Dust cloud combustion characterization of a mixture of LiBH_4 destabilized with MgH_2 for reversible H_2 storage in mobile applications

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ABSTRACT

This study discusses results of an experimental program to determine dust cloud combustion characteristics of $2\text{LiBH}_4 + \text{MgH}_2$ binary system in air. The determined parameters of hydrided and partially-dehydrided states of this system include: maximum deflagration pressure rise (P_{MAX}), maximum rate of pressure rise $(dP/dt)_{\text{MAX}}$, minimum ignition temperature (T_C), minimum explosible concentration (MEC), minimum ignition energy (MIE), and explosion severity index (K_{St}). Impact of dust particle size on the measured parameters is evaluated for the partially-dehydrided state. For dust of same mean particle size, results show the hydrided state to be more explosible in air compared to its partially-dehydrided state. Moreover, MIE of the partially-dehydrided mixture is identified in the test with lowest ignition delay time (IDT) and highest dust cloud concentration (DC). Taguchi's mixed-levels design of experiments (DoE) methodology is employed to calculate dust's MIE response surface as a function of DC and IDT . The one-at-a-time effect and interaction effect between DC and IDT on dust MIE are determined. The core insights of this contribution are useful for quantifying risks in mobile and stationary H_2 storage applications, informing H_2 safety standards, and augmenting property databases of H_2 storage materials.

Keywords: dehydrogenation; deflagration; dust cloud; hydrogen storage; lithium borohydride; magnesium hydride

1. Introduction

The Office of Energy Efficiency & Renewable Energy (EERE) of the U.S. Department of Energy (DOE) funded numerous independent material-based¹ R&D projects and Centers of Excellence (CoEs) to identify candidate hydrogen storage materials for on-board use in light-duty vehicles and for off-board uses such as stationary power generation and refueling infrastructure [1]. Understanding the reactivity of hydrogen storage materials continues to be one of the key targeted metrics of the DOE-funded independent and collaborative R&D efforts in order to demonstrate the safe use of these candidate materials and, hence, to support the widespread commercialization of hydrogen-fueled vehicles. Khalil's research [2-10], under DOE

¹ Material-based R&D includes reversible metal hydrides (such as borohydrides and destabilized metal hydrides), regenerable chemical hydrogen storage materials (such as liquid chemical hydrogen carriers and boron-based materials, and hydrogen sorbents (such as activated carbon metal-organic framework materials).

contract award # DE-FC36-07GO17032, provides examples of experimental and theoretical studies performed to better understand hydrogen storage materials reactivity and safety for on-board applications.

Lithium borohydride (LiBH_4), a low-Z complex metal hydride with a high H_2 gravimetric storage capacity, is one of the candidate solid-state hydrogen storage media that has been evaluated for use in an array of applications including transportation, stationary power, grid energy storage applications to facilitate penetration of the intermittent renewable energy sources such as wind and solar, portable power (e.g., gen-sets, consumer electronics, etc.), material handling equipment (MHE) such as forklift trucks, and airport ground support equipment (GSE) such as baggage and pushback tractors. Details of DOE 2015 and 2020 technical, cost and safety targets for these applications are provided in DE-FOA-0000827 [11].

Pure LiBH_4 has a molecular weight of 21.78 g/mole, density of 0.67 g/ml, 18.37 wt.% H_2 ($\approx 121 \text{ kg/m}^3 \text{ H}_2$), melting temperature of 268 °C, and enthalpy of formation (ΔH°_f) of -190 kJ/mole . This material can be thermodynamically destabilized using magnesium hydride (MgH_2) additive to improve its de-/rehydrogenation kinetics. Of interest to this research is the composite system $2\text{LiBH}_4 + \text{MgH}_2$ (2:1 molar ratio) where both LiBH_4 and MgH_2 are complex anion hydrides. Pure MgH_2 has a molecular weight of 26.32 g/mole, density of 1.45 g/ml, 7.6 wt. % H_2 ($\approx 110 \text{ kg/m}^3 \text{ H}_2$), melting temperature of 690 °C, and enthalpy of formation (ΔH°_f) of -75.73 kJ/mole .²

Hydrogen release from dehydriding pure LiBH_4 is 13.8 wt. % H_2 is described by Eq. (1):

This reaction takes place at 410 °C and shows that 75% of H_2 is desorbed at this temperature. However, the absorption side of this reaction is not possible under moderate conditions, i.e., at H_2 pressures < 100 bar and temperatures < 350 °C. Bosenberg et al. [12] and Orimo et al. [13] were able to hydride a mixture of boron (B) and lithium hydride (LiH) at conditions of 600 °C and 350 bars for 12 hours.

Beattie et al. [14] reported that H_2 desorbs with slow kinetics from MgH_2 at atmospheric pressure and $\approx 400 \text{ °C}$ according to Eq.(2). In the current study, we calculated a desorption enthalpy of 75.73 kJ/mole for this reaction using *HSC Chemistry*® [15]. Pozzo and Alfe [16] reported an experimentally measured value of $76.1 \pm 1 \text{ kJ/mole}$ for this desorption enthalpy and Felderhoff and Bogdanovic [17] calculated the dissociation pressure curve of MgH_2 as a function of temperature in the range 250-500 °C.

² The standard enthalpies of formation (ΔH°_f) and densities of LiBH_4 and MgH_2 are calculated in this work using *HSC Chemistry*, rev. 6.12, [13].

In the hydrided state of $2\text{LiBH}_4 + \text{MgH}_2$, the system contains a mixture of LiBH_4 and MgH_2 with 2:1 molar ratio. In its partially-dehydrided state, the system contains, asides from H_2 gas release, a powder mixture of LiBH_4 , MgH_2 , LiH , and MgB_2 . Dehydriding this composite system is described by Eq. (3) (*vide infra*):

The calculated H_2 release from this reaction is 11.45 wt. % H_2 . Vajo and Skeith [18] reported that the in-situ formed MgB_2 from this reaction tends to stabilize the dehydrided state and effectively destabilizes the LiBH_4 . Hydrogen absorption in LiH and B to form LiBH_4 takes place at 690°C and 200 bars (Zuttel et al. [19] and Bosenberg et al. [20]) and the absorption reaction requires a long time (> 12 hours). Barkhordarian et al. [21] called the $2\text{LiBH}_4 + \text{MgH}_2$ composite system a reactive hydride composite (RHC) and rehydriding this RHC is possible at pressures of about 50 bar H_2 and temperatures below 300°C (Vajo and Skeith [18], Barkhordarian et al. [21] & Bosenberg et al. [12]).

The objectives of the present study are as follows: 1) Discuss the results of an experimental program carried out to determine the dust cloud combustion characterization parameters of $2\text{LiBH}_4 + \text{MgH}_2$, in both its hydrided and partially-dehydrided states, for reversible H_2 storage in a wide range of mobile applications, 2) Evaluate impact of dust cloud mean particle size on the measured characterization parameters of this composite system, and 3) Use Taguchi's mixed-levels design of experiments (*DoE*) methodology [22] to assess the one-at-a-time effect and interaction effect of dust cloud concentration (*DC*) and test ignition delay time (*IDT*) on the dust cloud ignition energy. The study contributes novel insights to advance the current state of knowledge beyond what has been published to describe the thermodynamics and kinetics of dehydriding and rehydriding of the $2\text{LiBH}_4 + \text{MgH}_2$ composite system [12-21, 27-30]. Specifically, the insights generated from this contribution could be used for: i) improving the safe deployment of $2\text{LiBH}_4 + \text{MgH}_2$ composite system for H_2 storage in a wide range of mobile and stationary applications. ii) filling gaps in existing state of knowledge of potential hazards associated with use and transport of this energetic binary system. iii) providing data of significance to performing adequate risk quantification, process hazard analysis per NFPA-654 requirements [31]. iv) developing risk mitigation methods based on the identified hazards.

Nomenclature

<i>DC</i>	dust cloud concentration, g/m^3
<i>IDT</i>	ignition delay time, ms
<i>P</i>	pressure, bar-g
<i>t</i>	time, s
<i>V</i>	volume of the Kühner spherical test vessel, m^3

Dust cloud combustion characterization parameters

<i>K_{St}</i>	explosion severity index, bar-m/s, described by the <i>Cube Law</i> : $(dP/dt)_{\text{MAX}} V^{1/3}$
<i>MEC</i>	minimum explosible concentration, g/m^3
<i>MIE</i>	minimum ignition energy, mJ

P_{MAX}	maximum deflagration pressure rise, bar-g, above pressure in the 20-L Kühner test vessel at the time of ignition (1 bar-abs), during the course of a deflagration test
$(dP/dt)_{MAX}$	maximum rate of pressure rise, bar/s, in the 20-L Kühner test vessel during the course of a deflagration test
T_C	minimum autoignition temperature, °C

2. Experimental

2.1 Test methods for dust cloud combustion characterization

All tests discussed in this section are performed in accordance with *ASTM* standardized protocols [23-26] in order to generate reproducible and meaningful results to support future materials reactivity and safety studies of H₂ storage systems. In addition to their use for benchmarking purpose, the *ASTM* reference materials (Pittsburgh seam coal dust and Lycopodium spores) are also used for calibrating the test equipment described in this section. Unless otherwise stated, all tests are carried out on dusts that are dry (moisture content < 5%) and sieved through a No. 200-mesh screen (75 µm opening size).

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

The measured dust cloud combustion characterization parameters in accordance with this standardized test method [23] include P_{MAX} and $(dP/dt)_{MAX}$ which are determined by carrying out a series of tests over a wide range of dust concentrations (g/m³). To perform these tests, dust cloud is formed in the Kühner 20-liter (0.02 m³) spherical explosion test apparatus (Fig. 1) 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 occurs 60 ms of delay time (*DT*) after 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. The Kühner test apparatus is calibrated by performing the deflagration tests using the reference materials (Pittsburgh seam coal dust and Lycopodium spores). *ASTM E-1226* [23] provides a detailed discussion on selecting the initial dust concentration (g/m³) and how the optimal dust concentration is determined.

Fig. 1 - Schematic diagram of the Kühner 20-liter spherical explosion test apparatus.

The K_{St} index (bar-m/s), an internationally-recognized parameter that allows comparisons to be made between the test material and standardized reference dusts, is the volume-normalized maximum rate of pressure rise $(dP/dt)_{MAX}$ measured at the optimum dust concentration. Based on the calculated K_{St} value (rounded to the nearest integer), dusts are classified into four hazard classes as shown in Table 1 (*vide infra*).

Table 1 - Dust classification³ 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.

2.1.2 Minimum autoignition temperature (T_C) of combustible dusts

Test is performed according to an ASTM standardized test protocol [24] to determine T_C at which a dust cloud will autoignite when exposed to air heated to preset temperatures in an electrically heated furnace (Fig. 2). 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 , namely: dust concentration, dust particles size distribution, moisture content of the

³ Source: OSHA report 3371-008. <https://www.osha.gov/Publications/337/combustible-dust.pdf>

dust, and type of furnace⁴ used for heating the dust/air sample. Hence, 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 [24].

The employed 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 Figure 2. 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.

Fig. 2 - Godbert-Greenwald (G-G) furnace for determination of dust cloud minimum ignition temperature (T_C).

The dust is heated as it cascades down the vertical tube furnace (Fig. 2). 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

⁴ 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.

observed (*i.e.*, test result is a *No-Go*). ASTM E-1491 [24] provides sufficient guidance on selecting the initial dust concentration (in g/m^3) 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.

2.1.3 Minimum explosible concentration (MEC) of combustible dusts

This test describes a standardized protocol [25] for measuring *MEC* of an air-dispersed combustible dust capable of propagating a deflagration. The measured *MEC* value is dependent on 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. 1) and the dust 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. After plotting P_{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 $P_{MAX} > 1$ bar-g and the lowest concentration that produces a $P_{MAX} > 1$ bar-g. Again, P_{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 [26] determines *MIE* of a dust cloud in air by an igniter-generated spark. The modified Hartmann apparatus (Fig. 3) 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. In accordance with this standard [24], 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. Moreover, knowing the likelihood of ignition is important to designing adequate engineered safety features (*ESF*) to mitigate the risks of dust deflagration.

Fig. 3 - Modified Hartmann apparatus used for determining dust's minimum ignition energy (*MIE*).

To perform the *MIE* test, the dust sample is placed in a dish-shaped sample holder at the base of the tube (Fig. 3) and 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. 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 time⁵, the *MIE* value can be estimated by varying the dust concentration and the spark discharge energy. The *MIE* value 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 (that is: $E_1 < MIE < E_2$). 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

⁵ 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.

procedure is repeated at different dust concentrations until the lowest minimum ignition energy value is determined.

2.2 Dust sample preparation

The high-purity (99.9%) test materials (LiBH_4 powder and MgH_2 powder) were mixed using a laboratory SPEX mill. Samples, in 2 grams batches, were ball milled for one hour. The $2\text{LiBH}_4 + \text{MgH}_2$ powder samples were sieved with an ATM Corporation Sonic Sifter Separator model L3 and sieving was conducted for 30 minutes. This device employs two sieving motions: a vertical oscillating column of air, to prevent particle attrition and screen wear, and a repetitive mechanical pulse to help reducing sieve binding and rearranges clustered particles formed by agglomeration. The nominal sizes of the openings of sieve screens are specified in ASTM E11-04.⁶ The test samples were classified using U.S. standard 40, 70, 100, and 200 mesh screens.

Per ASTM Standards [23-26], two reference materials, namely, Pittsburgh seam coal dust and Lycopodium spores were employed to calibrating the test equipment and to provide baselines to compare against the samples experimental measurements. The reference samples passed through a 200-mesh screen ($d_p < 75 \mu\text{m}$). Also, drying of samples was done per ASTM testing requirements ($< 5\%$ moisture). The moisture content was determined by drying the samples in air at 60°C .

3. Results and discussion

This section is divided into the following eight subsections: 3.1) describes the ASTM reference materials' tests and 3.2) describes HSC Chemistry® software package [15] dehydrogenation enthalpy calculations to quantify the destabilizing effect of MgH_2 on dehydrating LiBH_4 . Subsections 3.3 through 3.6 discuss the results of dust cloud characterization parameters (P_{MAX} , $(dP/dt)_{\text{MAX}}$, T_C , MEC, and MIE, respectively) of the hydrided and partially-dehydrided states of this composite system. Subsection 3.7 discusses Taguchi's mixed-levels design of experiments (DoE) methodology [22] for quantifying the one-at-a-time effect and first-order interaction effect between DC and IDT (i.e., the main factors) on the dust cloud ignition energy (i.e., the response variable). Finally, subsection 3.8 summarizes key experimental observations and major insights.

3.1 Determination of dust cloud combustion characterization parameters of Pittsburgh seam coal dust and Lycopodium spores

The Kühner apparatus (used for determination of the parameters P_{MAX} , $(dP/dt)_{\text{MAX}}$, 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 standardized tests [23-26] using the aforementioned reference dusts. Table 2 compares the deflagration parameters of the reference materials as experimentally determined from this work versus the values reported in the applicable ASTM standards. Also provided in Table 2 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

⁶ ASTM E11-04. (1995). Standard Specifications for Wire Cloth and Sieve for Testing Purposes. West Conshohocken, PA: ASTM International.

reported values in ASTM standards was 5.7% and the maximum deviation was 33.3% (related to the *MEC* tests).

Table 2 - 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 Pressure Rise P_{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>
<i>MEC</i> , g/m ³	65	30	80	45
Minimum Ignition Temperature (T_C), °C	585	430	600	460

3.2 LiBH_4 destabilization by addition of MgH_2

Table 3 (*vide infra*) shows our calculated values of the dehydrogenation enthalpies [$(\Delta H)_f^\circ$] of pure LiBH_4 , pure MgH_2 , and the composite mixture $\text{LiBH}_4+\text{MgH}_2$ (2:1 molar ratio). The calculations were performed using the *HSC Chemistry* software package [15]. As can be seen in Table 3, the dehydrogenation enthalpies indicate that adding MgH_2 to LiBH_4 in the molar ratio 2:1 leads to destabilizing the borohydride by reducing the endothermic energy required to remove H_2 from LiBH_4 according to Eq. (3). In this reaction, the endothermic dehydrogenation enthalpy is 46.52 kJ/mole H_2 (@ 167 °C and 1 bar) as calculated by *HSC Chemistry* [15]. Using X-ray analysis, Vajo and Olson [29] confirmed the formation of the reaction products MgB_2 and LiH upon dehydrogenation of the $2\text{LiBH}_4+\text{MgH}_2$ system and they also cycled this reversible reaction five times without degradation.

Table 3 – LiBH₄ destabilization by addition of MgH₂			
Dehydrogenation Enthalpy	Lithium Borohydride (LiBH ₄)	Magnesium Hydride (MgH ₂)	Lithium Borohydride+Magnesium Hydride System (2LiBH ₄ +MgH ₂)
Dehydrogenation enthalpy (kJ/mole H ₂)	67.61 @ 410 °C and 1 bar H ₂ pressure. $\Delta G_R = - 0.268$ kJ/mole H ₂	79.78 @ 290 °C and 1 bar H ₂ pressure. $\Delta G_R = - 0.214$ kJ/mole H ₂	46.53 @ 167 °C and 1 bar H ₂ pressure. $\Delta G_R = - 0.034$ kJ/mole H ₂
% reduction in LiBH ₄ dehydrogenation enthalpy	$(67.61 - 46.53)/67.61 \approx 31.2\%$		

Table 3 also shows $\approx 31.2\%$ estimated enthalpy reduction of this reaction, Eq. (3), compared to dehydrogenating pure LiBH₄, Eq. (1). Moreover, the decrease in the required dehydrogenation temperature due to the addition of MgH₂ is $410\text{ °C} - 167\text{ °C} = 243\text{ °C}$. Because the dehydrogenation enthalpy of pure LiBH₄ is high, the equilibrium H₂ pressure is relatively low and, consequently, the required dehydrogenation temperature is high $\approx 460\text{ °C}$ (Vajo & Olson, [29]). However, when this borohydride is destabilized with the hydride additive (MgH₂), the dehydrogenation enthalpy of the binary system is reduced which increases the equilibrium hydrogen pressure and, thus, the required dehydrogenation temperature decreased to $\approx 167\text{ °C}$ (Vajo & Skeith [18] & Vajo & Olson [29]). Our insights are consistent with the findings discussed by Zuttel et al. [19] who also investigated the stability of tetraborohydrides (containing [BH₄]⁻ group), such as LiBH₄, for H₂ storage in mobile applications. They also found that adding SiO₂ to LiBH₄ lowers the desorption temperature but due a catalytic effect rather than due to a destabilization effect [19]. Finally, According to our *HSC Chemistry*® calculations (Table 3), the dehydrogenation temperature of pure MgH₂ is 290 °C and, hence, MgH₂ dehydrogenation temperature is also decreased by 123 °C (which is the difference between 290 °C and 167 °C). In other words, MgH₂ is also destabilized in the binary system as it is demonstrated by the decrease in the dehydrogenation enthalpy from 79.78 kJ/mole H_2 for pure MgH₂ to 46.32 kJ/mole H_2 for the binary system.

As discussed in subsections 3.3 through 3.7, the measured values of dust cloud characterization parameters P_{MAX} , $(dP/dt)_{MAX}$, and the calculated K_{St} index of the hydrided state of this composite system are greater than those of the partially-dehydrided state which could be attributed to the destabilizing effect of MgH₂ in the hydrided mixture 2LiBH₄+MgH₂. Moreover, the parameters T_C , MEC , and MIE of the hydrided state are found to be smaller than those of the partially-dehydrided state. These experimental observations are consistent with the findings reported by Vajo and Skeith [18] and Bosenberg et al. [12] which were based on thermodynamic and kinetic calculations, interpretation of the Van't Hoff plots for destabilized LiBH₄+MgH₂, pure LiBH₄ and pure MgH₂ as well as inspection of X-ray diffraction (XRD) patterns from 2LiBH₄+MgH₂.

Our experimental observations are also consistent with the conclusions made by Bosenberg et al. [12] who used high-pressure differential scanning calorimetry (HP-DSC), XRD analysis, and thermogravimetric (TG) measurements for the desorption reaction of $2\text{LiBH}_4 + \text{MgH}_2$.

3.3 Measurement of the maximum pressure rise, P_{MAX} , and maximum rate of pressure rise, $(dP/dt)_{MAX}$

For the hydrided and partially-dehydrided states of the binary system ($2\text{LiBH}_4 + \text{MgH}_2$), P_{MAX} , and $(dP/dt)_{MAX}$, 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 P_{MAX} and $(dP/dt)_{MAX}$ were the averages of the highest values of repeat tests over the range of concentrations of each of the dust types being examined (i.e., hydrided and partially-dehydrided samples).

Figures 4 through 7 summarize the measured values of P_{MAX} , and $(dP/dt)_{MAX}$ for the hydrided and partially-dehydrided states of the $2\text{LiBH}_4 + \text{MgH}_2$ composite system. The key insights that can be derived from this series of tests are as follows:

- 1) The partially-dehydrided dust cloud (with mean particle sizes 75 μm , 75-150 μm , and 420 μm , respectively) had the lowest P_{MAX} and $(dP/dt)_{MAX}$ values and, hence, the lowest K_{St} index compared to corresponding values of the hydrided state. With the exception of the finest dust (i.e., with mean particle size 75 μm), the partially-dehydrided dust was classified as weakly explosible (based on its calculated K_{St} value as shown in Table 5).
- 2) The higher air-reactivity of the hydrided $2\text{LiBH}_4 + \text{MgH}_2$ dust can be attributed to the MgH_2 destabilizing effect on LiBH_4 which made this borohydride more reactive. This higher reactivity manifested itself in greater measured values of P_{MAX} , $(dP/dt)_{MAX}$, and calculated value of K_{St} index. Thus, the hydrided dust was classified as highly explosible (see Table 4).
- 3) From a safety standpoint, postulated accident scenarios leading to hydrided dust cloud deflagration in air (Khalil et al. [8]) would have consequences that are more severe (due to the higher values of P_{MAX} , $(dP/dt)_{MAX}$, and K_{St} index) compared to the partially-dehydrided state of this composite system.
- 4) Tests with the higher dust concentration range (Figs. 4,6,7) required higher ignition energy of 10 kJ to ignite the dust cloud compared to the tests with the lower dust concentration range (Fig. 5) which required lower ignition energy of 2.5 kJ. In both cases, the finest dust ($\bar{d}_p = 75 \mu\text{m}$) resulted in the highest P_{MAX} and highest $(dP/dt)_{MAX}$ (Figs. 4 through 7). This observation can be attributed to the fact that as the dust particle size decreases, the surface area of contact, between particles and surrounding air, increases which makes the dust cloud in air more reactive.

Fig. 4 – Maximum pressure rise, P_{MAX} , and maximum rate of pressure rise, $(dP/dt)_{MAX}$, as a function of dust concentration, DC , for the hydrided $2LiBH_4+MgH_2$. Dust mean particle size: 75 μm . Igniter energy: 10 kJ.

As displayed in Fig. 4, the measured P_{MAX} is 10.7 bar-g and corresponds to 500 g/m³ dust concentration. The igniter energy used in this series of tests is 10 kJ and the dust concentration covered the range between 60 and 500 g/m³. Figure 4 also shows $(dP/dt)_{MAX}$ as a function of the dust concentration range (60 to 500 g/m³). The measured $(dP/dt)_{MAX}$ is 2036 bar/s at 500 g/m³ dust concentration.

For the partially-dehydrided samples, Fig. 5 shows the measured P_{MAX} , as a function of dust concentration (in the range 20 to 60 g/m³) and for dust mean particle sizes of 420 μm , 75-150 μm , and 75 μm , respectively. The employed igniter energy for this dust concentration range is 2.5 kJ. The measured value of P_{MAX} is 3.4 bar-g corresponding to 30 g/m³ dust concentration and 75 μm mean particle size. Fig. 6 shows P_{MAX} as a function of dust concentration in the range 30 to 350 g/m³. The mean particle sizes of the dust samples for this series of tests are 420 μm (coarsest), 75-150 μm , and 75 μm (finest). The igniter energy in this series of tests is 10 kJ. The measured P_{MAX} is 9.9 bar-g corresponding to 350 g/m³ dust concentration and 75 μm mean particle size. Fig. 7 displays $(dP/dt)_{MAX}$ as a function of dust concentration in the range 30 to 350 g/m³. The dust mean particle sizes being tested include 420 μm (coarsest), 75-150 μm (intermediate), and 75 μm (finest). The employed test igniter energy is 10 kJ. The measured $(dP/dt)_{MAX}$ is 1,225 bar/s corresponding to 350 g/m³ dust concentration and 75 μm mean particle size.

Fig. 5 – Maximum pressure rise, P_{MAX} , as a function of dust concentration, DC , for the partially-dehydrated $2LiBH_4+MgH_2$. Mean particle size of dust (*Data Series 1*: 420 μm ; *Data Series 2*: 75-150 μm ; *Data Series 3*: 75 μm). Igniter energy: 2.5 kJ.

Fig. 6 – Maximum pressure rise, P_{MAX} , as a function of dust concentration, DC , for the partially-dehydrided $2\text{LiBH}_4 + \text{MgH}_2$. Mean particle size of dust (series 1: $420\text{ }\mu\text{m}$; series 2: $75\text{-}150\text{ }\mu\text{m}$; series 3: $75\text{ }\mu\text{m}$). Igniter energy: 10 kJ .

Fig. 7 – Maximum rate of pressure rise, $(dP/dt)_{MAX}$, as a function of dust concentration, DC , for the partially-dehydried $2LiBH_4+MgH_2$. Mean particle size of dust (*Data Series 1*: 420 μm ; *Data Series 2*: 75-150 μm ; *Data Series 3*: 75 μm). Igniter energy: 10 kJ.

3.4 Measurement of the minimum autoignition temperature, T_C

Results of T_C tests of the hydrided and partially-dehydried states of $2LiBH_4+MgH_2$ are provided in Figs. 8 through 10. The reason for varying the dust concentration was to ensure that T_C 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 any concentration. The value of T_C was the lowest (150 °C) for the more energetic hydrides state compared to T_C values of the partially-dehydried state which varied according to the mean particle size of the dust cloud. The value of T_C was the lowest (230 °C) for the finest dust cloud (75 μm) and corresponded to a dust mass of 60 mg (Fig. 8). The T_C values were higher than 230 °C as the mean particle size increased but the dust cloud mass also varied (see Figs. 9 and 10).

Fig. 8 – Minimum ignition temperature (T_C), as a function of dust sample mass for the hydrided $2\text{LiBH}_4+\text{MgH}_2$. Mean particle size of dust is $75\text{ }\mu\text{m}$. $T_C = 150\text{ }^\circ\text{C}$. Also shown T_C for the partially-dehydrided $2\text{LiBH}_4+\text{MgH}_2$. Mean particle size of dust (series 3: $75\text{ }\mu\text{m}$). $T_C = 230\text{ }^\circ\text{C}$. Go: signifies a test result where a flame is observed in the test apparatus; No Go: signifies a test result where no flame is observed in the test apparatus.

Fig. 9 – Minimum ignition temperature (T_C), as a function of dust sample mass for the partially-dehydrated $2\text{LiBH}_4 + \text{MgH}_2$. Mean particle size of dust (series 2: 75-150 μm). $T_C = 320^\circ\text{C}$. Go: signifies a test result where a flame is observed in the test apparatus; No Go: signifies a test result where no flame is observed in the test apparatus.

Fig. 10 – Minimum ignition temperature (T_C), as a function of dust sample mass for the partially-dehydrated $2\text{LiBH}_4+\text{MgH}_2$. Mean particle size of dust (series 1: $420\text{ }\mu\text{m}$). $T_C = 270\text{ }^\circ\text{C}$. Go: signifies a test result where a flame is observed in the test apparatus; No Go: signifies a test result where no flame is observed in the test apparatus.

3.5 Measurement of the minimum explosible concentration, MEC

The results of *MEC* tests are provided in Figs. 11 and 12 for the hydride and partially-dehydrated states of $2\text{LiBH}_4+\text{MgH}_2$, respectively. As can be seen from Fig.11, the *MEC* value of hydrided $2\text{LiBH}_4+\text{MgH}_2$ dust mixture (with $75\text{ }\mu\text{m}$ mean particle size) was 30 g/m^3 . At this dust concentration, the deflagration pressure exceeded the 1 bar-g criterion. By comparison, the maximum deflagration pressure was below 1 bar-g for the tests with 20 g/m^3 and 25 g/m^3 dust concentrations. The igniter energy for this series of *MEC* tests was 2.5 kJ.

Fig. 11 – Minimum explosible concentration (*MEC*) as a function of dust concentration, *DC*, for the hydrided $2\text{LiBH}_4+\text{MgH}_2$. Mean particle size of dust: $75\text{ }\mu\text{m}$. Igniter energy: 2.5 kJ.

For the partially-dehydrated state of this composite dust system, Fig. 12 shows that *MEC* of the dust with $75\text{ }\mu\text{m}$ mean particle size was 30 g/m^3 , for dust with a mean particle size in the range $75\text{-}150\text{ }\mu\text{m}$ *MEC* value was 60 g/m^3 , and for the dust with $420\text{ }\mu\text{m}$ mean particle size, *MEC* value was 30 g/m^3 . In this series of *MEC* tests, the igniter energy was 2.5 kJ. Also at the aforementioned dust concentrations, the maximum deflagration pressure exceeded the 1 bar-g criterion.

Fig. 12 – Minimum explosible concentration (*MEC*) as a function of dust concentration, *DC*, for the partially-dehydrated $2\text{LiBH}_4+\text{MgH}_2$. Mean particle size of dust (series 1: 420 μm ; series 2: 75-150 μm ; series 3: 75 μm). Igniter energy: 2.5 kJ.

3.6 Measurement of the minimum ignition energy, *MIE*

For each of the dust type being examined (see Figs. 13 through 16), the experimentally determined *MIE* value was the minimum energy level (in mJ) sufficient to ignite the dust cloud. The standard protocol [26] provides 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. 13, the hydrided dust cloud has a *MIE* value < 9 mJ. In the *MIE* test series of the hydride state, the ignition delay time was 25 ms.

For the partially-dehydrated dust cloud, Fig. 14 shows that *MIE* value was < 9.2 for dust with 75 μm mean particle size. Fig. 15 shows that *MIE* value was between 22 and 47 mJ for the dust with a mean particle size in the range 75-150 μm . Fig. 16 shows that *MIE* was 20 mJ for the dust with a mean particle size of 420 μm . In *MIE* test series, the igniter delay time was 25 ms. It is obvious from the measured data that the bigger the mean particle size of the dust cloud, the more energy would be required to ignite it in air. Moreover, the lower the value of *MIE*, the easier it is to ignite the dust cloud and the higher the probability of occurrence of an external ignition source with energy sufficient to ignite the dispersed dust in air.

It should be noted that for *MIE* test series of the partially-dehydrated dust of 420 μm mean particle size, three ignition delay times (*IDT*) were employed, namely, 40, 50, and 100 ms, respectively. With longer *IDT*, more of the air-suspended particles inside the Kühner vessel will have the opportunity to settle to the bottom before ignition is applied and, hence, do not ignite. Also, the higher the dust cloud concentration inside the vessel, the easier it can ignite with less igniter energy. For the partially-dehydrated dust with 420 μm mean particle size, *MIE* value of 20 mJ occurred when the *IDT* value was 40 ms (i.e., the lowest *IDT*) and the associated dust concentration was the highest (500 g/m^3). Notice from Fig. 16 that all tests with the 250 g/m^3 dust samples and *IDT* values of 40, 50, and 100 ms, respectively, were No Go tests.

Fig. 13 – Minimum ignition energy (*MIE*) as a function of dust concentration (*DC*) for the hydrided $2\text{LiBH}_4+\text{MgH}_2$. Mean particle size of dust: 75 μm . *MIE* < 9 mJ. Ignition delay time: 25 ms. *Go*: signifies a test result where a flame is observed in the test apparatus; *No Go*: signifies a test result where no flame is observed in the test apparatus.

Fig. 14 – Minimum ignition energy (*MIE*) as a function of dust concentration (*DC*) for the partially-dehydrated $2\text{LiBH}_4+\text{MgH}_2$. Mean particle size of dust (series 3: $75\text{ }\mu\text{m}$). *MIE* < 9.2 mJ . *Go*: signifies a test result where a flame is observed in the test apparatus; *No Go*: signifies a test result where no flame is observed in the test apparatus.

Fig. 15 – Minimum ignition energy (MIE) as a function of dust concentration (DC) for the partially-dehydrated $2\text{LiBH}_4+\text{MgH}_2$. Mean particle size of dust (series 2: 75-150 μm). $22 < \text{MIE} < 47 \text{ mJ}$. Go: signifies a test result where a flame is observed in the test apparatus; No Go: signifies a test result where no flame is observed in the test apparatus.

Fig. 16 – Minimum ignition energy (MIE) as a function of dust concentration (DC) for the partially-dehydrated $2\text{LiBH}_4+\text{MgH}_2$. Mean particle size of dust (series 1: 420 μm). $\text{MIE}=20 \text{ mJ}$. Go: signifies a test result where a flame is observed in the test apparatus; No Go: signifies a test result where no flame is observed in the test apparatus.

3.7 Analysis using Taguchi's mixed-levels design of experiments (DoE)

This subsection discusses Taguchi's mixed-levels design of experiments (DoE) methodology [20] for quantifying the one-at-a-time effect (*i.e.*, separate effect) and first-order interaction effect between *DC* and *IDT* (*i.e.*, the main factors) on the dust cloud ignition energy (*i.e.*, the response variable). Also, Taguchi's mixed-levels DoE methodology [22] was employed for calculating the response surface of dust cloud ignition energy as a function of *DC* and *IDT*. The ignition energy data for the partially-dehydrated composite dust with 420 μm mean particle size were selected for Taguchi's analysis.

For Taguchi's analysis, the two main factors considered are: dust concentration (DC , g/m^3) and test ignition delay time (IDT , ms). The first main factor DC has two levels (namely, 250 and 500 g/m^3) and the second main factor IDT has three levels (40, 50, and 100 ms, respectively). Fig. 17 exhibits the one-at-a-time impact of each of the main factors (DC and IDT) on the mean ignition energy (IE) which is the response variable. This figure shows that IDT has the dominant impact on the IE of the dust cloud. In other words, the variability in the dust concentration (DC) has lesser impact on the dust cloud ignition energy (IE) compared to impact of variability in the ignition delay time (IDT). Fig. 18 shows the calculated response surface of dust cloud ignition energy (IE) of the partially-dehydrated composite system as a function of DC (g/m^3) and IDT (ms). As can be seen from Fig. 18, the dust MIE occurred in the test where IDT was 40 ms (i.e., the lowest IDT value) and DC was 500 g/m^3 (i.e., the highest DC value). Finally, Taguchi's analysis did not show an interaction effect between DC and IDT on the dust ignition energy.

Fig. 17 – One-at-a-time impact of the main factors (IDT in ms and DC in g/m^3) on the dust mean ignition energy (response variable).

Fig. 18 – Calculated response surface of the ignition energy (IE) of the partially-dehydrated composite system as a function of the dust cloud concentration ($DC, g/m^3$) and the test ignition delay time (IDT, ms).

3.8 Summary

3.8.1 Dust cloud characterization parameters

In the present experimental program, values of the dust cloud combustion characterization parameters of hydrided and partially-dehydrated $2LiBH_4+MgH_2$ composite system were measured in accordance with ASTM standardized test protocols [23-26]. The results of these tests are summarized in Tables 4 and 5 (*vide infra*). The measured parameters included P_{MAX} , $(dP/dt)_{MAX}$, T_C , MEC , and MIE . The explosion severity index (K_{St}) was calculated using the *Cube Law* ($K_{St} = (dP/dt)_{MAX} \cdot V^{1/3}$) to classify the degree of dust explosibility. Moreover, the corresponding parameters of the reference materials (*Pittsburgh seam coal and Lycopodium spores*) were measured and their K_{St} values were calculated.

Table 4 - Summary of results for hydrided $2LiBH_4-MgH_2$ dust cloud deflagration parameters.

Parameter	Hydrided $2LiBH_4+MgH_2$		Reference Materials	
	Dust $\bar{d}_p = 75 \mu m$		(Current Work)	
		Pittsburgh Seam Coal	Lycopodium Spores	
P_{MAX} , bar	10.7	7.3	7.4	
$(dP/dt)_{MAX}$, bar/s	2036	426	511	
K_{St} , bar-m/s ^(a)	553	124	139	
Dust class	St-3	St-1	St-1	
T_C , °C	150	585	430	
MEC , g/m ³	30	65	30	
MIE , mJ	< 9 ^(b)	110	17	

Table 5 – Summary of results for partially-dehydrided 2LiBH₄-MgH₂ dust cloud deflagration parameters.

	Partially-Dehydrided 2LiBH ₄ +MgH ₂			Reference Materials (Current Work)			
	Dust $\bar{d}_p$						
Parameter	75 μm	75 – 150 μm	420 μm	Pittsburgh Seam Coal (Current Work)	Lycopodium Spores	Pittsburgh Seam Coal (ASTM)	Lycopodium Spores
P_{MAX} , bar	9.9	6.2	6.0	7.3	7.4	7.0	7.0
R_{MAX} , bar/s	1225	153	118	426	511	430	555
K_{St} , bar-m/s	333	42	32	124	139	117	151
Dust class	St-3	St-1	St-1	St-1	St-1	St-1	St-1
T_C , °C	230	310	270	585	430	600	460
MEC , g/m ³	30	60	30	65	30	80	45
MIE , mJ	< 9.2	22 < MIE < 47	20	110	17	30-140	10-30

Footnotes:

- Explosion severity index $K_{St} = ((dP/dt)_{MAX}) \cdot V^{1/3}$, bar-m/s, where V = volume of the Kühner vessel = 20 liters = 0.02 m³
- The lowest controllable ignition spark energy in our test apparatus is 9 to 10 mJ. Because the sample material ignited during the test at the lowest controllable energy setting in the test apparatus, the dust MIE value is reported as < 9 mJ (see Table 4).

3.8.2 Impact of mean particle size ($\bar{d}_p$) on dust cloud combustion characteristics

For the hydrided composite system (with a mean particle size of 75μm), the dust cloud combustion characterization results indicated that this hydrided state is more air reactive compared to the partially-dehydrided state as demonstrated by the higher values of P_{MAX} (bar-g), $(dP/dt)_{MAX}$ (bar/s), and K_{St} (bar-m/s) and the lower value of T_C (°C) and MIE (mJ) as shown in Tables 4 and 5.

For partially-dehydrided composite system, the results of the dust cloud combustion characterization (Table 5) showed that:

- P_{MAX} (bar-g) decreased by ~ 37.4% and by ~ 39.4% as the dust mean particle size increased from 75 μm to a mean value in the range 75 – 150 μm and to 420 μm, respectively.
- $(dP/dt)_{MAX}$ (bar/s) and, hence, K_{St} (bar-m/s) decreased by ~ 87.5% and by 90.4% as the dust mean particle size increased from 75 μm to a mean value in the range 75 – 150 μm and to 420 μm, respectively.
- The value of MEC (g/m³) doubled as the mean particle size increased from 75 μm to a mean value in the range 75 – 150 μm.

- The value of T_C ($^{\circ}\text{C}$) increased by $\sim 34.8\%$ and by $\sim 17.4\%$ as the dust mean particle size increased from $75\text{ }\mu\text{m}$ to a mean value in the range $75 - 150\text{ }\mu\text{m}$ and to $420\text{ }\mu\text{m}$, respectively.
- The value of MIE (mJ) increased by $\sim 280\%$ and by $\sim 122\%$ as the dust mean particle size increased from $75\text{ }\mu\text{m}$ to mean value in the range $75 - 150\text{ }\mu\text{m}$ and to $420\text{ }\mu\text{m}$, respectively.
- For the partially-dehydrided state of the composite system, dust classification changed from *St-3* (i.e., *very strong explosibility*) to *St-1* (i.e., *weak explosibility*) as the mean particle size increased from $75\text{ }\mu\text{m}$ to a mean value in the range $75 - 150\text{ }\mu\text{m}$ and to $420\text{ }\mu\text{m}$, respectively (Table 5).

4. Conclusions

An experimental program was carried out to measure the dust cloud combustion characterization parameters of dehydrided and partially-dehydrided states of the binary system $2\text{LiBH}_4 + \text{MgH}_2$ for reversible hydrogen storage. This composite mixture has been considered, among other candidate H_2 storage materials, for use in a broad range of mobile and stationary applications. The main conclusions drawn from this study are as follows:

- While the purpose of adding MgH_2 to LiBH_4 powder is to improve the latter's de/rehydrogenation kinetics, the presence of this destabilizing additive has caused the experimentally observed very strong explosibility of the hydrided $2\text{LiBH}_4 + \text{MgH}_2$ dust cloud in air. Accordingly, the dust cloud of this hydrided state has been classified as *St-3* (corresponding to a calculated K_{St} of ≈ 553). For the partially-dehydrided state of this composite mixture, only the finest dust cloud (with a mean particle diameter of $75\text{ }\mu\text{m}$) has been classified as *St-3* (corresponding to a calculated K_{St} of ≈ 333).
- Taguchi's mixed-levels design of experiments (DoE) calculations show that: a) variability in test's ignition delay time (*IDT*) has a more dominant impact on the dust cloud ignition energy compared to the impact of variability in dust concentration (*DC*), b) there is no first-order interaction effect between *IDT* and *DC* on the dust *MIE*, and c) Taguchi's response surface of dust cloud ignition energy offers a means for identifying location of the dust minimum ignition energy as a function of *IDT* and *DC*.
- The core insights of this study are useful for quantifying risks associated with use of this complex solid-state medium for H_2 storage in mobile and stationary applications. Moreover, these insights can be used for supporting development of H_2 safety standards, augmenting H_2 storage material property data such as the IEA/DOE/SNL hydride databases,⁷ and designing adequate engineered safety features (ESF) such as explosion relief venting and isolation devices.

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⁷ IEA/DOE/SNL Hydride databases, Hydride Information Center, Sandia National Laboratories, <http://hypark.ca.sandia.gov>

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