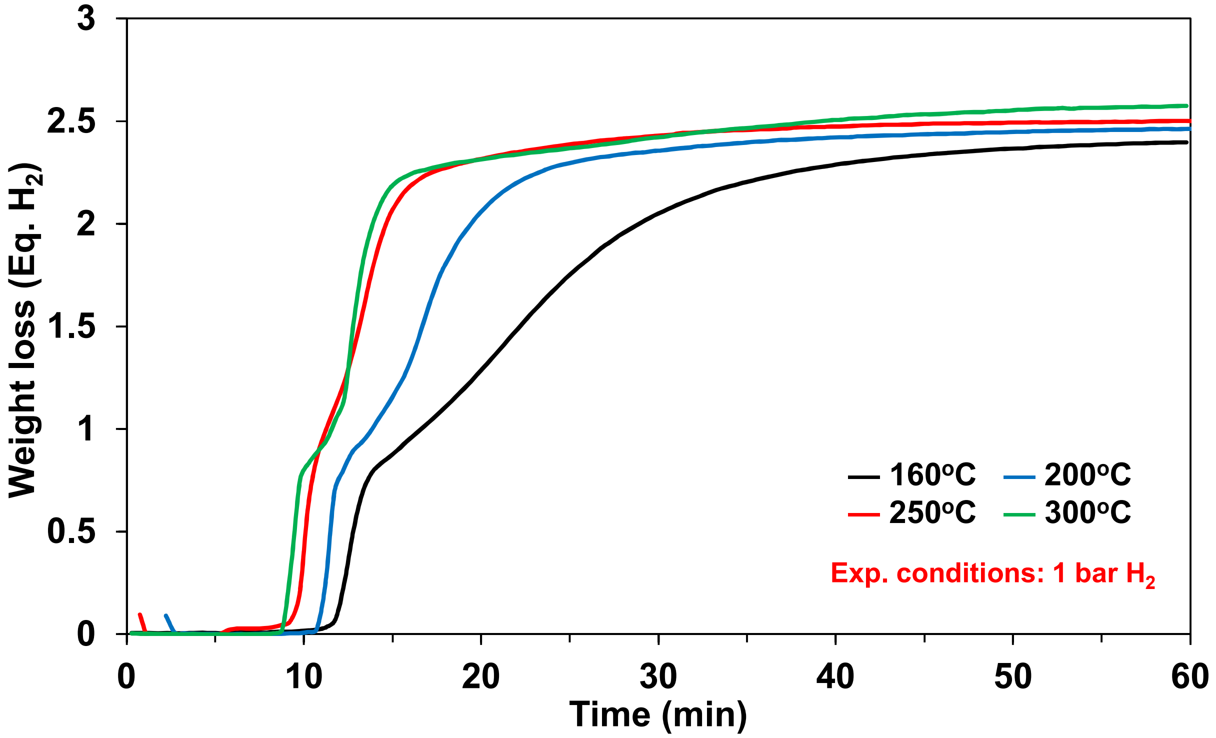
Front Figure

Hydrogen capacity and bulk kinetics comparisons of ammonia borane at 160°C, 200°C, 250°C and 300°C.



Kinetics Study of Solid Ammonia Borane Hydrogen Release – Modeling and Experimental Validation for Chemical Hydrogen Storage

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Abstract

Ammonia borane (AB), NH_3BH_3, is a promising material for chemical hydrogen storage with 19.6 wt% gravimetric hydrogen capacity of which maximum 16.2 wt% hydrogen can be released via and exothermic thermal decomposition below 200°C. We have investigated the kinetics of hydrogen release from AB and from an AB-methyl cellulose (AB/MC) composite at temperatures of 160-300°C using both experiments and modeling. The hydrogen release rate at 300°C is twice as fast as at 160°C. The purpose of our study was to show safe hydrogen release without thermal runaway effects and to validate system model kinetics. AB/MC released hydrogen at ~20°C lower than neat AB and with a faster release rate in that temperature range. Based on the experimental results, the kinetics equations were revised to better represent the growth and nucleation process during decomposition of AB. We explored two different reactor concepts; auger and fixed bed. The current auger reactor concept turned out to not be appropriate, however, we demonstrated safe self-propagation of the hydrogen release reaction of solid AB/MC in a fixed bed reactor.

1. Introduction

Hydrogen is an energy carrier and provides an alternative to technologies based on fossil fuels. A major challenge for using hydrogen as a fuel today, especially for vehicles, is to develop efficient and effective methods for hydrogen storage that cannot only store hydrogen safely, but supply it where and when it is needed. Hydrogen storage systems developed so far include compressed gas cylinders, cryo-compressed cylinders and solid-state storage materials. Compared to the physical approaches such as liquefaction and compression, hydrogen storage in the solid state has potential to be superior in terms of high volumetric and gravimetric hydrogen contents. Thus, development of solid-state hydrogen storage materials that work at sufficiently low temperatures has been identified as a key requirement for expanding hydrogen PEM fuel cell applications and increasing market acceptance. Substantial progress has been made in the past few years in the discovery of new materials.[1-2] Chemical hydrogen storage (CHS) materials typically release large amounts of hydrogen at low temperatures (<200°C), but cannot easily be rehydrided like a metal hydride. Instead, regeneration schematics have been developed and some of the most promising materials are ammonia borane, lithium alanate and alane.[3-5] Potential practical applications include not only storage for the transportation section, but other probable near-term fuel cell early-markets including portable power and stationary power.[2]

The work at the Pacific Northwest National Laboratory (PNNL) targets objectives to optimize performance characteristics and reduce the size, weight, and cost of a chemical hydrogen storage system. This is accomplished through a carefully engineered and integrated design approach, including application of advanced materials, use of micro-scale enhancements of heat and mass transfer, better understanding and tailoring of bulk storage media and system kinetics, and assessments of manufacturing and cost impact based on established models/approaches for technology tradeoff or “viability” studies.[6-8]

A key input parameter for reactor modeling is kinetics which is the topic of the current paper. Studies on reaction kinetics are valuable when engineering the size of a device that might be used to release hydrogen from hydrogen carriers. For example, bench-scale data and proven reactor models for chemical hydrogen storage systems are invaluable when working toward an optimal design. PNNL extended this analysis to develop models for a solid chemical hydrogen storage system, taking into account geometrical effects of the reactor on combined heat and mass transfer. Bench-scale kinetics measurements were obtained for solid AB to validate kinetics models and will be discussed in detail below. This data is used as input parameters to the transport and reactor models, which will ultimately provide predictions on the hydrogen release rate under varying operating conditions. Test data on small-scale chemical reactors is used to validate the component models, and the models is used to assist in the design of larger-scale reactor systems. It is worthwhile to note, that there was recently a similar effort reported by Bhouri et al[9] on reversible endothermic reactions, i.e. for titanium-doped sodium alanate.

To demonstrate a low-cost, high-performing on-board hydrogen storage through a fully integrated systems design and engineering approach, we chose the most investigated chemical hydrogen storage material, i.e. ammonia borane (AB), as a surrogate material since there are currently no material that meet all DOE system performance targets and AB is considered the best role model to learn requirements and needs of a chemical hydrogen storage material through experiments and system modeling. AB has recently received considerable attention because of its combined low molecular weight (30.86 g/mol) and high gravimetric storage capacity (19.6 wt.%). The dehydrogenation of AB occurs in three steps that are generally represented by the transformation of AB to polyaminoborane (PAB, $(H_2NBH_2)_x$) and H_2, PAB to polyiminoborane (PIB, $(HNBH)_x$) and H_2, and PIB to BN and H_2.[9-11] These steps can be described by the following equations (A), (B) and (C), respectively. The two first steps release ~16 wt% at PEM fuel cell relevant temperatures. [10-12]

$$NH_3BH_3 \rightarrow (NH_2BH_2)_x + H_2 \qquad (90 - 120^{o}C) \qquad (A)$$

$$(NH_2BH_2)_x \rightarrow (NHBH)_x + xH_2 \qquad (120 - 160^{o}C) \qquad (B)$$

$$(NHBH)_x \rightarrow BN + xH_2 \qquad (> 500^{o}C) \qquad (C)$$

The AB decomposition reaction is an irreversible chemical nucleation and growth reaction that occurs with hydrogen release. A major difference between reversible metal hydrides and exothermic chemical hydrogen storage (CHS) is that Sieverts data of a reversible metal hydride can be performed under equilibrium conditions by dosing hydrogen in aliquots to collect isotherms at a set temperature. For a CHS material with an exothermic hydrogen release reaction it is to some extent self-propagating, thus, temperature will not be fixed and equilibrium states are difficult to obtain, and to our knowledge, performing isotherms is most difficult. In the following we will report our experimental kinetics study and updated kinetics models. With the purpose to provide information on kinetics for future systems engineering, we developed a simple empirical model based on Avrami equations meant only for conditions where both the first and second equivalents of hydrogen are produced. We also performed a scale-up experiment with a fixed bed reactor to demonstrate safe, self-propagated hydrogen release reaction of ammonia borane.

2. Experimental apparatus and procedures

2.1. Materials

The starting materials, ammonia borane (NH_3BH_3, 97%) from JSC Aviabor (Nizhny Novgorod region, Russia) and methyl cellulose (99.9%) from Sigma-Aldrich (Milwaukee, WI), were used as received without any further purification. All the material handling was carried out in a glove box filled with purified argon, which can keep a low oxygen concentration (less than 1 ppm) by a recycling purification system to protect samples and starting materials from oxidation and/or hydroxide formation. The composites of ammonia borane and methyl cellulose (referred to as "AB/MC composites" hereafter) were prepared according to the procedures described in the following. Approximately 10 g of AB and MC in a weight ratio of 8 : 2 were added to the reaction flask which contains a tetrahydrofuran (THF) solution. The reaction flask was stirred for 16 hours at room temperature. Then, the THF was removed by rotary evaporation to yield a white solid powder.

2.2. Hydrogen release properties of AB and AB/MC composites

The hydrogen release properties of AB or AB/MC composites were evaluated by using a commercial Sieverts' type apparatus (PCT Pro-2000, Setaram) upon heating to 100 ~ $350^{o}C$ at a heating rate of 10 ~ $13^{o}C/min$ and hydrogen back pressures of 1 bar. To design the kinetics experiments, we followed the recommendations in DOE's "Recommended best practices for the characterization of storage properties of hydrogen storage materials" by Gross (2012).[13] About 40 mg of the sample is loaded into a stainless steel vial as loose powder, which is then sealed inside the PCT autoclave in the glove box. Hydrogen pressures were measured by a Teledyne Taber model 206 piezoelectric transducer in the range of 0 ~ 20 MPa, with a resolution of 10^{-4} MPa. During dehydrogenation, the sample temperature and applied pressure were monitored and recorded by a Lab View-based software program. The amount of hydrogen release was calculated by the pressure changes in calibrated volumes, of which the details are described elsewhere.[13] In order to capture the volatile by-products such as borazine ($N_3B_3H_6$) or diborane (B_2H_6) during the hydrogen release, a cold trap (Setaram) with dry ice was installed between the sample and the pressure transducer. By capturing the by-products we can study the rate of the hydrogen release.

2.3 Fixed bed reactor design

To demonstrate safe hydrogen release and to directly observe heat and reaction propagation, we designed and assembled a fixed bed reactor with solid AB or AB/MC, shown in Figure 9. The dimensions of the reactor were 26 mm OD and 25 mm ID Quartz tube. The 300 mm long reactor was fitted with a 24/40 slip joint top, a side arm inlet near the bottom with 3mm ID, and a 5 mm hole centered in the flat bottom of the tube. A programmable Weller model WD 1M with WP 60 heating cartridge was used as a heat source. A Weller LTB 2.4mm soldiering chisel tip was inserted through the bottom hole, sealed in place with a 2-008 silicone O-Ring and silicone RTV rubber. A series of twelve 0.6mm holes located 10 mm a part along one side of the reactor tube allowed insertion of Type 'K" thermocouples (OMEGA part KMQSS) which were sealed with silicone RTV rubber. One additional thermocouple was inserted through the side arm inlet and impinged on the soldiering tip. The reactor was designed to be operated with or without alumina insulation surrounding the reactor.

The AB and AB/MC powders were loaded in various forms and amounts: loose powder, granules or single pellets, from 0.25 grams to 5.0 grams, through the taper joint top. The taper joint top vented to a dry acetone bubbler and then to a Wet Test Meter, and finally to an open face hood. Dry Nitrogen was used to purge the reactor of oxygen via the side arm inlet prior to reacting the AB. The entire system was located behind a safety shield, and in an Open Faced hood. AB reactions were initiated by means of the soldering tip which was programmed to rapidly heat to a predetermined temperature. The soldering tip temperature could also be adjusted during the experiment. Observations were recorded via the thermocouples / data logger, a Sony visible light video camera, Cincinnati IRRIS-256ST Infrared Imaging System. Gas evolution (both rate and total volume) was recorded using the Wet Test Meter and video.

3. Results and discussion

3.1. Kinetics study of solid AB and AB/MC composites

Kinetics is a key parameter for practical hydrogen storage systems performance and therefore a key parameter in the systems modeling of hydrogen storage material. We have performed experiments in a temperature interval relevant to current application to validate the systems models.

For hydrogen storage, kinetics is the rate of hydrogen release (desorption) and, if the material is reversible also the rate for rehydrogenation (sorption). The outcome of a kinetics study reveals how the material approaches equilibrium and what influences how it gets there. The kinetics of the material subdued to system operating conditions will limit the practical amount of available hydrogen. Pressure and temperature will have an effect on kinetics and so will intrinsic properties, including phase changes, reaction mechanism, surface interactions and heat transfer. It is well known that temperature has an effect on the rate of a reaction. When temperature is increased, the atoms vibrates more which increases the number of collisions and ability to rearrange atoms, thus, reaction rate increases.

To obtain system models that accurately describe materials performance, it is important to describe the intrinsic rate-controlling mechanism. To quantify kinetics performance, kinetics measurements are performed to identify the intrinsic mechanism controlling hydrogen release (and uptake if material is reversible). Heat transfer is considered to be the most rate-limiting effect in practical applications. Surface interactions, hydrogen diffusion, mass transport and chemical bond breaking/forming mechanisms also contribute. Transport mechanisms also depend on packing density, particles size and thermal contact. The “Recommended Best Practices for Characterization of Hydrogen Storage Materials” by Karl Gross has an excellent summary of information related to kinetics measurements and other characterization methods.[13]

In this section, studies of hydrogen capacity and bulk reaction kinetics of AB and AB/MC composites at various operating conditions have been conducted to provide the system modelers with necessary information to update their kinetics models. Solid AB has been reported to meet most of the minimum criteria of the DOE system targets including the storage capacity, reaction enthalpy, the kinetics of hydrogen release reactions and the dehydrogenation temperatures. The main hurdles are excessive foaming upon hydrogen release, generation of volatile impurities, and costly regeneration schemes. To avoid the issue with foaming, AB/MC composite materials, which maintain form factor and reduce foaming upon hydrogen release, are here considered as a solid-based chemical hydrogen storage fuel system. Previously, measurements on AB have been performed up to 160°C using a PNNL-made Burette system and obtaining isothermal data.[13] However, in order to be able to measure at higher temperatures, a Sieverts type pressure-composition-temperature (PCT) gas-solid reaction instrument (Setaram) was adopted to characterize the kinetics of hydrogen release reactions of AB and AB/MC composites at various target temperatures (160~300^{o}C) under 1 bar of hydrogen back pressure. To demonstrate the hydrogen capacity and bulk reaction kinetics, dehydrogenation of neat AB and AB/MC composites were performed using the Sieverts apparatus, and the detailed results are given below.

It is noted that two different types of sample holders (i.e. microdoser and standard container from Setaram) were tested in order to try to achieve heating conditions close to isotherm. However, due to the temperature ramping in the Sievert's apparatus, we could not obtain truly isothermal measuring conditions. Therefore, temperature-programmed desorption (TPD), which is a common technique for surveying the overall hydrogen storage behavior of solid hydride materials, was applied in this study. During TPD, temperature is ramped up at a constant heating rate. The pressure change during the temperature ramping is measured in a calibrated volume and converted to corresponding percentages of hydrogen release. A cold trap filled with dry ice was adopted between the pressure transducer and the sample holder to capture undesirable and condensable by-products such as borazine ($N_3B_3H_6$) or diborane (B_2H_6) during the dehydrogenation process. Our preliminary results indicated that the amount condensable by-product is temperature dependent. We assumed that the pressure change from the large amount of hydrogen gas would not be substantially impacted by the gas cooling and the condensable by-products removal. By removing the by-products we can study the kinetics of hydrogen release without impact of other species.

Figure 1 shows the TPD profiles of neat AB, which compare the hydrogen capacity and bulk kinetics at various temperatures. The first equivalent of hydrogen can clearly be observed, followed by the release of the second equivalent. Approximately 40 mg samples under atmospheric H_2-pressure were heated up to 160 ~ 300°C at a ramping rate of 10 ~ 13°C/min, thereafter held at applied temperature for a pre-determined length of time. As pointed out earlier, because of not being able to measure isothermally, AB starts to decompose during the ramping process, which caused a time-lag on the x-axis during the first 10 minutes. It can be observed in Figure 1 that the total weight loss between 160 ~ 300°C amounted to 2.4 ~ 2.6 equivalents under 1 bar hydrogen pressure within 1 hour. The majority of the hydrogen capacity (≥ 2.0 equivalents) was released during about 30 minutes in all cases, with total hydrogen capacities reaching 2.5 equivalents as can be seen in Figure 1. The results also indicate that the dehydrogenation kinetics of neat AB accelerated as the target temperatures increased from 160 to 300^{o}C, as expected. In addition, the distinction between 1st and 2nd steps in the dehydrogenation of AB,[10-11] which correspond to above equations (A) and (B), respectively, becomes less pronounced at higher temperature.

Based on the maximum release rates of 1st equivalent, the value of hydrogen release rate at 300^{o}C per gram AB (0.79 mg/s•1g AB) increased almost twice compared with that of release rate at 160^{o}C (0.38 mg/s•1g AB). The hydrogen release rate was calculated from the experimental slope (displayed in Figure 1) occurring during heating (after the induction period) by simply calculating the gram of release hydrogen per gram AB.

Figure 2 presents a comparison of the hydrogen capacity and bulk kinetics of AB/MC composite from 160 to 300^{o}C. The kinetics is very rapid and the sharp feature of the curve is most likely due to slow software response to data collection. The dehydrogenation experiments were carried out under the same conditions as described above. A time-lag can be observed in all the measurements, which is attributed to the non-isothermal heating process. First of all, the measured hydrogen capacities of AB/MC were comparable to the theoretical value, *i.e.* ~2.5 equivalents, or ~16.2 wt% of hydrogen, between 160 and 300^{o}C under 1 bar hydrogen pressure.

Note that the experimental weight loss from AB/MC composites is normalized. Secondly, the TPD profiles in Figure 2 indicate that there are substantial differences in the onset dehydrogenation temperature and time for complete hydrogen release between neat AB and AB/MC composites. The result shows that the first equivalent hydrogen started to release at ~ 95^{o}C from AB/MC composites, which is approximately 22°C lower than that of neat AB. In addition, more than 2.0 equivalents of hydrogen were released within 16 minutes from AB/MC composites, which is considerably faster than that from neat AB. When comparing desorption of AB and AB/MC in Figure 1 and 2, it can be seen that the hydrogen release rate for AB/MC is significantly faster than for AB. The release rate of AB/MC is so fast that our instrument couldn't record it fast enough, hence, the curves initially have the features of straight lines that eventually forms a curve like feature. Due to not being able to record the release rate adequately, it is difficult to provide an estimate for how much faster the hydrogen release rate of AB/MC is compared to AB, but roughly at least two times faster.

Overall, the measured hydrogen capacities of AB and AB/MC composites were comparable to the theoretical value. The hydrogen release rates of AB were as expected faster as the target temperatures increased from 160 to 300^{o}C under 1 bar hydrogen pressure. Due to the excessive foaming upon hydrogen release, spent AB is sticky and therefore difficult to remove from the sample holder which indicates poor ability to physically move the material within a system. However, AB/MC composites maintained form factor and reduced foaming (no foaming observed under these conditions) on hydrogen release under the experimental conditions and the powder can thus be easily removed from the sample holder which is necessary for being able to move the sample throughout a system.

The desorption kinetics from the Sieverts apparatus compared to PNNL's Burette system are shown in Figure 3. Since the hydrogen release from AB was recorded as a function of time at isothermal reaction temperatures in the Burette system[14], a time-lag from AB and AB/MC composites in the PCT measurement was offset for the direct comparison. Maximum hydrogen capacity, *i.e.* ~2.5 equivalents or ~16.2 wt% of hydrogen for the Burette system and ~2.25 equivalents or 14.6 wt% for PCT system, was obtained after about 30 minutes in all cases at 160^{o}C under atmospheric H_2-pressure. It is noted that the reaction rates (mg/s•1g AB) of 1st equivalent of hydrogen are ~1.37 (AB-Burette), ~0.38 (AB-PCT) and ~3.73 (AB/MC-PCT). The obtained kinetic information from the high-temperature experimental data will be further validated with the developed kinetic models in the following section 3.2.

To illustrate the need for operating AB at temperatures above 160°C, Figure 4 shows six hydrogen release experiments between 100°C and 350°C. As can be seen, at 100°C, hydrogen release is very slow and only a fraction of maximum hydrogen capacity can be obtained within six hours. For practical applications, the temperature needs to be 160°C and above to obtain necessary hydrogen release rate and hydrogen capacity for practical applications.

When operating a fuel cell, there will be a back pressure of hydrogen. Therefore, although it's very common to measure release rates of hydrogen storage materials under vacuum, we also measured under 1 and 5 bar of hydrogen pressure at 160°C and the result is plotted in Figure 5. Overall kinetics is not largely affected by the pressure, however the hydrogen capacity did increase with pressure.

3.2 Isothermal and Ramped-Temperature Modeling of Ammonia Borane Thermolysis

The experiments in the previous section 3.1 were used to validate the kinetics models and it was revealed that an update of the equations is required. With the purpose of developing a model that has a sufficient level of details for input to systems engineering, we developed a simple empirical model meant only for conditions where both the first and second equivalents of hydrogen are produced (e.g. greater than 110°C). These are the temperatures that are of interest for modeling the reaction because the fraction of hydrogen released from AB and its rate are sufficiently high to be applicable to a vehicle-level storage system. The results for the temperature range of greater than 110°C is clarified in the text below.

Avrami equations have previously been used for modeling of an endothermic chemical hydrogen storage material, i.e. alane (AlH_3), as well as for ammonia borane, as has been reported by

Greatz and Reilly[15] and by Ismail and Hawkins[16]. They showed that the correlation between theory and experiments is adequate, thus, we chose to use Avrami equations for our models.

Ammonia borane releases approximately one mol of H_2 per mol of AB when heated for extended periods above 70°C and below ~110°C. The measured release kinetics of the first molar equivalent of H_2 gas from AB under isothermal reaction conditions from 70 to 90°C were used to predict the stability or shelf-life of solid AB stored at 50°C and 60°C by Rassat et al. 2010. [17] The investigation showed that plots of AB reaction progress as a function of time at temperature were sigmoidal (S-shaped), characteristic of nucleation and growth phenomena in solids. The reaction was represented by a generalized Avrami kinetics expression of the form

$$\chi(t) = \chi_1 \alpha(t) = \chi_1 \left\langle 1 - \exp\left\{ - \left[k(t - \tau) \right]^n \right\} \right\rangle \ ; \quad 0 \text{ for } t \le \tau \tag{1}$$

where χ_1 and $\chi(t)$ are, respectively, the maximum and time-dependent absolute conversion of the solid reactant to H_2 gas (i.e., mol H_2/mol AB). The bracketed term in Eqn. (1) is the time-dependent fractional conversion, $\propto(t)$, where k is the reaction rate constant, τ is the incubation or induction time period in which H_2 release does not occur, and n is the nucleation-growth index. Rassat et al. (2010)[17] found that χ_1 was approximately 1.0 for isothermal reactions from 70°C to 90°C, and that the induction period for the thermolytic release of this 1st H_2 equivalent from neat AB was on the order of 10 minutes at ~90°C and increased by about an order of magnitude per decade of decrease in isothermal reaction temperature. Assuming the trend continues to higher temperatures, the induction period would be a fraction of a minute or less at 110°C and above.

As shown below, AB reaction temperatures greater than ~110°C produce up to ~2.5 molar equivalents of H_2. Brooks et al.[7] used a linear combination of Avrami kinetics expressions of the form given by Eqn. (1) to empirically model hydrogen release in these higher temperature AB reactions, assuming the induction time is negligible

$$\begin{aligned} \chi(t) &= \chi_1 \left\{ 1 - \exp\left[- (k_1 t)^{n_1} \right] \right\} + \chi_2 \left\{ 1 - \exp\left[- (k_2 t)^{n_2} \right] \right\} \\ &= \chi_1 \alpha_1(t) + \chi_2 \alpha_2(t) \end{aligned} \tag{2}$$

Here, χ_1 and χ_2 are the maximum absolute molar equivalents of H_2 released in the 1st and 2nd "sequential" release processes (e.g., a first lower-temperature or initial reaction step and subsequent conversion of the 1st reaction product to release more H_2 in a second step). The kinetics parameters describing the fractional conversion in time of the "1st" and "2nd" equivalents, $\propto_1(t)$ and $\propto_2(t)$, are unique, as indicated by the variable subscripts i = 1 and 2. Equation (2) has been and can be used to reasonably represent the conversion profiles of AB isothermal reactions at ≥110°C. However, the independence of the 1st and 2nd terms allows the "2nd" equivalent of H_2 to be released before the "1st" reaction has occurred, which is mechanistically dubious. The following variation overcomes this issue,

$$\chi(t) = \chi_1\alpha_1(t) + \chi_2\alpha_1(t)\alpha_2(t) \tag{3}$$

where $\propto_1(t)$ and $\propto_2(t)$ are defined in Eqn. (2). As given by Eqn. (3), the progress of the 2nd equivalent H_2 release reaction is dependent on the first step. This assures that some first-step AB reaction product is formed in an initial, precursor H_2 release event leading to further H_2 release during formation of the 2nd and higher equivalent spent AB products. Note that this does not mean that the complete 1st equivalent of H_2 is released from all the AB before the 2nd equivalent starts to release. Effectively, release of the 2nd H_2 equivalent is both a sequential process, e.g., following formation of some first-step AB product, and a parallel process, e.g., while first-step AB product is still being formed elsewhere.

With the goal of developing a ramped-temperature AB reaction model, Eqn. (3) was first fit to isothermal reaction data obtained for thin films of ammonia borane solid at 130, 145, and 160°C using a hydrogen gas Burette measurement system designed by Zheng et al. in 2008.[14] A range of χ_i and n_i values provide good fits to the data, and the best values vary to some extent with reaction temperature. Subject to an imposed requirement that $\chi_1 + \chi_2 = 2.5$ mol H_2/mol AB (i.e., a maximum of 2.5 total equivalents of H_2 released), the following values were found to be representative and applicable to all three data sets: $\chi_1 = 0.6$; $\chi_2 = 1.9$; $n_1 = 5$; and $n_2 = 0.6$. Using these values, Eqn. (3) was further fit to the H_2 release vs. reaction time data to solve for k_1 and k_2 values at each reaction temperature (e.g., using KaleidaGraph™ software). The increase in reaction rate with absolute reaction temperature, T, is well characterized by an Arrhenius expression of the form

$$k_i = A_i \exp\left(-\frac{E_{a,i}}{RT}\right) \tag{4}$$

where R is the ideal gas constant, A_i is the pre-exponential factor, and $E_{a,i}$ is the apparent activation energy for rate constant k_i. Table 1 shows the Arrhenius kinetic constants obtained from the three-point fit of the isothermal reaction data. Using the fit parameters from the table in Eqn. (4) to solve for k_i, and subsequently using these in Eqn. (3) along with the χ_i and n_i values specified above, the hydrogen release (molar equivalents) as a function of reaction time at any isothermal reaction temperature greater than ~110°C can be estimated. The results of this isothermal reaction modeling approach are compared to the 130, 145, and 160°C basis data in Figure 6.

The isothermal reaction model cannot be applied directly to assess H_2 release from ammonia borane under non-isothermal reaction conditions. For example, Figure 7 shows the PCT experimental results for a relatively quick ramp from room temperature to 160°C and the isothermal model results at that temperature (repeated from Figure 6). Figure 7 also shows the greatly improved representation of the PCT data using a ramped-temperature reaction model, which is described below.

Effectively, modeling the extent of hydrogen release as a function of time in a non-isothermal system requires integrating the reaction rate over the reaction time. The reaction rate (mol H_2 released/mol AB reacted/time) is the derivative with respect to time of Eqn. (3)

$$\frac{d\chi(t)}{dt} = \chi_1 \frac{d\alpha_1(t)}{dt} + \chi_2\left[\alpha_2(t)\frac{d\alpha_1(t)}{dt} + \alpha_1(t)\frac{d\alpha_2(t)}{dt}\right] \tag{5}$$

where

$$\alpha_i(t) = 1 - \exp\left[-(k_i t)^{n_i}\right]$$

and

$$\frac{d\alpha_i(t)}{dt} = n_i k_i^{n_i} t^{n_i - 1} \exp\left[-(k_i t)^{n_i}\right]$$

The reaction rate is a function of time, temperature (through k_i), and the current extent of reaction $\propto_i(t)$, which is likewise a function of time and temperature. In Eqn. (5), t is either: 1) *Isothermal System* – the duration at temperature for systems that are isothermal from the start of reaction ($t = 0$) to t (= elapsed clock time); or 2) *Non-Isothermal System* – the effective time, t_{eff}, at the current system temperature $T(t)$ to achieve the same overall extent of reaction. Whereas the elapsed clock time t is generally known or specified, the effective time at temperature of non-isothermal systems must be solved. For a given overall reaction progress $\chi(t)$ and current reaction rate constants, $k_i[T(t)]$, the effective time $t_{eff}(t)$ can be solved numerically from Eqn. (3) (i.e., find t_{eff} such that the left and right hand sides of the equation are equal). With reaction rate and t_{eff} defined, the extent of hydrogen release in time for a specified reaction temperature profile (T vs. t) can be estimated by integration. For example, the following step-wise integration process was used to model the PCT data:

- Specify parameters: initial conditions, T and χ at $t = 0$; fixed kinetic model parameters ($\chi_1 = 0.6$, $\chi_2 = 1.9$, $n_1 = 5$, and $n_2 = 0.6$); integration time step size, Δt; and reaction duration, t_{end}
- Assumption: the reaction rate is negligible for reaction temperatures <100°C (i.e., the multiple-equivalent H_2 release kinetic model is only applied for temperatures ≥100°C)
- Loop calculations or integrate in t as follows:
    - Advance time by Δt ($t = t + \Delta t$)
    - Specify or calculate T at t
    - Calculate $k_i(T)$ [using Eqn. (4) and Table 1]
    - Solve for $t_{eff}(k_i, \chi)$ [using Eqn. (3)]
    - Calculate reaction rate $d\chi/dt$ (k_i, t_{eff}) [using Eqn. (5)]
    - Advance molar equivalents of H_2 released χ by ~$(d\chi/dt)\Delta t$ [$\chi = \chi + (d\chi/dt)\Delta t$]
    - Repeat until $t = t_{end}$

This non-isothermal model process was implemented using Mathcad© (v. 14.0) software. PCT experiment temperature ramps [i.e., $T(t)$] were first fit to multi-order polynomials for subsequent use in the non-isothermal reaction model. The PCT temperature and hydrogen release data and the corresponding model representations are shown in Figure 6 for ultimate PCT temperatures of 160, 200, and 250°C. Results for a PCT experiment ramped to 300°C and the model results are nearly identical to those shown in Figure 8 for 250°C. This is so because the temperature ramps nearly overlap for the first ~15 minutes, up to 185 to 190°C, by which point > 2.0 molar equivalents of H_2 were released. Note that the experimental data shown in Figure 8 justify the model assumption of negligible reaction for temperatures <100°C. The model predictions are very good overall, especially in tracking the onset and profile of the initial H_2 release reaction. Above ~2.0 molar equivalents of H_2 released, however, the model tends to over predict the H_2 release rate. Other than the temperature inputs to the reaction model, no PCT experimental data were used to "fit" the model hydrogen release profiles. As described above, these were based on the isothermal kinetics experiments and model fits shown in Figure 6. However, a visual comparison of the non-isothermal model to PCT data in Figure 8 was used to help guide the final selection of the n_i and χ_i kinetic parameters in the isothermal model. Because of the complex kinetics, it is difficult to directly extract fundamental kinetic information for hydrogen release from ammonia borane from the ramped-temperature PCT tests.

3.3 Fixed bed reactor with AB or AB/MC

The purpose of our experiments with a fixed bed reactor was to better understand thermal heat propagation in AB and AB/MC composite. With the set up for a fixed bed reactor described in the Experimental section 2.3 and shown in Figure 9, we studied heat propagation of 2.5 gram of AB and AB/MC in a temperature range of 160-400°C at 1 atm by collecting thermal images with an IR camera. We observed that neat AB chips foamed and did not propagate heat well in the current design. However, AB/MC composite powder did not foam, and Figure 10 shows heat propagation in the IR camera images. Heat propagation was not fast and it took 4 minutes for the temperature to peak and that is with an initial point of 300°C. The hot spot that develops from 236 seconds-260 seconds we believe is a reflection and not real. The temperatures along the column of the bed was measured with an array of thermocouples and it can be seen in Figure 11 comparing AB with AB/MC, that the heat is propagating in AB/MC, but, not much in AB. Table 2 summarizes key observations. Based on our current observations, the key conclusion is that the AB/MC mixture allows for safe heat propagation.

We also measured hydrogen evolution in another set up with an autoclave loaded with 2.5 gram of AB/MC and inserted into a tubular furnace that was heated up to 300°C under 10.5 atm, (155 psi) argon. As can be seen in Figure 12, about 3.5 liters of hydrogen evolved, corresponding to ~2.5 equivalents, confirming full hydrogen release.

3.4 Flow Through (Auger) Reactor

We investigated the feasibility of a flow through (auger) reactor as a source of hydrogen generation from solid AB. The reactor, which is known as a plasticating single screw extruder and the most common equipment in the polymer industry,[19-20] was outfitted for generating hydrogen in the present work. The purpose of experimental validation includes: 1) validate the concept of flow through reaction with an auger, 2) verify sufficient heat transfer to AB at required feed rate, 3) measure hydrogen generation vs. AB feed rate. The experiments were conducted according to the procedures described below.

As shown in Figure 13, the extruder consists of a hopper that holds the AB powder and the extruder barrel which can be conceptually divided into three sections on the basis of function. These are called the feed, compression, and metering sections. In the feed section, the solid AB powder is conveyed by the rotating screw from the hopper to the compression zone where the AB is forced against the heated walls of the barrel do to the action of electrical heaters and mechanical heat. By the time the AB reaches the metering zone, all the AB has finished to dehydrogenate, and the shearing action of the screw rotating against the inner wall of the extruder barrel forces the spent AB out of the extruder and through a nozzle. During extrusion, the feed section of the barrel was maintained at room temperature with cold water cooling lines, whereas the compression and metering zones were sustained at 150^{o}C and 70^{o}C, respectively. To neutralize sudden generation of hydrogen and undesired volatile by-products throughout the thermal decomposition process of AB, the experiments were carried out in a shielding box filled under flowing nitrogen gas. As the AB powder moved from the hopper to the screw channel and the screw rotated, the solid bed was compacted, transported down the channel, and then released hydrogen in the compression zone. However, due to the excessive pressures from the hydrogen generation as well as the frictional forces between the barrel and the AB powder, the barrel and screw in the extruder nozzle clogged. Therefore, with the current screw and nozzle design, we were not able to validate the concept of flow through reaction with an auger as a solid AB reactor.

Conclusions

We have demonstrated feasibility of safely using solid ammonia borane, preferably mixed with methylcellulose (AB/MC) to reduce foaming, for self-propagated hydrogen release in a fixed bed reactor. We measured kinetics of hydrogen release from AB and from AB/MC composites and found that it is necessary to operate at temperatures above 110°C to obtain rapid kinetics for practical applications. The experimental data was used to validate kinetics models and the equations were revised to better represent the nucleation and growth behavior of the AB decomposition reaction.

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Table 1. Arrhenius kinetic constants obtained from the three-point fit of the isothermal reaction data

	$\underline{k_1}$	$\underline{k_2}$
A_i (sec^{-1})	$5.2724 \cdot 10^4$	$2.7228 \cdot 10^{15}$
E_i (kJ/mol)	38.14	131.58

Table 2. Summary of key observations from fixed bed reactor tests on AB and AB/MC

AB	**AB/MC**
Melts and foams during hydrogen release	Does not foam during hydrogen release
Reaction propagation not observed	Reaction propagation observed but not self-sustained at low pressures; self-sustained at high pressures (in furnace set-up)
Thermal runaway not observed	Thermal runaway not observed
Hydrogen release accompanied with sublimation	Rapid hydrogen release, similar to kinetics data
Product very sticky	Product not sticky
NMR of product indicates 2+ equivalents	NMR of product indicates 2+ equivalents

Figure Captions:

Figure 1 Hydrogen capacity and bulk kinetics comparisons of AB at 160°C (black), 200°C (blue), 250°C (red) and 300°C (green) measured at 1 bar H_2.

Figure 2 Hydrogen capacity and bulk kinetics comparisons of AB/MC at 160°C (black), 200°C (blue), 250°C (red) and 300°C (green) measured at 1 bar H_2.

Figure 3 Hydrogen capacity and bulk kinetics comparisons of AB and AB/MC at 160°C and 1 bar H_2.

Figure 4. Hydrogen capacity and bulk kinetics of AB at 100-350°C (0 bar H_2-pressure).

Figure 5. Hydrogen capacity and bulk kinetics of AB at 0, 1 and 5 bar H_2-pressure at 160°C.

Figure 6. Hydrogen release data (+) from ammonia borane at 130, 145, and 160°C compared to isothermal reaction model results (– – –)

Figure 7. Hydrogen release data from ammonia borane in a PCT Experiment at 160°C compared to isothermal and ramped-temperature reaction model results

Figure 8. Temperature and hydrogen release profiles in PCT experiments at 160°C (Bottom), 200°C (Middle), and 250°C (Top) compared to ramped-temperature reaction model results

Figure 9. a) Photo and b) schematics of fixed bed reactor with solid ammonia borane pellets loaded into quartz vial equipped with thermo couples

Figure 10. Thermal imaging of fixed bed reactor with 2.5 grams of AB/MC heated to 160°C from the bottom, under 1 bar H_2, illustrating heat propagation. The pink color in the bottom is the heat source. Red represents the hottest temperature and blue the coldest temperature. Time in seconds was recorded.

Figure 11. Fixed bed reactor; comparison of a) AB and b) AB/MC during hydrogen release as measured by thermocouples placed through the length of the quartz tube.

Figure 12. Hydrogen gas evolution monitored during decomposition of 2.5 grams of AB/MC powder heated in an autoclave inserted in a tubular furnace. The gas evolution is represented by the green diamonds. Temperatures of the furnace (blue) and the powder (red) were recorded

Figure 13. Flow through (auger) reactor for concept validation with AB.

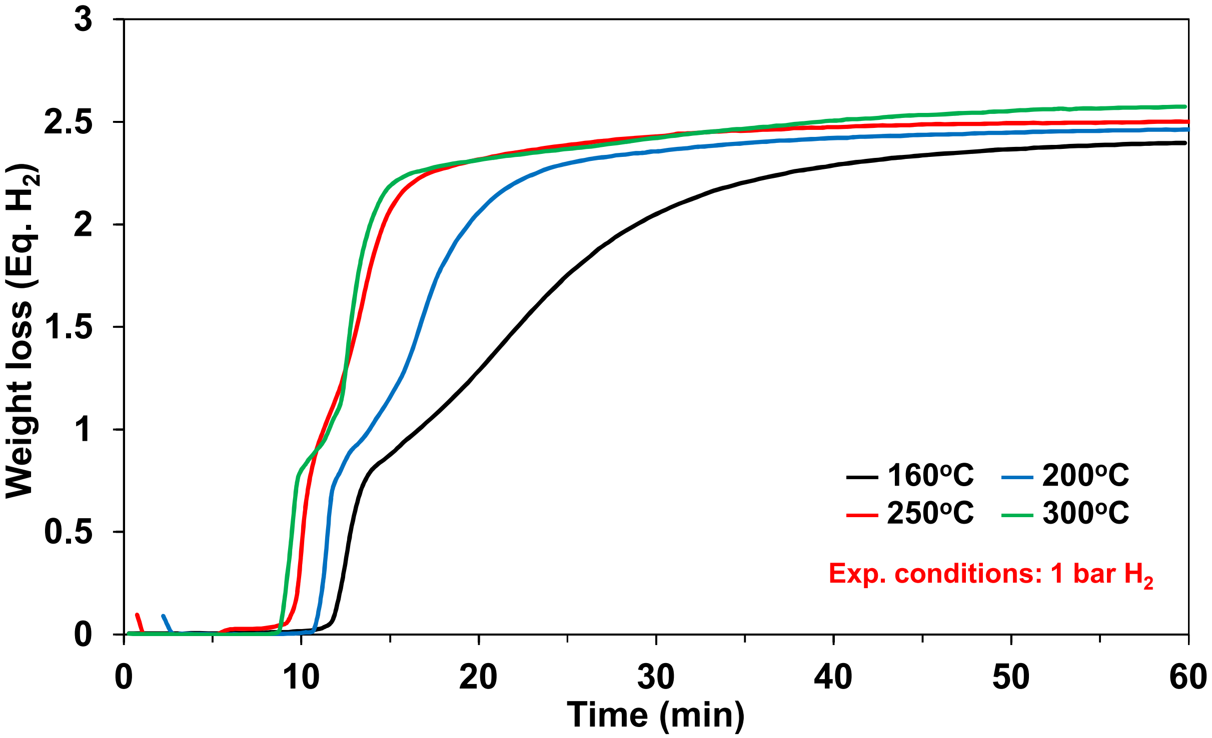

3
2.5
2
1.5
1
0.5
0
Weight loss (Eq. H_2)
0
10
20
30
40
50
60
Time (min)
160°C
200°C
250°C
300°C
Exp. conditions: 1 bar H_2

Figure 1

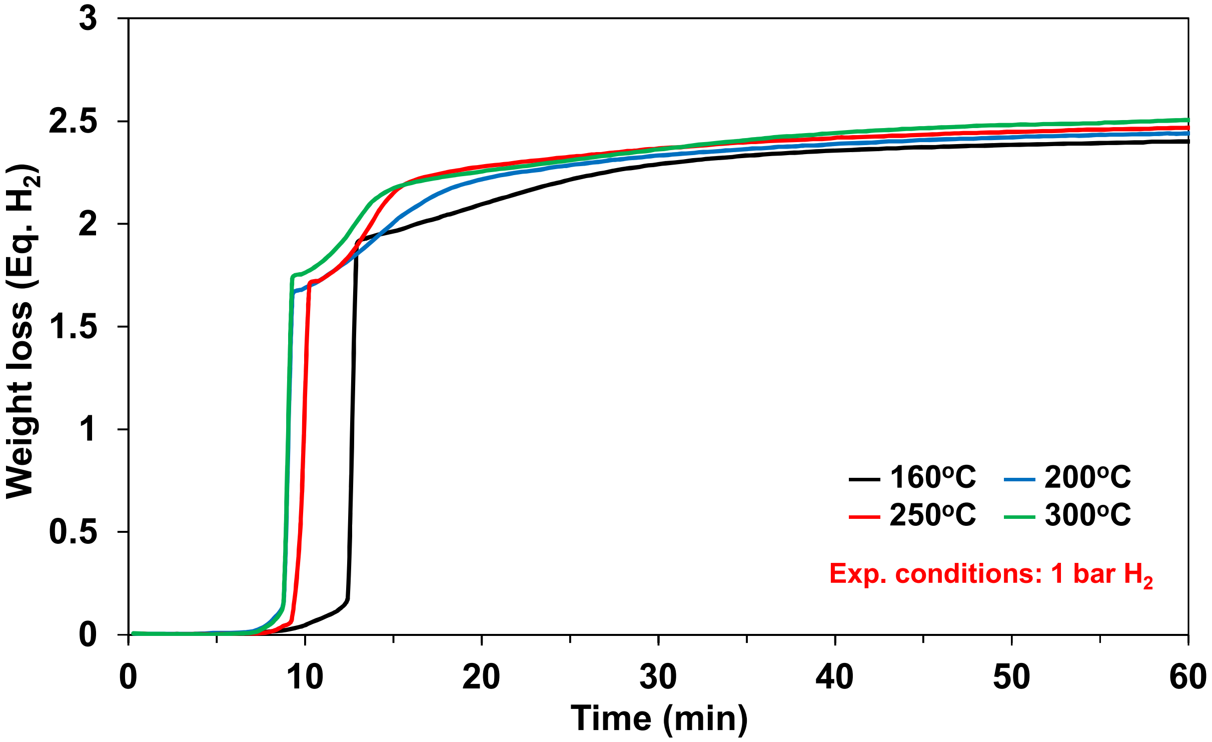
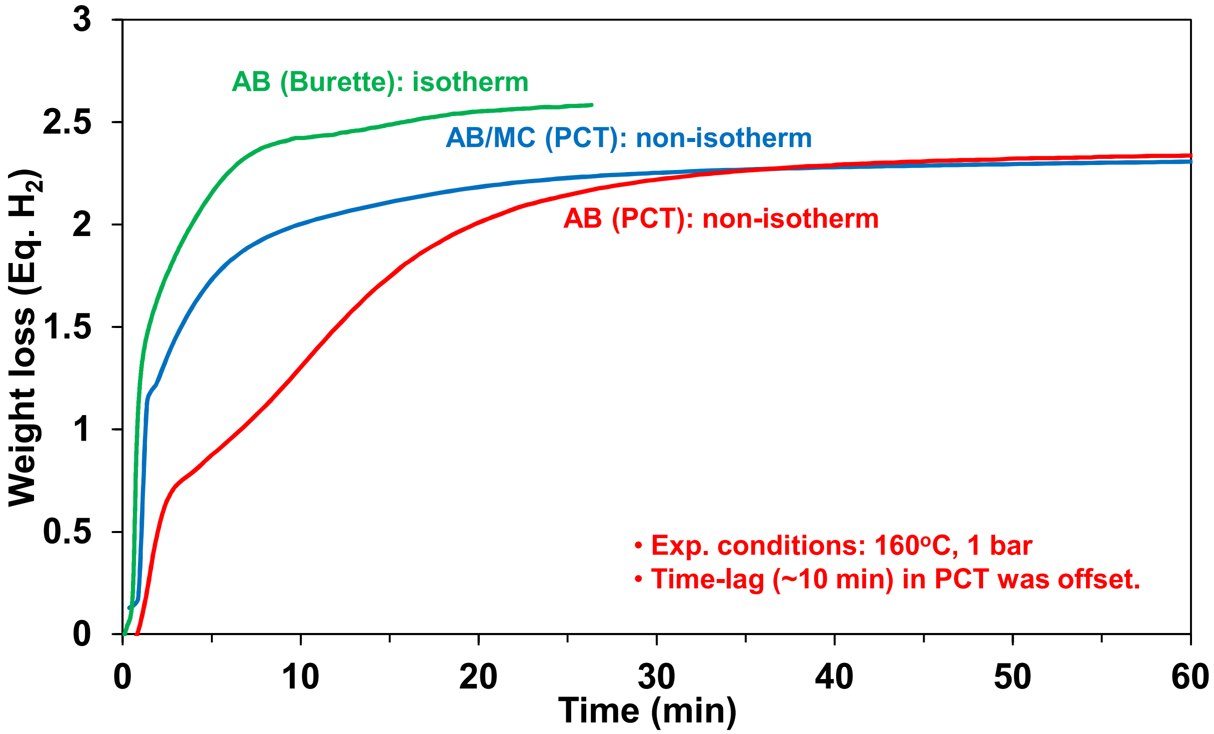

3
2.5
2
1.5
1
0.5
0
Weight loss (Eq. H_2)
0
10
20
30
40
50
60
Time (min)
160°C
200°C
250°C
300°C
Exp. conditions: 1 bar H_2

Figure 2


AB (Burette): isotherm
AB/MC (PCT): non-isotherm
AB (PCT): non-isotherm
• Exp. conditions: 160°C, 1 bar
• Time-lag (~10 min) in PCT was offset.
Weight loss (Eq. H_2)
Time (min)
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0.5
1
1.5
2
2.5
3
0
10
20
30
40
50
60

Figure 3

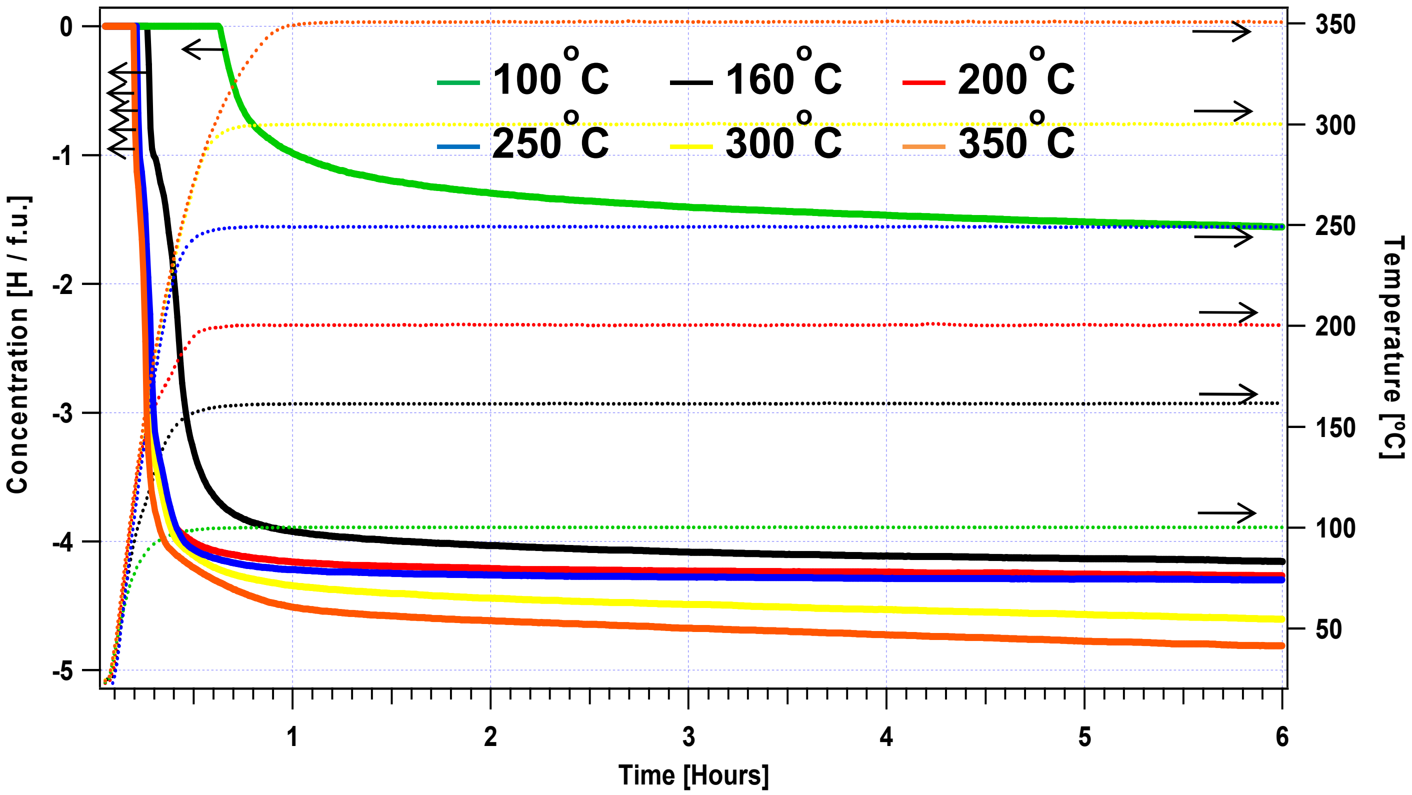

100°C
160°C
200°C
250°C
300°C
350°C
Concentration [H / f.u.]
0
-1
-2
-3
-4
-5
Temperature [°C]
350
300
250
200
150
100
50
Time [Hours]
1
2
3
4
5
6

Figure 4

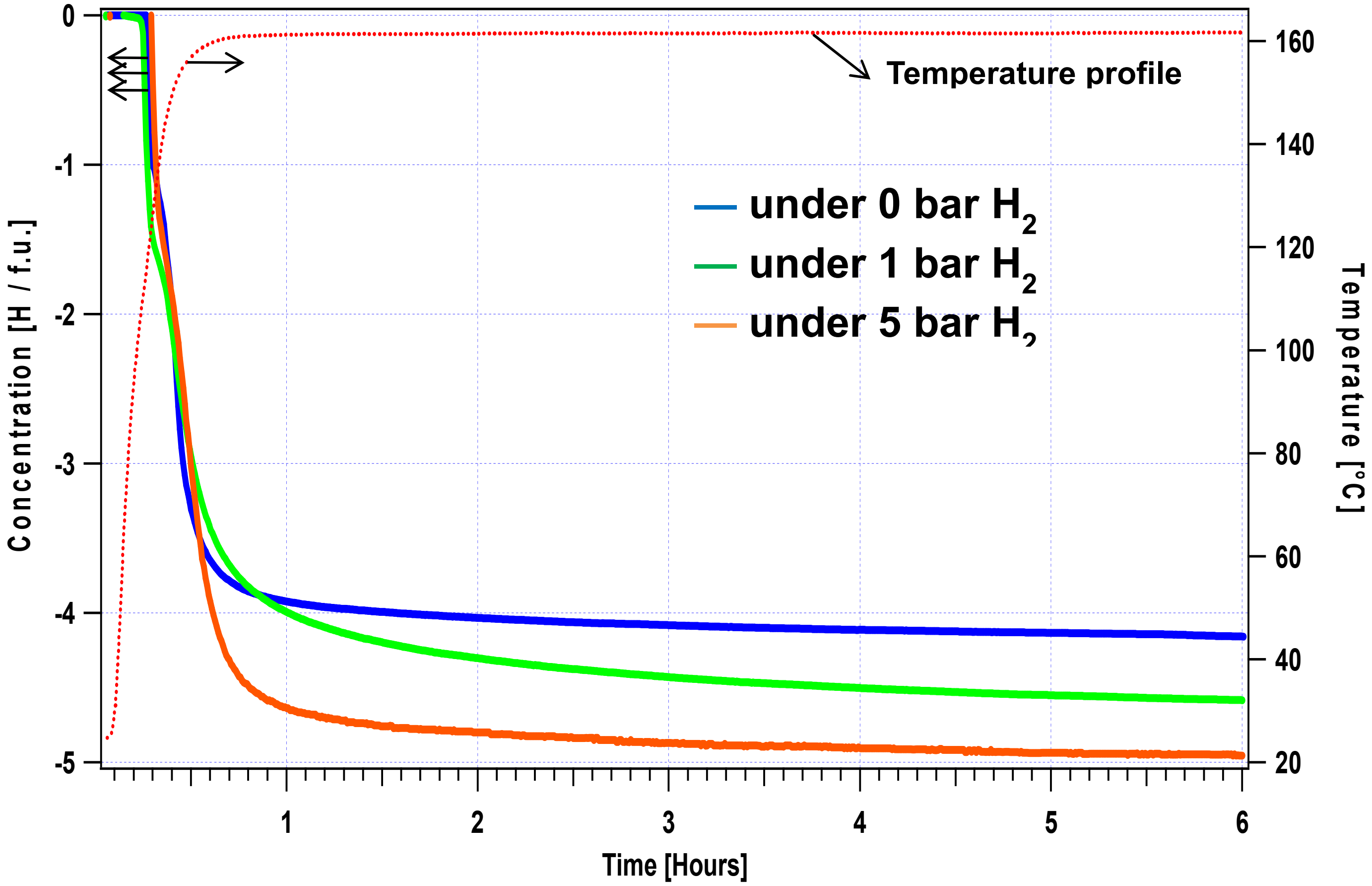

0
-1
-2
-3
-4
-5
Concentration [H / f.u.]
160
140
120
100
80
60
40
20
Temperature [°C]
1
2
3
4
5
6
Time [Hours]
Temperature profile
under 0 bar H_2
under 1 bar H_2
under 5 bar H_2

Figure 5

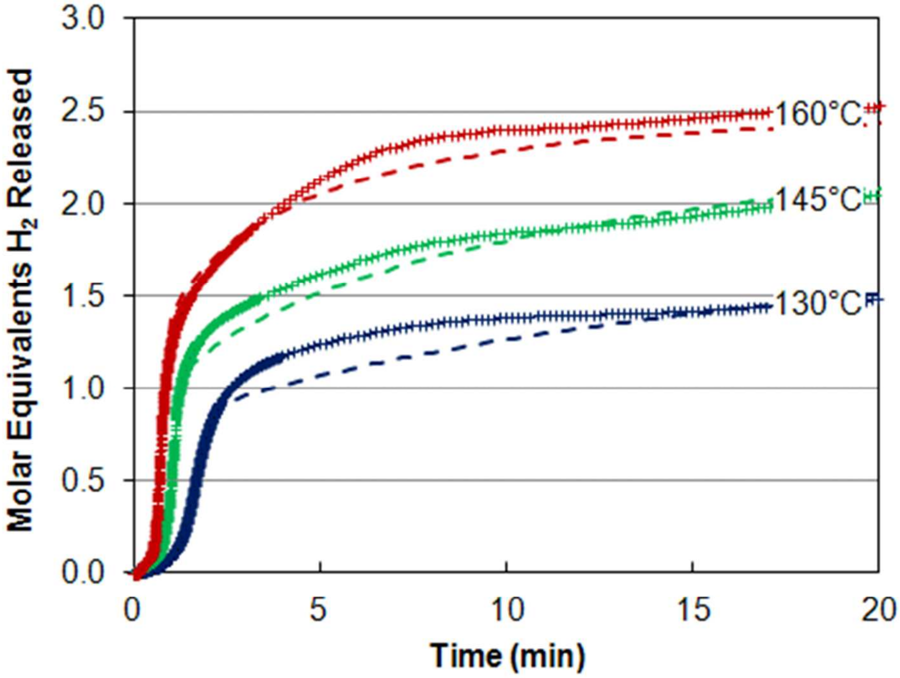


Figure 6.

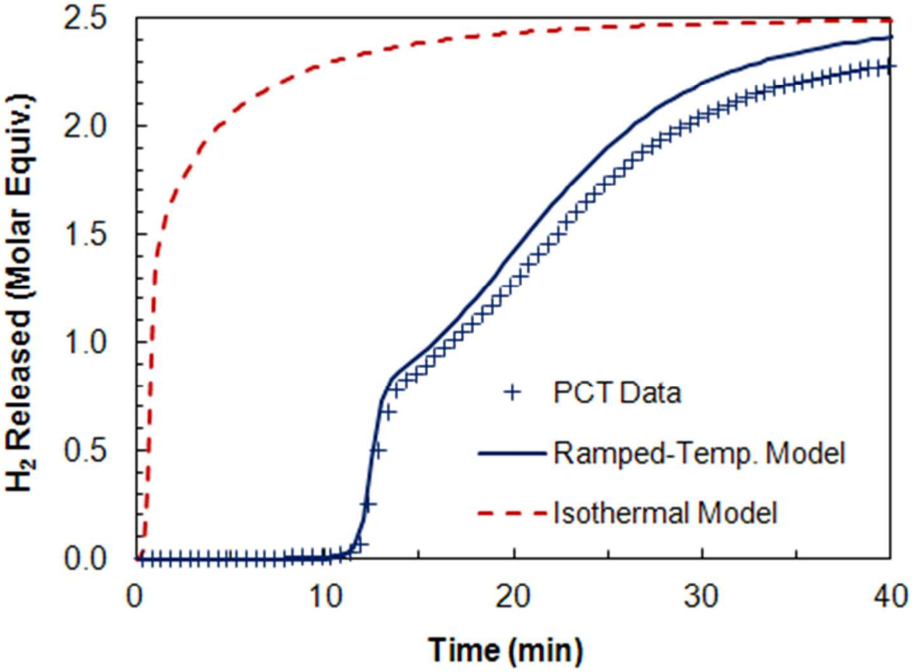
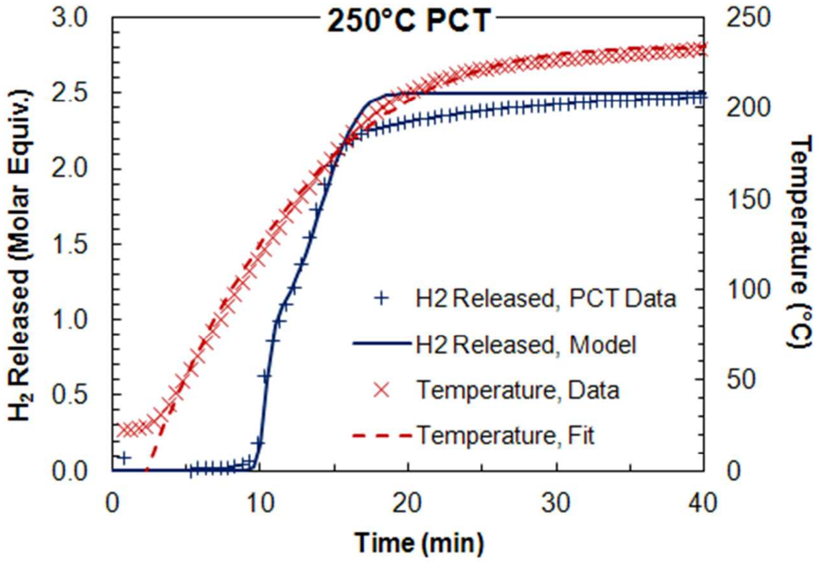
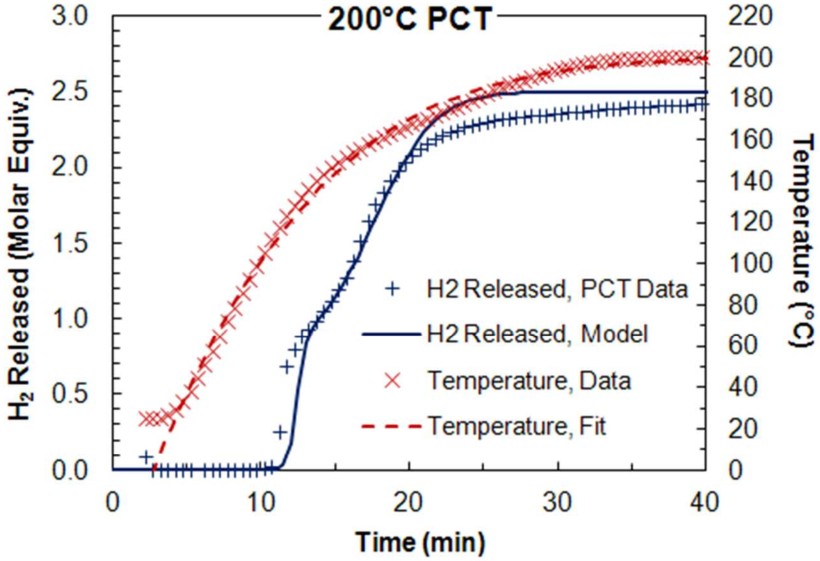


Figure 7.


250°C PCT
H$_2$ Released (Molar Equiv.)
Temperature (°C)
Time (min)
H2 Released, PCT Data
H2 Released, Model
Temperature, Data
Temperature, Fit
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
50
100
150
200
250
0
10
20
30
40


200°C PCT
H$_2$ Released (Molar Equiv.)
Temperature (°C)
Time (min)
H2 Released, PCT Data
H2 Released, Model
Temperature, Data
Temperature, Fit
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0.5
1.0
1.5
2.0
2.5
3.0
0
20
40
60
80
100
120
140
160
180
200
220
0
10
20
30
40

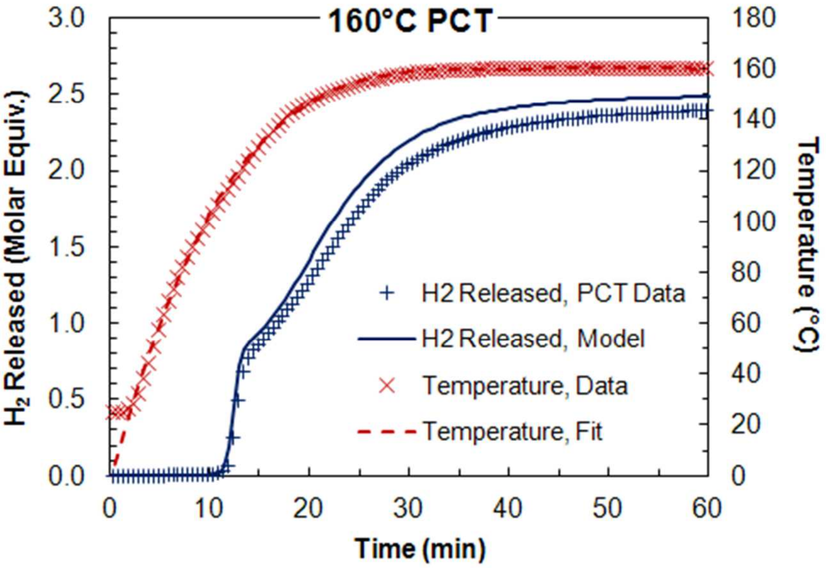

160°C PCT
H2 Released (Molar Equiv.)
Temperature (°C)
Time (min)
H2 Released, PCT Data
H2 Released, Model
Temperature, Data
Temperature, Fit
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
20
40
60
80
100
120
140
160
180
0
10
20
30
40
50
60

Figure 8.

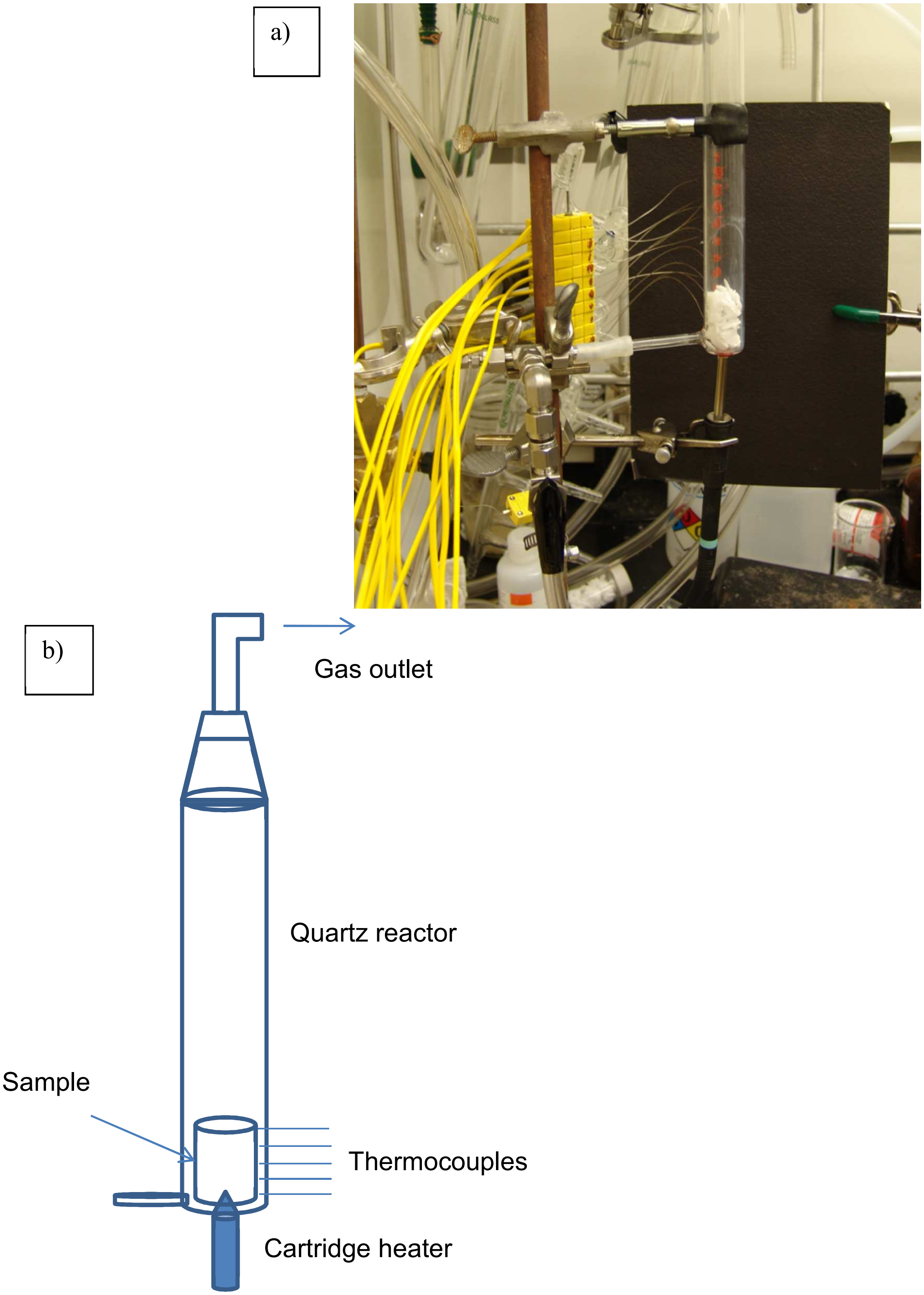
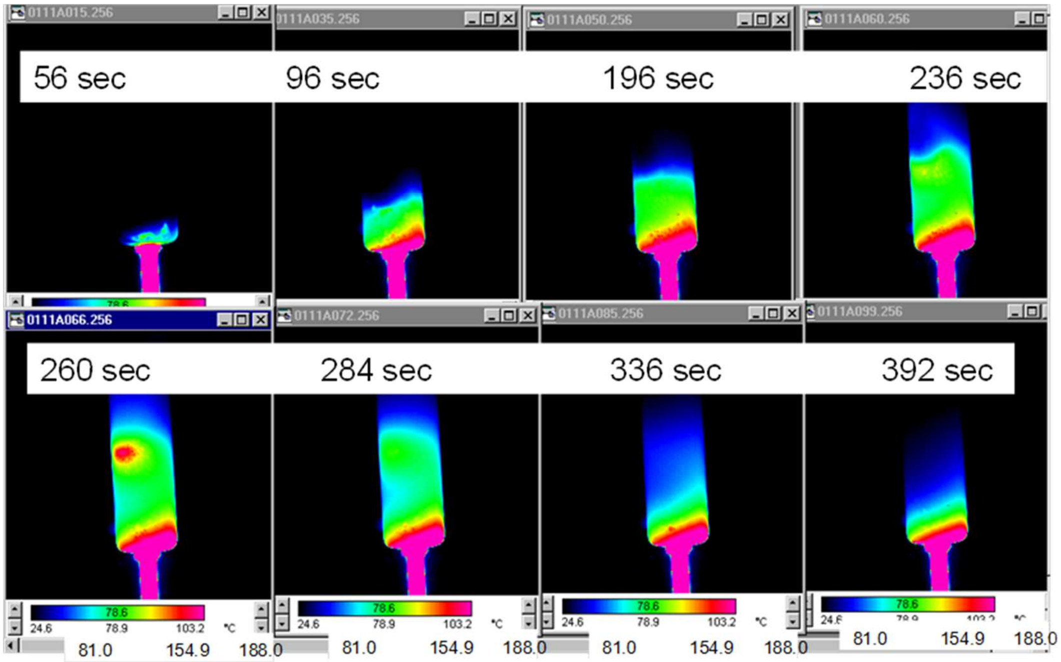

a)
b)
Gas outlet
Quartz reactor
Sample
Thermocouples
Cartridge heater

Figure 9.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56 sec
96 sec
196 sec
236 sec
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0111A085.256
0111A099.256
260 sec
284 sec
336 sec
392 sec
78.6
24.6
78.9
103.2
°C
81.0
154.9
188.0

Figure 10.

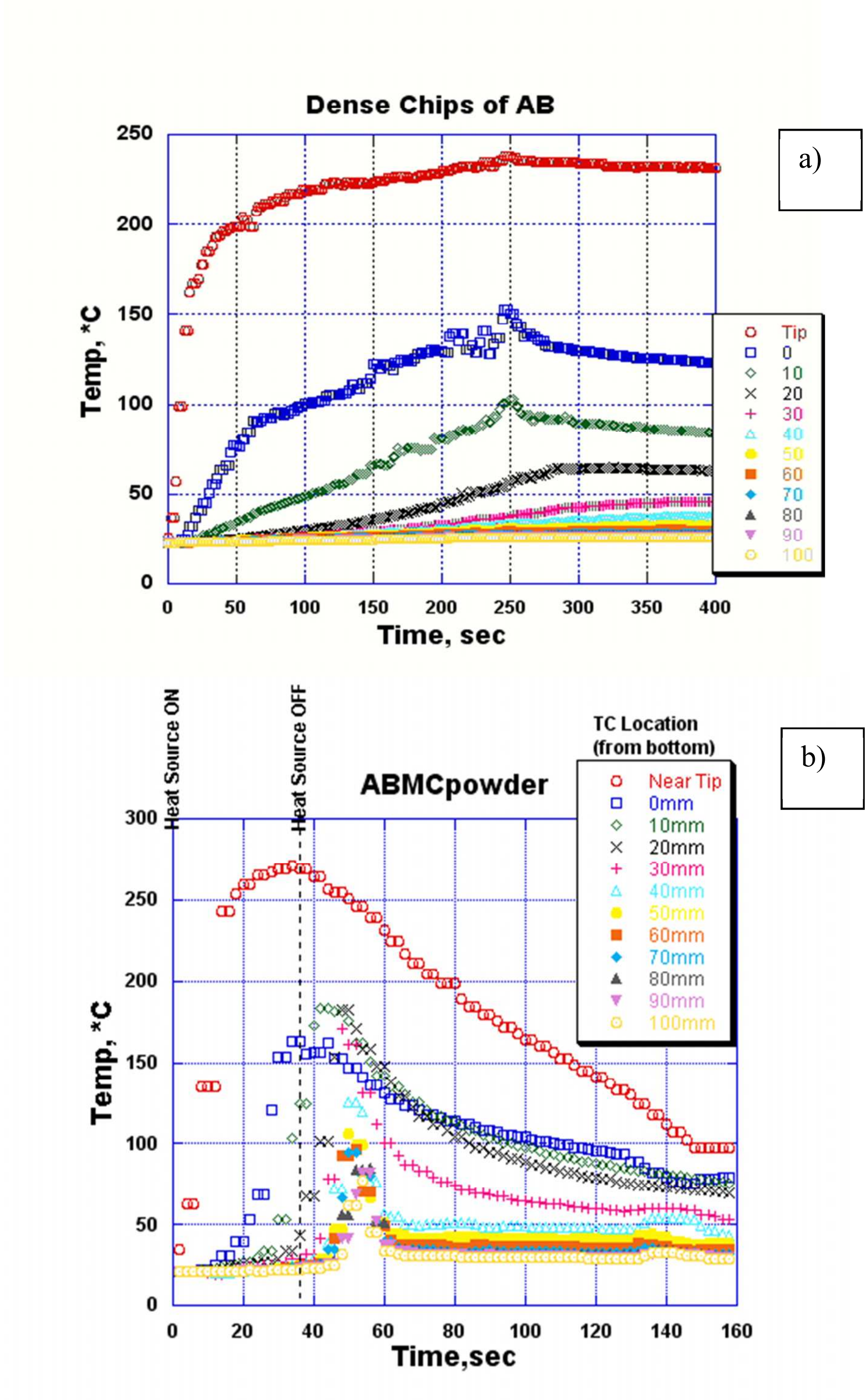
Dense Chips of AB
a)
Temp, *C
0
50
100
150
200
250
Time, sec
0
50
100
150
200
250
300
350
400
Tip
0
10
20
30
40
50
60
70
80
90
100
Heat Source ON
Heat Source OFF
ABMCpowder
b)
TC Location
(from bottom)
Near Tip
0mm
10mm
20mm
30mm
40mm
50mm
60mm
70mm
80mm
90mm
100mm
Temp, *C
0
50
100
150
200
250
300
Time,sec
0
20
40
60
80
100
120
140
160

Figure 11.

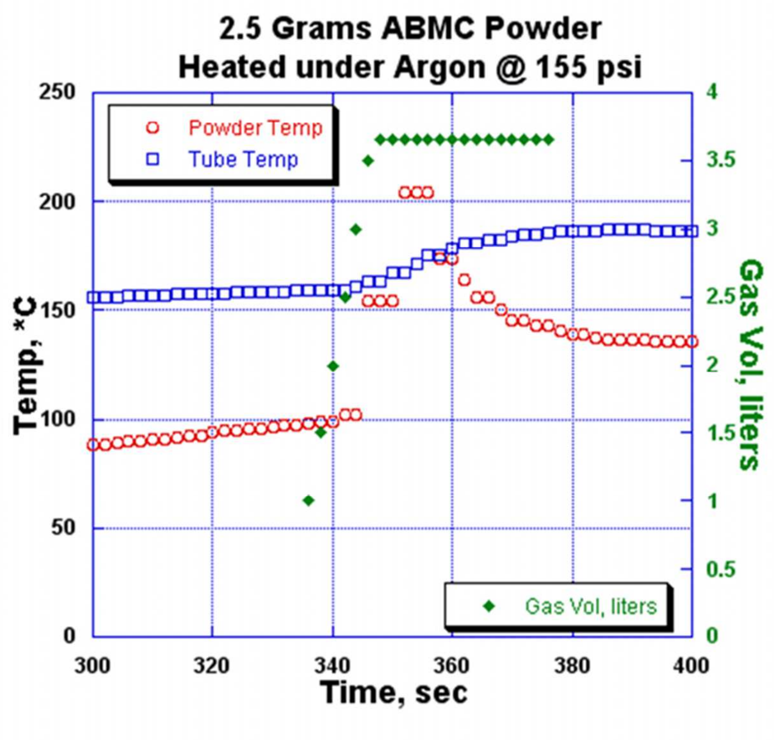

Figure 12.

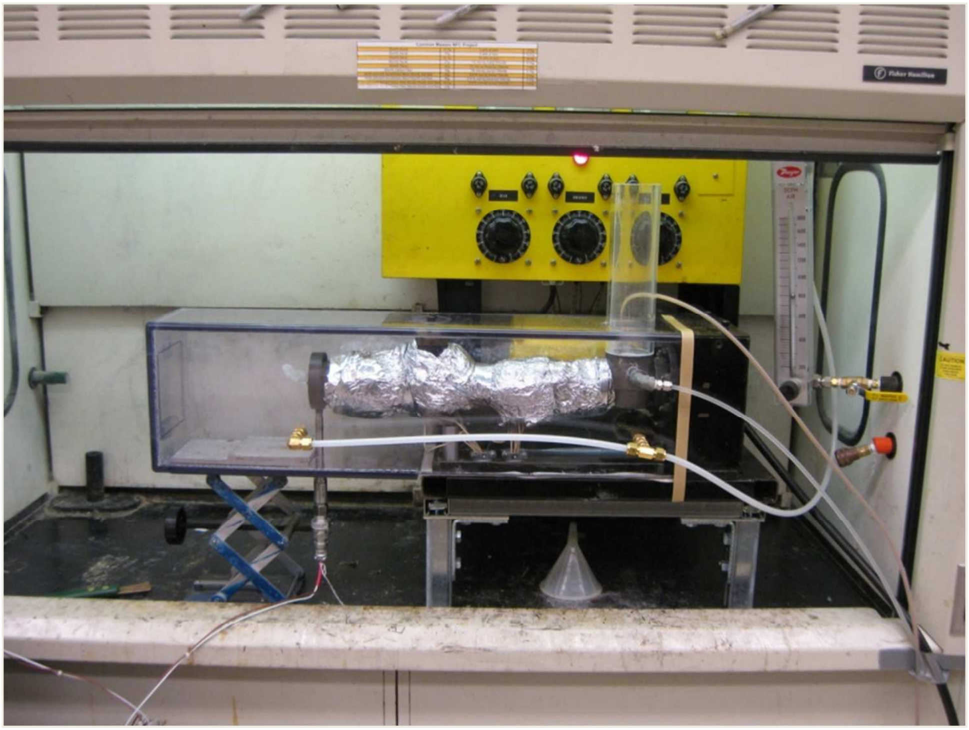

Figure 13.