Experimental Determination of Dust Cloud Combustion Parameters of α -AlH₃ Powder in its Charged and Fully Discharged States for H₂ Storage Applications

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ABSTRACT

This study discusses results of an experimental program for determination of dust cloud combustion parameters of charged and fully discharged states of metastable alane (aluminum hydride, α -AlH₃ polymorph) powder in air. The measured characterization parameters include: maximum deflagration pressure rise (ΔP_{MAX}), maximum rate of pressure rise $(dP/dt)_{MAX}$, minimum ignition temperature (T_C), minimum explosible concentration (MEC), and minimum ignition energy (MIE). These measured values are used for calculating the associated explosion severity (ES) index, and volume-normalized maximum rate of pressure rise (K_{St}). The experimental results show values of MEC and T_C of fully discharged alane to be greater than those of the charged alane but measured MIE values are about the same. Moreover, the results show higher reactivity of fully discharged alane dust cloud in air compared to its charged state. For example, ES and K_{St} of discharged alane dust cloud in air are about 300% and 35% greater, respectively, than ES and K_{St} of charged alane dust. The higher air reactivity of fully-discharged (primarily Al powder) dust cloud compared to its charged state can be attributed to the higher surface energy (J/m²) of Al compared to that of α -AlH₃. These experimental insights have safety implications in postulated risk scenarios involving light-duty vehicles powered by PEM fuel cells. The core insights and critical data provided by this contribution are useful for supporting development and promulgation of hydrogen safety standards and augmenting property databases of hydrogen storage materials.

Keywords: charged alane; aluminum powder; dust cloud; hydrogen storage; off-board regenerable

1. Introduction

The development of low-cost, thermodynamically- and kinetically-efficient hydrogen (H₂) storage materials is essential for successful deployment of H₂-based technologies in mobile applications such as PEM¹ fuel cells (PEMFC) powered light-duty vehicles, unmanned aerial vehicles (UAV) powered by PEMFC, light-weight man-portable power generators, and material handling equipment (MHE) such as forklift trucks, pallet jacks, and airport baggage and pushback tractors.² To encourage conducting of fundamental research in this area, the U.S. Department of Energy (DOE) sponsors materials discovery R&D programs which aim to identify

¹ PEM = proton exchange membrane

² Material handling equipment (MHE) is an example of specialty vehicle applications which also includes airport ground support equipment (GSE).

novel hydrogen storage media that can meet its 2020 technical, cost, and most importantly safety targets for on-board H_2 storage and for man-portable power equipment. Details of DOE targets are described in many of its reports, such as DOE multi-year plan (US DOE, 2012) and funding opportunity announcements (FOA) like DE-FOA-0000827 (2013).

With respect to performing fundamental research related to H_2 storage materials reactivity and safety, Khalil (2010a, 2010b, 2011a, 2011b, 2013a, 2013b, 2014) experimentally determined dust cloud deflagration parameters of selected H_2 storage materials including metal hydrides, complex metal hydrides, chemical hydrides, and adsorbents. Khalil et al. (2010, 2013c) experimentally and theoretically investigated strategies for mitigating sodium alanate ($NaAlH_4$) reactivity risks during postulated accident scenarios involving exposure to air or water. Khalil and Modarres (2010) applied probabilistic risk assessment (PRA) methods to determine the safety importance measures for a conceptual baseline design on an on-board reversible hydrogen storage system that uses $NaAlH_4$ (sodium alanate) as a solid-state H_2 storage medium.

Aluminum hydride or alane (AlH_3) is one of the candidate metal hydrides (MH) that has been proposed for solid-state H_2 storage in mobile applications such as PEMFC-powered light-duty vehicles, forklifts, man-portable power generators, and PEMFC-powered unmanned aerial vehicles, UAV, (Klebanoff and Keller, 2010; 2012). This metal hydride has also been considered for other uses such as a rocket propellant, a reducing agent, and as an explosive material (Deluca and Rossetini, 2009).

The present study discusses the results of an experimental research program designed to determine dust cloud combustion characterization parameters of aluminum hydride (alane, AlH_3) as one of the candidates of solid-state H_2 storage media for mobile applications including PEMFC-powered light-duty vehicles. Both charged and fully-discharged alane have been tested in this experimentally-focused fundamental research program. The alane material being tested has a mean particle size of 75 μm and the dust cloud combustion characterization tests are performed per standardized test protocols (ASTM E-1226-05, 2005; ASTM E-1491-06, 2006; ASTM E-1515-07, 2007; ASTM E-2019-03, 2008). Furthermore, this study focuses only on solid-state alane for H_2 storage and, hence, alane slurries (*e.g.*, alane powder in ionic liquids, supercritical fluids, mineral oil, etc.) are not discussed here.

The remainder of this manuscript is organized as follows: Subsection 1.1 discusses the current state of knowledge of AlH_3 as a solid-state H_2 storage material and subsection 1.2 discusses the novelty and significance of the present experimental study. Section 2 presents the experimental methods employed to meet the objectives of this study. Section 3 discusses the experimental results of this research program and section 4 provides conclusions and recommendations based on the insights generated.

1.1 A brief account of the current state of knowledge of AlH_3 as a solid-state H_2 storage material

Alane, a covalently-bonded binary hydride, has a molecular weight of 30 g/gmole, a gravimetric H_2 storage capacity of 10.1 wt%, and a volumetric H_2 storage capacity of 0.148 kg H_2 /L (Sandrock et al., 2005; Hwang et al., 2007). Alane has several polymorphs, namely: α - AlH_3 , α' - AlH_3 , β - AlH_3 , and γ - AlH_3 phases. While the first polymorph (α - AlH_3) is metastable at

room temperature, the other three polymorphs are less stable. According to Graetz et al. (2011), at temperatures above 100°C, the three polymorphs (α' -AlH₃, β -AlH₃, and γ -AlH₃) tend to exothermally transition to α -AlH₃ without H₂ release. The exothermic transition energies of α' -, β -, and γ -AlH₃ are -1.1, -1.0, and -1.9 kJ/mole H₂, respectively (Graetz, 2012). The resulting α -AlH₃ from these transition reactions then decomposes, without side reactions, to Al metal and H₂. Graetz et al. (2011) suggested that metallic Al that forms on the surface of α -AlH₃ particles during its thermolysis reaction further accelerates H₂ release leaving behind a porous aluminum structure which enhances H₂ diffusion to the particle's surface.

1.1.1 Alane synthesis, regeneration, desorption, and destabilization

With respect to alane synthesis, this hydride is not commercially available but can be synthesized by several processes including reacting lithium borohydride (LiBH₄) with either aluminum chloride (AlCl₃) or a strong acid like hydrochloric acid (HCl) or sulfuric acid (H₂SO₄) in diethyl ether (Et₂O) (Graetz et al. ,2011; Graetz, 2012). Other alane synthesis processes include the electrochemical approach proposed by Savannah River National Laboratory (SRNL) but material's durability under H₂ absorption/ desorption cycling conditions and its structural stability remain unproven (Klebanoff and Keller, 2010; 2012). Also, Brookhaven National Laboratory (BNL) explored direct hydrogenation of metallic Al to form alane adducts using amines such as dimethylethylamine (C₄H₁₁N), triethylenediamine (C₆H₁₂N₂), and quinuclidine (C₇H₁₃N) at 300°K and pressures below 60 bar (Graetz et al. 2006). Nonetheless, these alane synthesis pathways still require further optimization.

With regard to alane regeneration, Graetz et al. (2006) cited several technical challenges need to be resolved to enable cost-efficient utilization of alane as a H₂ storage material for the on-board vehicular application where the resulting spent fuel (Al powder) would need to be off-board regenerated/ recharged. Additionally, alane regeneration energy could be as high as 70% of the energy contained in 1 mole of H₂ (namely, 240 kJ/mole H₂) and, hence, the DOE fuel cycle target of 60% well-to-tank (WTT) efficiency cannot be realized (Graetz, 2012). Also because α -AlH₃ thermolysis reaction is irreversible, formation of α -AlH₃ by rehydrogenating metallic Al powder requires H₂ gas pressure greater than 25,000 bars depending on the temperature in the Al-H₂ pressure-temperature (P-T) phase diagram. Other research efforts include Hwang, S-J et al. (2007) who applied a series of NMR tests to characterize various alane samples (including those samples provided by UTRC). For example, they used NMR signature to characterize the transformation of γ -AlH₃ to α -AlH₃ for a wide range of temperature from room and high temperatures. Also, Turley and Rinn (1969) who examined the crystal structure of aluminum hydride, AlH₃ as well as aluminum deuteride, AlD₃, using X-Ray and neutron powder diffraction.

With respect to alane desorption, it is worth noting that some of the past researchers have focused on alane desorption including Ojwang et al. (2009) who developed a reactive force field, REAXFF, based on the density functional theory (DFT) to describe the dynamics of alane desorption/thermal dissociation and hydrogen release. Maehlen, et al. (2007) performed thermal desorption spectroscopy (TDS) for α -AlH₃ desorption. Their results suggested that alane particles could be covered by protective Al₂O₃ layers that act as kinetic barriers to the

decomposition process. The extent of Al_2O_3 formation depends on the age of the sample being experimentally examined.

Finally, since enhancement of $\alpha\text{-AlH}_3$ desorption kinetics at temperatures below 100°C is desirable for the on-board vehicular application, scientists such as Graetz and his research team at BNL (Graetz et al., 2006; Graetz et al., 2011; Graetz, 2012) and Ojwang and his collaborators (2009), among many others, were inspired to examine approaches to destabilize $\alpha\text{-AlH}_3$ polymorph using dopants such as transition elements (e.g., Ti) and alkali hydrides such as KH, NaH, and LiH. Other researchers like Sandrock et al. (2005) have experimentally demonstrated that by reducing $\alpha\text{-AlH}_3$ particle size and doping this polymorph with 20 mol% lithium hydride (LiH), the decomposition kinetics and, hence, H_2 release can be enhanced over the temperature range being considered in their tests. Furthermore, the induction period before H_2 release can be reduced by destabilizing $\alpha\text{-AlH}_3$ decomposition reaction. Detailed discussion on AlH_3 synthesis, polymorph structures, decomposition thermodynamics, reaction kinetics, decomposition destabilization, and regeneration can be found in the review article by Graetz (2012).

1.1.2 Aluminum dust cloud explosions (published literature)

The key published work on aluminum dust cloud explosions include Marmo et al. (2004) who described various conventional tools for conducting risk analysis such as failure modes and effects analysis (FMEA) and fault tree analysis (FTA). The authors applied these tools to a case study involving aluminum dust explosion associated with aluminum sheets surface finishing through grinding operations. They also reviewed consequence quantification methods for pressure waves resulting from dust cloud explosions. Myers, T.J. (2008) who described an inerting process to reduce aluminum dust ($75\text{ }\mu\text{m}$ mean diameter) explosion hazard resulting from buffing operations. He discussed the use of an inerting material, such as flame retardants, to reduce dust explosion risk. He also compared the explosion pressures (bar-g) with and without presence of flame retardants. Dufaud et al. (2010) who modeled the pressure rise during aluminum dust explosion using a shrinking core model and have experimentally studied the impact on aluminum dust explosion of humidity content and particles' sizes (7, 11, 27, and $42\text{ }\mu\text{m}$ mean diameter, respectively). Their testing protocols followed the ICE standards. In their humidity tests, aluminum dust samples were either pre-exposed to humid air till sorption equilibrium is reached (via water chemisorption or physisorption) or, alternatively, water vapor was introduced into the air contained in the test sphere. Based on their water-laden dust tests, they noted that hydrogen release during the ignition of aluminum dust has added to the explosion severity. For the tests in which dry aluminum dust was introduced into the air contained in the test sphere, they reported that dust explosion was less severe. The authors concluded that humidity in the air had an inhibiting effect on dust ignition. In addition, the authors found that aluminum dust oxidation to be depended on the particle's shape (e.g., spherical, ellipsoidal, or flakes) and particle's surface roughness. Finally, Li et al. (2011) who investigated the explosion characteristics of nano-aluminum dust of different particle sizes (35, 75, 100 nm, respectively). They employed testing protocols per ISO 6184-1 standards. They also compared the explosion

characteristics of the nano-Al particles versus Al particles with 75 μm mean diameter. Their aluminum dust was 98% pure with 2% impurities (a mixture of Fe, Cu, Si, and H_2O). They noted that the explosion results were dependent not only on the chemical composition of the aluminum dust but also on particles' shape and surface roughness as well as on the moisture and oxygen content in the air contained in the test vessel. As can be observed from their pressure-time plots, the ignition delay time (IDT) varied between 105 ms (for the nano-Al dust) to 159 ms (for the micro-size Al dust).

In this author's opinion, performing one-to-one comparison between the aforementioned published dust explosion characterization parameters of aluminum dust and the measured dust explosion characterization parameters of fully-discharged alane (this work) would lead to drawing erroneous conclusions for several reasons as follows:

- a) Differences in physical, morphological, and chemical compositions of the tested dust samples.
- b) Use of different testing standards (e.g., *ISO*, *IEC*, or *ASTM* standards).
- c) Difference in moisture content (chemisorbed or phisorbed) in the dust particles being tested.
- d) Potential presence of different types of impurities in the dust samples.³
- e) Employment of different igniter energy in MEC tests.⁴

1.1.3 Potential risks associated with using alane powder for hydrogen storage in mobile applications

To identify potential risks associated with using alane powder as a H_2 storage medium in light-duty vehicles, Khalil (2011a) developed a baseline design of an off-board regenerable H_2 storage system using alane (AlH_3) as the solid-state storage medium (Fig. 1) and performed design failure mode and effects analysis (d-FMEA) for the proposed system's configuration (Khalil, 2011a). Fig 1 shows the various key components of this on-board vehicular H_2 storage and delivery system including storage of the charged alane (fresh fuel) and the discharged alane (spent fuel). Table 1 summarizes potential safety-significant failure modes for this alane-based system as follows: a) Failure to transport the fresh alane powder (fresh fuel) through the on-board system, b) Failure of thermal management subsystem of the on-board alane thermolysis reactor and c) Accidental exposure of the charged alane (fresh fuel) or fully-discharged alane (spent fuel) powder to ambient air leading to potential dust cloud explosion and H_2 fires. The

³ In some cases, it is possible that such impurities could act as flame retardants to suppress the pressure rise and rate of pressure rise.

⁴ For example, larger igniter energy may influence the results by overriding the explosion (Myers, 2008).

conditions under which dust cloud explosion could occur are discussed in previous work by Khalil (2013a; 2013b; 2014). The aforementioned accidental exposure of alane dust to air could be encountered under postulated scenarios involving PEMFC vehicular collisions which lead to rupture of the charged alane storage tank, spent fuel (i.e., full-discharged alane) storage tank, or both.

The present experiment research program has been motivated by the outlined safety concerns as described in Table 1 with primary focus on the potential for alane (in its charged or fully-discharged states) dust cloud explosion accidents. In his previous research, Khalil (2010a; 2010b; 2011a; 2011b; 2013a; 2013b; 2014) discussed dust cloud explosions associated with other candidate solid-state H₂ storage materials.

Table 1

Critical failure modes and failure causes for the off-board regenerable alane system (Khalil, 2011a).

Critical Failure Modes	Failure Causes
1. Failure to transport the fresh AlH ₃ powder (fresh fuel) through the on-board system.	Failure of the variable-speed motor to operate or jamming of the connected driving piston leading to failure to deliver the fresh AlH ₃ to the thermolysis reactor and, hence, failure to generate H ₂ gas to feed the on-board PEM fuel cells.
2. Failure of thermal management of the on-board AlH ₃ thermolysis reactor.	Failure of the H ₂ burner or the pump that circulates the thermos-fluid heat transfer medium that heats the thermolysis reactor.
3. Accidental exposure of the charged alane (fresh fuel) or fully-discharged alane (spent fuel) powder to ambient air leading to dust cloud explosion.	Rupture of the pressure boundary of any of the following components in the on-board system: charged alane (fresh fuel) thermolysis reactor, connecting pipes, fully-discharged alane (spent fuel) separation chamber or the spent fuel collection tank.

Fig. 1. A schematic diagram of a baseline design of the off-board regenerable alane system (Khalil, 2011a).

1.2 Novelty and significance of the present experimental study

1.2.1 Novelty

This contribution provides novel safety-related insights based on an experimental research program designed to determine dust cloud combustion characterization parameters of alane (aluminum hydride, $\alpha\text{-AlH}_3$) powder in its charged and fully-discharged states. These insights should advance the current state of knowledge beyond what has been published to date on alane physical characteristics, synthesis, regeneration, desorption and destabilization (as discussed in subsections 1.1.1 through 1.1.4, respectively).

1.2.2 Significance

The significance of insights to be gained from determination of dust cloud combustion characterization parameters of alane (in its charged and fully-discharged forms) include:

- i) Advancing the safe deployment of alane for H_2 storage in a wide range of mobile applications such as PEMFC-powered light-duty vehicles, unmanned aerial vehicles (UAV) powered by PEMFC, material handling equipment (MHE), airport ground support equipment (GSE), man-portable power systems for military and civilian use. For example, knowledge of the maximum deflagration pressure rise, ΔP_{MAX} , and maximum rate of pressure rise, $(dP/dt)_{MAX}$, could be used for designing adequate engineered safety features (ESF) such as deflagration vents and isolation devices for the on-board systems.
- ii) Filling existing knowledge gaps about safety precautions related to handling and transport of this energetic material. For example, the calculated ES index and K_{St} index could be used to assign an appropriate hazard classification for alane powder.

- iii) Supporting data-driven quantitative risk assessment (QRA) and process hazard analysis per NFPA-654 requirements (2006). To elucidate this point, Khalil and Modarres (2010) leveraged measured dust cloud combustion characterization parameters (such as the *MIE* value) to quantify the safety importance measures of various components in a conceptual baseline design of an on-board reversible hydrogen storage system.
- iv) Developing risk mitigation methods based on potential risks of alane use. To elucidate this point, Khalil (2010a) and Khalil et al. (2010) discussed risk mitigation methods for selected candidate hydrogen materials for on-board light-duty vehicles. Also, Khalil et al. (2013c) have successfully demonstrated the risk mitigation benefits of compacting sodium aluminum hydride (sodium alanate, NaAlH_4) instead of using loose powder of this material for on-board hydrogen storage. They found that powder compaction has completely eliminated the air pyrophoricity hazard associated with sodium alanate powder (Khalil et al., 2013c).
- v) Complementing insights generated by other researchers such as Dedrick et al. (2008) who examined the consequences of accidental exposure of alane powder to air by developing theoretical models to describe the kinetics of alane reaction with oxygen (O_2) and water (H_2O). They also estimated the associated release of H_2 , O_2 , and H_2O from $\alpha\text{-AlH}_3$ reaction with O_2 .

2. Experimental methods

2.1 Test methods for dust cloud combustion characterization

Alane dust cloud combustion characterization tests discussed in this section are performed in accordance with *ASTM* standardized protocols (*ASTM* E-1226-05, 2005; *ASTM* E-1491-06, 2006; *ASTM* E-1515-07, 2007; *ASTM* E-2019-03, 2008) in order for the generated results to be reproducible and meaningful for on-going and future H_2 storage materials reactivity and safety studies. Also as part of this experimental program, dust cloud combustion parameters of the *ASTM* reference materials (Pittsburgh seam coal dust and Lycopodium spores) are measured to: 1) serve as benchmarks for the alane dust being tested and 2) calibrate the test equipment described in this section. Unless otherwise stated, all tests are carried out on dust samples that are dried (moisture content < 5%) and sieved through a No. 200-mesh screen (75 μm opening size).

2.1.1 Maximum deflagration pressure rise, ΔP_{MAX} , and maximum rate of pressure rise, $(dP/dt)_{MAX}$, of combustible dusts

The measured dust cloud combustion characterization parameters in accordance with this *ASTM* standardized test method (*ASTM* E-1226-05, 2005) include maximum deflagration pressure rise, ΔP_{MAX} , and maximum rate of pressure rise, $(dP/dt)_{MAX}$. These parameters can be defined as follows:

ΔP_{MAX} = maximum deflagration pressure rise (bar-g) above atmospheric pressure in the 20-L Kühner test vessel at the time of ignition. This parameter is determined by carrying out a series of tests over a wide range of dust concentrations (g/m^3).

$(dP/dt)_{MAX}$ = maximum rate of pressure rise (bar/s) during the deflagration test. This parameter is determined by carrying out a series of tests over a wide range of dust concentrations (g/m^3).

To perform the deflagration tests, dust cloud is formed in the Kühner 20-liter (0.02 m^3) spherical explosion test apparatus (Fig. 2) by pneumatically introducing the dust sample with air into the pre-evacuated vessel (at -0.60 bar-g) from a reservoir pressurized with air to 20 bar-g. Ignition is initiated after 60 ms of delay time (DT) from the start of dust injection at which time the vessel pressure reaches 1-bar absolute (0 bar-g). The pressure-time profile generated during the deflagration test is measured using two piezoelectric pressure transducers with the output signals automatically processed by the test control and data acquisition system (Fig. 3). The Kühner test apparatus is calibrated by performing the deflagration tests using the reference materials (Pittsburgh seam coal dust and Lycopodium spores). Selection of dust concentration range and method of determination of the optimum concentration are performed according to ASTM E-1226-05 (ASTM E-1226-05, 2005).

It should be noted that a 60-ms ignition delay time (IDT) was employed in the tests. Based on the author's past experience with dust cloud combustion characterization tests (Khalil, 2013a; Khalil, 2013b; Khalil, 2014), the choice of IDT value is critically important. For example, using longer IDT greater than 60 ms would result in some settling of the air-suspended dust inside the Kühner vessel before ignition is applied and, hence, that dust fraction would not contribute to dust cloud ignition.

Fig. 2. Schematic diagram of the Kühner 20-liter spherical explosion test apparatus.

Fig. 3. Simplified diagram of the automated test rig including the data acquisition system and the Kühner test apparatus.

The K_{St} index (bar-m/s) is the volume-normalized maximum rate of pressure rise $(dP/dt)_{MAX}$ measured at the optimum dust concentration and can be calculated by the following “Cube Law”:

$$K_{St} = \left(\frac{dP}{dt} \right)_{MAX} \cdot V^{1/3} \quad (1)$$

Where: P = pressure, bar, t = time, s, and V = volume of the Kühner spherical vessel, m^3 .

The K_{St} index is an internationally-recognized parameter that allows comparisons to be made between the test material and standardized reference dusts. Based on the calculated K_{St} value (rounded to the nearest integer), dusts are classified into four hazard classes as displayed in Table 2 (*vide infra*).

Table 2

Dust classification⁵ based on the K_{St} value.

Dust Class	K_{St} (bar-m/s)	Dust Cloud Characteristics
<i>St-0</i>	0	None explosive. Dust is incapable of propagating a deflagration.
<i>St-1</i>	> 0 and ≤ 200	Weak explosibility.

⁵ Source: OSHA report 3371-008. <https://www.osha.gov/Publications/337/combustible-dust.pdf>

Dust Class	K_{St} (bar-m/s)	Dust Cloud Characteristics
<i>St-2</i>	> 200 and ≤ 300	Strong explosibility.
<i>St-3</i>	> 300	Very strong explosibility.

Note: The calculated K_{St} index in this study is based on a 20-L test chamber (Kühner apparatus).

2.1.2 Minimum autoignition temperature (T_C) of combustible dusts

This test is performed according to an *ASTM* standardized test protocol (ASTM E-1491-06, 2006) to determine the minimum temperature (T_C) at which a dust cloud will autoignite when exposed to air heated to preset temperatures in an electrically heated furnace (Fig. 4). Dust ignition is determined by visual observation of the resulting flame. For a given dust type, there are several experimental factors that affect the measured T_C value including dust concentration, dust particles size distribution, moisture content of the dust as well as the type of furnace⁶ being used for heating the dust/air sample. Hence, in order to generate reproducible results and establish a common basis for comparing the deflagration parameters of different dust types, testing should be performed in accordance with aforementioned standardized protocol (ASTM E-1491-06, 2006).

The test apparatus contains a means for dispersing the weighted dust sample into the top of a vertical tube furnace having a bore diameter of 3.8 cm and a length of 30.5 cm. The outside of the test tube is wound with an electric heater surrounded by an insulating material. The furnace temperature is measured using a type-N thermocouple positioned 1.6 mm from the heated wall. This apparatus, referred to as the Godbert-Greenwald (G-G) furnace, is shown schematically in Fig. 4. The reference dusts (Pittsburgh seam coal and Lycopodium spores) are tested first to establish the initial calibration of the G-G furnace and validate the testing protocol.

The dust sample is heated as it cascades down the vertical tube furnace (Fig. 4). Ignition is deemed to have occurred if a flame appears at the bottom outlet of the furnace. The reported minimum dust cloud ignition temperature (T_C) is the average of the lowest test temperature at which ignition is observed (*i.e.*, test result is a *Go*) and the highest test temperature at which ignition is not observed (*i.e.*, test result is a *No-Go*). ASTM E-1491-06 (2006) provides sufficient guidance on selecting the initial dust concentration (in g/m³) to be tested as well as on varying the dust concentration to ensure that the autoignition temperature is measured at the most easily ignited concentration.

⁶ The 0.27-L Godbert-Greenwald (G-G) Furnace, the 0.35-L BAM Oven, the 1.2-L Bureau of Mines Furnace, and the 6.8-L Bureau of Mines Furnace.

Fig. 4. Godbert-Greenwald (G-G) furnace for determination of dust cloud minimum ignition temperature (T_C).

2.1.3 Minimum explosible concentration (MEC) of combustible dusts

This test describes a standardized protocol (ASTM E-1515-07, 2007) for measuring the minimum explosible concentration (MEC) of an air-dispersed combustible dust capable of propagating a deflagration. This measured MEC value is sensitive to several experimental conditions such as the igniter energy and uniformity of dust dispersion inside the test chamber.

Tests are carried out in a Kühner 20-liter test vessel (Fig. 2) and the dust sample is pneumatically injected into the pre-evacuated vessel (at -0.60 bar-g) from a reservoir pressurized with air to 20 bar-g. Dust dispersion within the test vessel is achieved using a standard nozzle assembly. Ignition of the dust cloud is achieved using a 2.5 or 5 kJ pyrotechnic igniter that is positioned in the center of the vessel. Ignition occurs 60 ms after the start of dust injection at which time the vessel pressure reaches 1 bar absolute (i.e., 0 bar-g). The pressure-time profile developed during the deflagration is measured using two piezoelectric pressure transducers with the output signals automatically processed by the test control and data management system (Fig. 3).

After plotting ΔP_{MAX} as a function of dust concentration (in g/m^3), the minimum explosible concentration (MEC) is reported as the average of the highest concentration that does not produce a $\Delta P_{MAX} > 1$ bar-g and the lowest concentration that produces a $\Delta P_{MAX} > 1$ bar-g. Again, ΔP_{MAX} is the maximum pressure rise in the Kühner test vessel reached during the course of a single deflagration test.

2.1.4 Minimum ignition Energy (*MIE*) of combustible dusts

This *ASTM* standardized test protocol (ASTM E-2019-03, 2008) determines the minimum ignition energy (*MIE*) of a dust cloud in air by an igniter-generated spark. The modified Hartmann apparatus (Fig. 5) is employed for conducting the *MIE* tests. The apparatus consists of a cylindrical Lucite test tube with internal dimensions of 50 mm I.D. by 260 mm long. The igniter's electric circuit is used to generate electric sparks of precisely controlled energy in the range of 5 to 10,000 mJ. These tests are carried out by causing an electric spark discharge to occur between pointed electrodes that are surrounded by the dust cloud.

Fig. 5. Modified Hartmann apparatus used for determining dust's minimum ignition energy (*MIE*).

In accordance with this standard (ASTM E-2019-03, 2008), the *MIE* value represents the amount in energy which is sufficient to ignite the dust cloud at its most easily ignitable concentration in air, given the specified test conditions. Because the *MIE* value increases with increased dust moisture content, it is important to dry the dust sample to a moisture content $\leq 5\%$ before testing. Knowledge of the *MIE* value of a given dust type is a useful input to risk quantification in many applications including the on-board hydrogen storage systems. Also, knowing the likelihood of ignition is important to designing adequate engineered safety features (ESF) to mitigate the risks of dust deflagration.

The dust sample is placed in a dish-shaped sample holder at the base of the tube. Air from a pressurized reservoir is directed into the sample holder causing the dust to be dispersed as a cloud in the test volume. The top of the test volume is fitted with a paper diaphragm that retains the dispersed dust but bursts on dust ignition. A pair of pointed ignition electrodes (tungsten, graphite or stainless steel) is located at the center of the test volume. Sparks are generated using a multi-capacitor, variable high voltage (HV) power supply. The spark circuit contains two capacitive components: a) Ionization capacitor; and b) HV capacitor. The ionization capacitor has a capacitance of 0.47 μF and is hydrided to a voltage typically between 160 and to 200 V. This capacitor contributes up to 9.4 mJ to the total spark energy. The HV capacitor is selected from a bank of capacitors having values from 0.005 to 0.5 μF . The HV capacitor is hydrided to

voltages from 500 to 4000 V. On triggering the ionization capacitor, energy is dehydrated through an ignition coil resulting in a voltage jump to several thousand volts at the electrodes that creates an ionized field in the electrode gap. Electric current flows out of one electrode, through the ionized field into the opposite electrode. The gap between electrode tips is maintained at 3 to 6 mm. The initial voltage (V_i) and final voltage (V_f) of the HV capacitor are measured using a JCI-148 electrostatic voltmeter. The energy delivered at the spark gap is calculated as shown in Eq. (5):

$$E = \frac{\left\{ (C \cdot V^2)_{\text{IONIZATION}} + (C \cdot [V_i^2 - V_f^2])_{\text{MAIN}} \right\}}{2} \quad (2)$$

Where: E = dehydrated energy (J), C = total capacitance of the discharge circuit in farads (F), and V_i and V_f = measured values of the initial and final voltages of the hydrated capacitor (V).

An electronic timing circuit is used to regulate the time delay between the start of dust dispersion and the discharge of the spark. The pressure of the air reservoir is adjusted as required to establish full and uniform dust dispersion in the test volume.

Tests are conducted by discharging the stored electrical energy, at various values of the capacitance or capacitor charge potential, across the spark gap in dust clouds of fixed concentration. Ignition is deemed to have occurred if the paper diaphragm is ruptured or if flame is observed in the test vessel. The Go (*i.e.*, occurrence) / No-Go (*i.e.*, nonoccurrence) of flame is recorded for each test. For the specified ignition delay time⁷, the *MIE* value can be estimated by varying the dust concentration and the spark discharge energy.

The minimum ignition energy, *MIE*, lies between the highest energy, E_1 , at which ignition fails to occur in successive attempts to ignite the dust-air mixture and the lowest energy, E_2 , at which ignition occurs at least once within the successive attempts:

$$E_1 < MIE < E_2 \quad (3)$$

The *MIE* test starts with a value of a spark energy that will reliably cause ignition of a given dust concentration in air and the spark energy is then reduced in steps at the given dust concentration until the dust cloud no longer ignites in any of the repeat tests at a given ignition energy. The procedure is repeated at different dust concentrations until the lowest minimum ignition energy value is determined.

3. Results and discussion

Experimental determination of alane (in its charged and fully-discharged states) dust cloud combustion characterization parameters provides useful insights not only for safe use and

⁷ Ignition delay time (*IDT*, t_d) is the time between the onset of dust sample dispersion inside the test chamber and the activation of the ignition source.

handling of this candidate H₂ storage material PEMFC-powered light-duty vehicles,⁸ but also for a wide range of other mobile applications such as portable power generators, forklifts, etc.

This section is divided into eight subsections as follows: 3.1) discusses dust samples preparation and handling, 3.2) describes the *ASTM* reference materials' tests and 3.3) provides a brief summary of the calculated thermodynamic parameters of alane thermal decomposition using *HSC Chemistry*® software package (Roine et al., 2006). Subsections 3.4 through 3.7 discuss the results of dust cloud characterization parameters (P_{MAX} , $(dP/dt)_{MAX}$, T_C , MEC , and MIE , respectively) of the charged and fully-discharged states of this H₂ storage material. Finally, Subsection 3.8 summarizes key testing results and insights in tabular formats.

3.1. Dust samples preparation and handling

The dust samples of charged alane (α -AlH₃) as well as its fully-discharged (primarily aluminum metal) have a mean particle size of 75 μ m. Also, per *ASTM* Standards (ASTM E-1226-05, 2005; ASTM E-1491-06, 2006; ASTM E-1515-07, 2007; ASTM E-2019-03, 2008), two reference materials, namely, Pittsburgh seam coal dust and Lycopodium spores are employed to calibrate the test equipment and to provide baselines for comparison against the dust types being tested. The reference samples also have a mean particle size of 75 μ m. Finally, drying of the test and reference dust samples is done per *ASTM* testing requirements (< 5% moisture). The moisture content was determined by drying the samples in air at 60 °C.

To eliminate exposure of alane dust samples to the atmosphere which may alter or degrade their properties, a laboratory glove box (Fig. 6) has been employed to prepare, store, and handle the dust samples. An inert and dry gas (nitrogen in this case) is continuously passed through the glove box to displace air and to maintain a dry atmosphere. Also, a laboratory electronic scale is placed inside the glove box to weigh the required amounts of dust samples. The samples are then stored in small disposable plastic cups with airtight snap-on lid. The test samples are then passed through the access chamber of the glove box to the test apparatus.

⁸ For PEMFC light-duty vehicles, about 124 kg of AlH₃ would be loaded into the on-board system to supply H₂ gas to an 80-kW PEMFC stack (@ 45% efficiency) to cover an expected driving range of 300 miles (Ahluwalia et al., 2015).

Fig. 6. Laboratory glove box where alane dust samples are prepared and stored before being tested.

3.2 Determination of dust cloud combustion characterization parameters of Pittsburgh seam coal dust and Lycopodium spores (reference dust types per ASTM standards)

The Kühner apparatus (used for determination of the parameters ΔP_{MAX} , $(dP/dt)_{MAX}$, and MEC), the Godbert-Greenwald furnace (used for determination of T_C), and the modified Hartmann apparatus (used for determination of MIE) were first calibrated by conducting the *ASTM* standardized tests (ASTM E-1226-05, 2005; ASTM E-1491-06, 2006; ASTM E-1515-07, 2007; ASTM E-2019-03, 2008) using the aforementioned reference dusts. Table 3 (*vide infra*) compares the deflagration parameters of the reference materials as determined from this work versus the values reported in the applicable *ASTM* standards. Also provided in Table 3 is the dust explosion severity classification based on the calculated K_{St} index.

With respect to the deflagration parameters of the Pittsburgh seam coal dust, the minimum deviation between the measured values in this work and the reported values in *ASTM* standards was 0.9% and the maximum deviation was 22.7% (related to the *MIE* tests). For the deflagration parameters of the Lycopodium spores, the minimum deviation between the measured values in this work and the reported values in *ASTM* standards was 5.7% and the maximum deviation was 33.3% (related to the *MEC* tests).

Table 3

Summary of reference materials dust cloud combustion characteristics in Air.

Deflagration Parameters	Pittsburgh Seam Coal Dust	Lycopodium Spores	Pittsburgh Seam Coal Dust	Lycopodium Spores
	<i>(this work)</i>		<i>(per ASTM standards)</i>	
Maximum Deflagration Pressure Rise ΔP_{MAX} , bar-g	7.3	7.4	7.0	7.0
Maximum Rate of Pressure Rise $(dP/dt)_{MAX}$, bar/s	426	511	430	555
Volume-normalized maximum rate of pressure rise, K_{St} , bar-m/s	124	139	117	151
Dust class based on K_{St}	<i>St-1</i>	<i>St-1</i>	<i>St-1</i>	<i>St-1</i>
MEC , g/m ³	65	30	80	45
Minimum Ignition Temperature (T_C), °C	585	430	600	460

3.3 Estimation of alane desorption thermodynamic parameters

In this study, HSC Chemistry software package (Roine et al., 2006) has been used to calculate the dehydrogenation enthalpy (ΔH), entropy change (ΔS), and Gibbs free energy (ΔG) for α -AlH₃ irreversible thermolysis as described by reaction (4). This reaction is mildly endothermic and thermodynamically favorable as shown in Fig. 7.

According to HSC calculations at 25°K, α -AlH₃ thermal decomposition (*i.e.*, dehydrogenation) reaction has a ΔH value of about 7.6 kJ/mole H₂, ΔS of about 129.5 J/moleH₂/°K, and ΔG of about -31.0 kJ/mole H₂ (calculations at 25°C are not shown in Fig. 7). At 150°C, the endothermic heat required to decompose 1 mole AlH₃ and produce 1.5 moles H₂ is about 9.43 kJ/mole H₂ (or about 14.15 kJ/mole AlH₃). This endothermic heat represents $\approx$ 2.6% of the energy stored in 1.5 moles H₂.⁹

⁹ This calculation is based H₂ lower heating value (LHV) of 240 kJ/mole H₂ or 33.3 kWh/kg H₂

In general, our HSC thermodynamic calculations are consistent with the experimentally determined alane thermolysis thermodynamics using differential scanning calorimetry (DSC) as reported in the review paper by Graetz (2012) and Ahluwalia et al. (2015).

Fig. 7. Reaction enthalpy and Gibbs free energy for AlH_3 decomposition as a function of temperature.

3.4 Measurement of the maximum deflagration pressure rise, ΔP_{MAX} , and maximum rate of pressure rise, $(dP/dt)_{MAX}$

For the charged and fully-discharged states of alane, the maximum deflagration pressure rise, ΔP_{MAX} , and the maximum rates of pressure rise, $(dP/dt)_{MAX}$, were determined from the pressure-time record of each dust concentration. In each test, the pressure inside the 20-L Kühner vessel at time of ignition was 1 bar. The value of $(dP/dt)_{MAX}$ for a given deflagration test at a given dust concentration was the maximum slope of the pressure-time plot or the highest value on the rate of pressure rise trace. The values of ΔP_{MAX} and $(dP/dt)_{MAX}$ were the averages of the highest values of repeat tests over the range of concentrations of the two dust types being examined (i.e., charged and fully-discharged dust samples).

Table 4 summarizes the measured values of ΔP_{MAX} , and $(dP/dt)_{MAX}$ for the charged and fully-discharged alane samples. The key insights derived from this series of tests are as follows:

- 1) The fully-discharged alane dust cloud produced higher ΔP_{MAX} and $(dP/dt)_{MAX}$ values and, hence, higher K_{St} index and ES index compared to the corresponding values of charged alane. However it should be noted that while the fully-discharged alane tests were conducted with a 10-kJ igniter, the charged alane tests used 2.5-kJ igniter (as it was

noticed that the 10-kJ ignition energy caused personnel safety concerns due to the encountered violent acoustic sound inside the Kühner vessel).

The higher air-reactivity of the fully-discharged alane, compared to the charged alane, dust can be attributed to exothermic energy release due to Aluminum metal (spent fuel) oxidation in air inside Kühner vessel. Al has higher surface energy (J/m^2) compared to that of AlH_3 (see Subsection 4.1 for more details on the surface energy of Al and AlH_3). The higher the surface energy, the more reactive the surface would be. Another argument which may likely support this observation is the pacification effect of Al_2O_3 layers that forms around AlH_3 particles during its thermal decomposition in air. This argument is consistent with what Maehlen, et al. (2007) have suggested regarding the formation of a protective Al_2O_3 layer that act as a kinetic barrier to AlH_3 decomposition process in air.

- 2) The consequences of postulated accident scenarios leading to fully-discharged alane dust cloud deflagration and potential fires are likely to be more severe due to the higher ΔP_{MAX} , $(dP/dt)_{MAX}$, ES , and K_{St} values compared to those of charged alane dust.
- 3) For fully-discharged alane dust cloud in air, ΔP_{MAX} corresponded to 250 g/m^3 dust concentration in the Kühner vessel and 10-kJ ignition energy. For this series of deflagration tests, the dust concentration covered the range between 125 and 250 g/m^3 . For deflagration tests with charged alane dust, ΔP_{MAX} of 4.6 bar-g was achieved at 125 g/m^3 dust concentration and 2.5 kJ ignition energy. The dust concentration for this series of deflagration tests covered the range between 30 and 125 g/m^3 .
- 4) For the fully-discharged alane dust, the rate of pressure rise was measured as a function of dust concentration range (125 to 250 g/m^3). The measured $(dP/dt)_{MAX}$ was 4,082 bar/s at 250 g/m^3 dust concentration. For the charged alane dust, the rate of pressure rise was measured as a function of dust concentration in the range 30 to 125 g/m^3 . The measured $(dP/dt)_{MAX}$ was 3,000 bar/s at dust concentration of 125 g/m^3 .
- 5) Both types of dust were classified as Class-II combustible dusts based on their calculated ES values as depicted in Table 4.

Table 4

Maximum deflagration pressure rise, ΔP_{MAX} , and maximum rate of pressure rise, $(dP/dt)_{MAX}$, for charged and fully charged alane powder.

	Charged Alane Powder	Fully-Discharged Alane Powder
ΔP_{MAX} , bar-g	4.6	10.3
$(dP/dt)_{MAX}$, bar/s	3,000	4082
K_{ST} , bar-m/s	815	1,100
Explosion Severity, $ES^{(1)}$	4.4	13.5
Dust Classification	Class-II Combustible	

⁽¹⁾ $ES = [\Delta P_{max} \cdot (dP/dt)_{max}]_{test\ dust} / [\Delta P_{max} \cdot (dP/dt)_{max}]_{reference\ dust}$

The reference dust represents the Pittsburgh seam bituminous coal dust.

3.5 Measurement of the minimum autoignition temperature, T_C

Results of the minimum autoignition temperature (T_C) tests for the charged and fully-discharged alane are provided in Fig. 8. A 'No Go' test result signifies ignition was not observed and the 'Go' test result signifies that ignition was observed. The test sample weight in these tests has been varied to ensure that the minimum autoignition temperature is measured at the most easily ignited concentration. The value of T_C of each dust type was the average of the lowest temperature at which ignition is reproducibly observed and the highest temperature at which ignition is not observed at a given dust concentration. As an example for the charged alane dust, the lowest temperature at which ignition is reproducibly observed was 220°C and the highest temperature at which ignition was not observed was 180°C. Hence, the value of T_C for charged alane would be 200°C (observed at 69 mg dust weight). For the more energetic fully-discharged alane, the lowest temperature at which ignition is reproducibly observed was 720°C and the highest temperature at which ignition was not observed was 700°C. Hence the value of T_C for charged alane would be 710°C (observed at 69 mg dust weight). It should also be noticed that for both dust types, the test results were 'No Go' at the lower test sample weight (*i.e.*, 40 mg).

Fig. 8. Minimum autoignition temperature of charged and fully-discharged alane (the solid circles correspond to the charged alane samples and the open circles correspond to the fully-discharged alane).

3.6 Measurement of the minimum explosible concentration, MEC

The Kühner test vessel (20 L) was employed for conducting the alane dust cloud *MEC* tests. The results of these *MEC* tests are provided in Figs. 9 and 10 for the charged and fully-discharged states of alane. As can be seen from Fig. 9, the *MEC* value of charged alane dust was 30 g/m³. At this dust concentration, the deflagration pressure exceeded the 1 bar-g criterion. The corresponding igniter energy for this series of *MEC* tests was 2.5 kJ. For the fully-discharged alane, the *MEC* value was 125 g/m³. At this dust concentration, the deflagration pressure exceeded the 1 bar-g criterion and the corresponding igniter energy for this series of *MEC* tests was 10 kJ.

Fig. 9. Deflagration pressure (bar-g) as a function of dust concentration (g/m³) for charged and fully-discharged alane.

Fig. 10 displays the Go/ No Go test results for the charged and fully-discharged alane dust as a function of the ignition energy and the sample dust concentration. It should be noted that in some of the tests, the charged alane samples ignited inside the Kühner test vessel even before the igniter energy was introduced and the corresponding dust concentration covered the range between 65 and 100 g/m³. Similarly it was observed in some of the fully-discharged alane tests,

the dust ignited inside the Kühner test vessel before the igniter energy was introduced. These experimental observations are indicative of the strong air reactivity of both alane dust types and, thus, have safety implications in postulated accident scenarios involving PEMFC vehicular collisions leading to dispersal of the on-board stored alane (fresh and/ or spent) powder.

Fig. 10. Go / No Go test results vs. ignition energy for MEC determination of alane dust types (charged and fully-discharged). The solid diamonds signify the fully-discharged alane and the open circles signify the charged alane samples.

3.7 Measurement of the minimum ignition energy, MIE

For each of the two alane dust types being examined, the experimentally determined *MIE* value was the minimum energy level (in mJ) sufficient to ignite the dust cloud. The standard protocol (ASTM E-2019-03, 2008) describes the determination of a single *MIE* value by calculating the average of the minimum energy level just sufficient to ignite the dust cloud and the highest of the energy level at the same concentration not capable of igniting the dust cloud in successive repeat tests. As can be seen from Fig. 11, both types of alane dust clouds have an *MIE* value of less than 10 mJ. In the *MIE* test series of the alane fully-discharged state, the applied ignition energy covered the range between 10 and 62.4 mJ. For the *MIE* test series of the alane charged state, the applied ignition energy covered the range between 10 and 33.3 mJ. Such low

MIE values (< 10 mJ) of both alane states have safety implications during postulated PEMFC vehicular collisions leading to dispersal of the on-board stored alane powder in air where the generated dust cloud can easily ignite by an external ignition source with energy < 10 mJ.

Fig. 11. Minimum ignition energy (*MIE*) of charged and fully-discharged alane. The solid diamonds signify the fully-discharged alane and the open circles signify the charged alane samples.

3.8 Summary

In the present experimental research program, dust cloud combustion characterization parameters of alane in its charged and fully-discharged states were measured in accordance with *ASTM* standardized test protocols (*ASTM* E-1226-05, 2005; *ASTM* E-1491-06, 2006; *ASTM* E-1515-07, 2007; *ASTM* E-2019-03, 2008). The results of these tests are summarized in Table 5 (*vide infra*). The measured parameters included ΔP_{MAX} , $(dP/dt)_{MAX}$, T_C , *MEC*, and *MIE*. The volume-normalized maximum rate of pressure rise index (K_{St}) was calculated, using Eq. (1) and used for classify the alane hazard class. Moreover, the corresponding parameters of the *ASTM* reference materials (*Pittsburgh seam coal* and *Lycopodium spores*) were measured and reported in Table 5.

Table 5

Summary of results for alane (in charged and fully-discharged states) dust clouds deflagration parameters.

Parameter	Alane Dust Type		ASTM Reference Materials (<i>Current Work</i>)	
	Charged	Fully-Discharged	Pittsburgh Seam Coal	Lycopodium Spores
	Dust $\bar{d}_p = 75 \mu\text{m}$			
ΔP_{MAX} , bar	4.6	10.3	7.3	7.4
$(dP/dt)_{MAX}$, bar/s	3,000	4,082	426	511
K_{St} , bar-m/s ^(a)	815	1,100	124	139
<i>Explosion Severity (ES)</i>	4.4	13.5		
<i>Dust class</i>	Class-II Combustible		St-1	St-1
T_C , °C	200	710	585	430
MEC , g/m ³	30	125	65	30
MIE , mJ ^(b)	< 10	< 10	110	17

Footnotes:

- (a) Explosion severity index $K_{St} = ((dP/dt)_{MAX}) \cdot V^{1/3}$, bar-m/s (Eq. (1) where V = volume of the Kühner vessel = 20 liters = 0.02 m³)
- (b) The lowest controllable ignition spark energy in our test apparatus is 9 to 10 mJ. Because the material sample ignited during the test at the lowest controllable energy setting in the test apparatus, the dust MIE value is reported as < 10 mJ.

4. Conclusions and recommendation for future work

4.1 Conclusions

This study discussed the results of an experimental research program carried out to determine dust cloud combustion characterization parameters of alane powder in its charged and fully-discharged states. The following conclusions can be drawn from the results of this study:

- If solid-state alane is to be pursued for H₂ storage in mobile applications like the on-board vehicular application, R&D effort has to be continued to identify more practical and cost effective approaches for off-board recharging/ rehydrogenation of the spent fuel (which is primarily Aluminum powder).
- Fully-discharged alane dust is more air reactive compared to the charged alane state. This conclusion is supported by the observed higher values of ΔP_{MAX} , $(dP/dt)_{MAX}$, ES index, and K_{St} index of discharged alane dust compared to the corresponding values of charged alane dust. The higher air reactivity of fully-discharged alane dust compared to the charged alane can be attributed to the higher surface energy (J/m²) of Al compared to α -AlH₃. More specifically, Al (100) surface has a surface energy of 0.94 J/m² and Al (111) surface has a surface energy of 1.1J/m² (Kuznetsov et al., 1998). By comparison, the surface energy of α -AlH₃ (100) and

(111) are 0.69 J/m^2 and 0.70 J/m^2 , respectively (Vajeeston et al., 2011). The higher the surface energy, the more reactive the surface would be.

- The tendency of discharged alane dust to be more explosible in air has safety implications that should be addressed in the design stage of systems (whether in mobile or stationary applications) that use alane powder for H_2 storage.
- Accidental dispersal of charged alane dust in air is also problematic from a fire safety standpoint as supported by observation that T_C and MEC values of charged alane dust are about 28% and 24%, respectively, of T_C and MEC values of fully-discharged alane dust.
- Both charged and fully-discharged alane dust have low MIE values ($< 10 \text{ mJ}$) and, thus, can be easily ignited. This conclusion presents another safety concern in postulated accident scenarios where alane dust becomes suspended in air in conjunction with presence of an external source of energy $< 10 \text{ mJ}$.
- The core insights and critical data provided by in this study are useful for quantifying risks associated with use of this solid-state medium for H_2 storage in mobile applications such as PEMFC powered light-duty vehicles. Additionally, these insights can be used for supporting development and promulgation of H_2 safety standards, augmenting H_2 storage material property data such as the IEA/DOE/SNL hydride databases,¹⁰ and for designing adequate engineered safety features (ESF) such as explosion relief venting and isolation devices.

4.2 Recommendations for future work

Similar to the dust cloud combustion characterization tests performed under this research program, it would be useful to build on the work done by Sandrock et al. (2005) by performing additional tests to determine the impact of adding dopants such as LiH and Ti (which are intended to improve $\alpha\text{-AlH}_3$ thermal decomposition kinetics) on the dust cloud combustion parameters. The insights of these additional tests are particularly important because dopants such as Ti powder could cause the metastable $\alpha\text{-AlH}_3$ to become unstable even at ambient temperature (Graetz et al., 2011).

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¹⁰ IEA/DOE/SNL Hydride databases, Hydride Information Center, Sandia National Laboratories, <http://hypark.ca.sandia.gov>

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Table 1
Critical failure modes and failure causes for the off-board regenerable alane system (Khalil, 2011a).

Critical Failure Modes	Failure Causes
1. Failure to transport the fresh AlH ₃ powder (fresh fuel) through the on-board system.	Failure of the variable-speed motor to operate or jamming of the connected driving piston leading to failure to deliver the fresh AlH ₃ to the thermolysis reactor and, hence, failure to generate H ₂ gas to feed the on-board PEM fuel cells.
2. Failure of thermal management of the on-board AlH ₃ thermolysis reactor.	Failure of the H ₂ burner or the pump that circulates the thermos-fluid heat transfer medium that heats the thermolysis reactor.
3. Accidental exposure of the charged alane (fresh fuel) or fully-discharged alane (spent fuel) powder to ambient air leading to dust cloud explosion.	Rupture of the pressure boundary of any of the following components in the on-board system: charged alane (fresh fuel) thermolysis reactor, connecting pipes, fully-discharged alane (spent fuel) separation chamber or the spent fuel collection tank.

Table 2Dust classification¹ based on the K_{St} value.

Dust Class	K_{St} (bar-m/s)	Dust Cloud Characteristics
<i>St-0</i>	0	None explosive. Dust is incapable of propagating a deflagration.
<i>St-1</i>	> 0 and ≤ 200	Weak explosibility.
<i>St-2</i>	> 200 and ≤ 300	Strong explosibility.
<i>St-3</i>	> 300	Very strong explosibility.

¹ Source: OSHA report 3371-008. <https://www.osha.gov/Publications/337/combustible-dust.pdf>

Table 3

Summary of reference materials dust cloud combustion characteristics in Air.

Deflagration Parameters	Pittsburgh Seam Coal Dust	Lycopodium Spores	Pittsburgh Seam Coal Dust	Lycopodium Spores
	<i>(this work)</i>		<i>(per ASTM standards)</i>	
Maximum Deflagration Pressure Rise ΔP_{MAX} , bar-g	7.3	7.4	7.0	7.0
Maximum Rate of Pressure Rise $(dP/dt)_{MAX}$, bar/s	426	511	430	555
Volume-normalized maximum rate of pressure rise, K_{St} , bar-m/s	124	139	117	151
Dust class based on K_{St}	<i>St-1</i>	<i>St-1</i>	<i>St-1</i>	<i>St-1</i>
MEC , g/m ³	65	30	80	45
Minimum Ignition Temperature (T_C), °C	585	430	600	460

Table 4

Maximum deflagration pressure rise, ΔP_{MAX} , and maximum rate of pressure rise, $(dP/dt)_{MAX}$, for charged and fully charged alane powder.

	Charged Alane Powder	Fully-Discharged Alane Powder
ΔP_{MAX} , bar-g	4.6	10.3
$(dP/dt)_{MAX}$, bar/s	3,000	4082
K_{ST} , bar-m/s	815	1,100
Explosion Severity, $ES^{(1)}$	4.4	13.5
Dust Classification	Class-II Combustible	

$$^{(1)} ES = [\Delta P_{max}, (dP/dt)_{max}]_{test\ dust} / [\Delta P_{max}, (dP/dt)_{max}]_{reference\ dust}$$

The reference dust represents the Pittsburgh seam bituminous coal dust.

Table 5

Summary of results for alane (in charged and fully-discharged states) dust clouds deflagration parameters.

Parameter	Alane Dust Type		ASTM Reference Materials (<i>Current Work</i>)	
	Charged	Fully-Discharged	Pittsburgh Seam Coal	Lycopodium Spores
Dust $\bar{d}_p = 75 \mu\text{m}$				
ΔP_{MAX} , bar	4.6	10.3	7.3	7.4
$(dP/dt)_{MAX}$, bar/s	3,000	4,082	426	511
K_{St} , bar-m/s ^(a)	815	1,100	124	139
<i>Explosion Severity (ES)</i>	4.4	13.5		
<i>Dust class</i>	Class-II Combustible		St-1	St-1
T_C , °C	200	710	585	430
MEC , g/m ³	30	125	65	30
MIE , mJ ^(b)	< 10	< 10	110	17

Footnotes:

- (a) Explosion severity index $K_{St} = ((dP/dt)_{MAX}) \cdot V^{1/3}$, bar-m/s (Eq. (1) where V = volume of the Kühner vessel = 20 liters = 0.02 m³)
- (b) The lowest controllable ignition spark energy in our test apparatus is 9 to 10 mJ. Because the material sample ignited during the test at the lowest controllable energy setting in the test apparatus, the dust MIE value is reported as < 10 mJ.

Fig. 1. A schematic diagram of a baseline design of the off-board regenerable alane system (Khalil, 2011a).

Fig. 2. Schematic diagram of the Kühner 20-liter spherical explosion test apparatus.

Fig. 3. Simplified diagram of the automated test rig including the data acquisition system and the Kühner test apparatus.

Fig. 4. Godbert-Greenwald (G-G) furnace for determination of dust cloud minimum ignition temperature (T_C).

Fig. 5. Modified Hartmann apparatus used for determining dust's minimum ignition energy (*MIE*).

Fig. 6. Laboratory glove box where alane dust samples are prepared and stored before being tested.

Fig. 7. Reaction enthalpy and Gibbs free energy for AlH_3 decomposition as a function of temperature.

Fig. 8. Minimum autoignition temperature of charged and fully-discharged alane (the solid circles correspond to the charged alane samples and the open circles correspond to the fully-discharged alane).

Fig. 9. Deflagration pressure (bar-g) as a function of dust concentration (g/m^3) for charged and fully-discharged alane.

Fig. 10. Go / No Go test results vs. ignition energy for MEC determination of alane dust types (charged and fully-discharged). The solid diamonds signify the fully-discharged alane and the open circles signify the charged alane samples.

Fig. 11. Minimum ignition energy (*MIE*) of charged and fully-discharged alane. The solid diamonds signify the fully-discharged alane and the open circles signify the charged alane samples.