Characterisation of paraffin-based hybrid rocket fuels loaded with nano-additives

Md. Zishan Akhter\textsuperscript{a} and M. A. Hassan\textsuperscript{b}

\textsuperscript{a}Department of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore; \textsuperscript{b}Department of Mechanical Engineering, Birla Institute of Technology -Mesra (Patna Campus), Patna, India

\textbf{ABSTRACT}

In this work, a new composition based on Paraffin wax and HTPB fuel, loaded with nanoparticles has been proposed for hybrid propulsion system. Lithium aluminium hydride (LiAlH\textsubscript{4}) and Magnesium hydride (MgH\textsubscript{2}) nanoparticles have been used as additives. A detailed rheological, thermal and ballistic characterisation has been carried out. The Magnesium hydride doped hybrid fuel exhibits lower viscosity as compared to the Lithium aluminium hydride doped one, leading to comparatively enhanced entrainment-aided combustion. LiAlH\textsubscript{4} doped hybrid fuels also exhibit solid-like behaviour and thus greater stability in the solid phase in contrast to the MgH\textsubscript{2} doped fuel. LiAlH\textsubscript{4} doped fuel is thermally more stable and produces relatively greater residual-mass. The loading of nanoparticles significantly improves the fuel regression performance during ballistic firing. This can be attributed to the release of nascent hydrogen and metal nanoparticles during dehydrogenation of metal hydrides. Regression rate enhancement in the range of 350\%–475\% is observed in comparison to the conventional HTPB hybrid fuels. A power law governing regression rate has been proposed for the tested hybrid fuels.

\textbf{1. Introduction}

Hybrid rockets fuel offer several advantages over the conventional rocket fuel based systems. It combines the benefits of both solid and liquid fuels. Advantage of hybrid fuel include reduced de-bonding and crack sensitivity, fuel insensitivity to combustion instability, and increased specific impulse ($I_{sp}$) in comparison to its solid counterpart. Hybrid fuel-based rocket engines offer the possibility of throttling and on-demand thrust termination/restart. Likewise, superiority of hybrid rocket system over the liquid ones broadly includes intrinsic safety from explosion hazard due to phase-separation among propellants. It also leads to simpler engine design due to the expulsion of regenerative cooling system from nozzle and combustion chamber. Hybrid propellants demonstrate greater flexibility in fuel/oxidiser selection with minimal environmental impacts. These features make it a suitable alternative to the conventional systems for various space applications.
such as, sounding rockets, first-stage boosters, upper-stage launch vehicles, orbital injection systems, and sub-orbital and orbital human space flight involving space tourism [1]. However, there are certain limitations associated with hybrid propulsion system such as low fuel regression rate and varying mixture ratio (O/F) during combustion. The low regression of polymeric fuels and the subsequent poor combustion efficiency is largely attributed to the diffusion-flame-limited-combustion model of hybrid propulsion system [2].

Over the years, several improvements were proposed to enhance hybrid fuel regression rate. These modifications included non-conventional grain designs having multi-port geometries [3,4] and embedded diaphragms [5,6], and altered oxidiser flow streams using swirl and radial injection techniques [7,8]. However, these regression enhancement measures led to complexity in design and manufacturing. Further effort for enhancement of regression rate led to investigations on cryogenic hybrid fuels like n-pentane which reported 5–10 times higher regression rate than conventional polymeric fuels [9,10]. Karabayoglu et al. used long-chained hydrocarbons like paraffin wax, which remain solid at room temperature. A 3–4 times enhancement in regression rate was obtained [11]. This high regression rate can be attributed to entrainment contribution to the mass flow rate, reduced effect of blocking due to two-phase flow and enhanced heat transfer due to increased surface roughness [12]. The proposed theory was validated by scale-up tests conducted on larger engines [13]. The mass flow rate due to entrainment is quantified in literature as

\[ \dot{m}_{ent} \propto \frac{p_{dyn}^{\alpha} h^{\beta}}{\mu^{\gamma} \rho^{\pi}} \]  

(1)

The entrainment exponential terms (\(\alpha\), \(\beta\), \(\gamma\) and \(\pi\)) in the above correlation play an important role in mass flow rate. Magnitude of these parameters are available in literature [11,14,15]. The correlation (1) suggests that mass entrainment is dependent on dynamic pressure (\(p_{dyn}\)), melt layer thickness (\(h\)), viscosity (\(\mu\)) as well as surface tension (\(\rho\)) of the fuel grain and hence affects the fuel regression rate.

However, combustion efficiency and mechanical integrity are decisive attributes of the solid hybrid grains for their applicability in space industry. Pure paraffin wax (C\(_{24}\)H\(_{50}\), PW) has poor structural integrity and cannot possibly sustain flight inertial loads, thermal load and/or shocks, thrust and radial combustion pressure. Several attempts had been made towards improving the mechanical properties of paraffin-based hybrid fuels using additives [16–19]. It has also been tested in composition with other binder fuels [20–22]. Hydroxyl-terminated poly butadiene (HTPB) is a favoured binder due to its relatively decent regression rate, greater solid loading (90% wt.) and high carbon/hydrogen ratio [23,24].

A novel approach towards regression enhancement could be doping solid fuels with energetic micro or nano-sized additives such as metals and light metal hydrides [25]. These additives improve fuel regression behaviour by raising the theoretical flame temperature, besides reducing gasification heat and mitigating blocking phenomenon. Increased radiative heat transfer to the grain surface results in reduction in viscosity of melted fuel thereby enhancing entrainment [26].
To the best of author’s knowledge, effect of nano metal hydride additives on PW-HTPB hybrid fuel has not been reported in literature. Therefore, in this work a blend of PW and HTPB based hybrid rocket fuel was developed and loaded with selected nano-sized light metal hydrides- Lithium aluminium hydride (LiAlH₄, LAH) and Magnesium hydride (MgH₂, MGH) nanoparticles. These metal hydrides have high hydrogen content and are accordingly predicted to contribute significantly towards fuel-regression enhancement [27]. To investigate the proposed fuel characteristics and performance, a detailed experimental analysis involving rheological, thermal and ballistic has been performed. The rheometry was performed to investigate the effects of nano-additives on viscosity as well as storage and loss moduli with respect to temperature and oscillatory frequency. The thermal and ignition behaviour of the prepared fuels were analysed using Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) techniques to assess the variations triggered by doping of LAH and MGH nanoparticles. Eventually, static ballistic firings were conducted to predict the regression rate of the developed fuels. Ballistic characterisation enabled us to evaluate the relative enhancement in fuel regression produced due to the loading of light metal hydride nanoparticles in the fuel matrix.

2. Materials and methods

2.1. Hybrid fuel preparation

The constituents of developed fuels included a blend of PW and HTPB as the base fuel along with nano-sized light metal hydride additives namely LAH and MGH all procured through commercial suppliers. Requisite quantity of curing agents – Diocetyl adipate (C₂₂H₄₂O₄, DOA), Toluene diisocyanate (C₉H₆N₂O₂, TDI) and Glycerol (C₃H₈O₃, GLY) sourced from Sigma Aldrich were used. The physiochemical properties of constituent fuel and additives are summarised in Table 1. All components of hybrid fuel were used without any further purification or modification. The average particle size of nano-additives LAH and MGH are different due to commercial availability.

The fuel formulations for proposed hybrid rocket fuels are tabulated in Table 2. The required amount of HTPB is ensured to be free of static electric charge. Requisite quantities of DOA and GLY, as given in Table 2, were added to the HTPB and mixed thoroughly for 1 h using controlled overhead stirrer. It was followed by addition of TDI and mixing is continued for another 10 min. PW was separately heated in water bath at a constant temperature of 100 °C. The nano light metal hydride additive was accurately weighed and stored separately in nitrogen atmosphere. Molten PW, along with the additive was poured into the HTPB mixture and stirred vigorously for 20 min to obtain a homogeneous slurry. A small fraction of prepared test fuel was stored overnight in a hot air oven at 45 °C to facilitate curing for further material characterisation.

| Properties               | PW  | HTPB | LAH   | MGH  |
|--------------------------|-----|------|-------|------|
| Molecular mass (g/mol)   | 380 | 3000 | 37.95 | 26.32|
| Density (g/cm³)          | 0.89| 0.913| 0.92  | 1.45 |
| Average particle size    | –   | –    | 25 nm | 50 nm|
| Melting point (°C)       | 53 – 57 | – | 125 | 285 |
| Boiling point (°C)       | 341 | 350.5| –     | –   |
| ΔHf(J/mol)               | –   | –    | –117.15| –90.79|
Remaining composition was used to prepare fuel grain for ballistic performance analysis, where it is poured gently into the mould of length—185 mm, outer diameter—40 mm and port diameter—15 mm. The mould’s inner-wall was coated with grease to facilitate grain removal upon solidification. The process of motor casting was performed in multiple steps. Only small amount of molten fuel was poured slowly and allowed to shrink before next pouring to prevent bubble formations and other possible imperfections in the solid grain. Visual inspection of the prepared grains was carried out and the acceptable grains were stored overnight in a hot air oven at 45 °C to facilitate curing. Similar procedure was followed for preparation of all test fuels.

2.2. Rheological characterisation

The rheological characterisation was conducted on Anton Paar MCR-302 dynamic compact rheometer to evaluate the viscoelastic properties of the prepared fuels. The measurements were carried out using parallel-plate geometry, where the sample is mounted between two coaxial plates and subjected to shearing by the top rotating plate while the bottom plate remains stationary. The plates used in the experiments were of 25 mm diameter, placed at a gap of 1 mm to load the fuel samples. The rheometer is fitted with Peltier heating-cooling system and circulatory fluid-bath for fine temperature control. The temperatureal effects on the rheological behaviour of test samples were investigated over the range of 30–110 °C. Suitable care was taken over the liquid-state temperature regimes to prevent bubble formation. Likewise, pre-shearing effects were avoided by loading fresh samples before each rheological measurement.

The rheological characterisation involved investigation of viscosity/shear modulus along with corresponding elastic/storage and viscous/loss moduli of the test samples. The relation between viscosity/shear modulus and the moduli (storage and loss) can be expressed as:

\[
\mu = G' + iG''
\]

where, \(\mu\) – viscosity/shear modulus, is expressed as the sum of storage modulus – \(G'\) and loss modulus – \(G''\). Further, the storage and loss moduli can be computed as

\[
G' = \frac{\sigma_o}{\varepsilon_o} \cos(\psi)
\]

\[
G'' = \frac{\sigma_o}{\varepsilon_o} \sin(\psi)
\]

where \(\sigma_o\) and \(\varepsilon_o\) depicts stress and strain amplitudes, while \(\psi\) denotes the phase shift between them.

| Fuels         | PW  | HTPB | DOA  | TDI | GLY | Additive |
|---------------|-----|------|------|-----|-----|----------|
| PW-HTPB      | 50% | 27%  | 19.1%| 3.5%| 0.4%| –        |
| PW-HTPB-MGH4 | 46% | 27%  | 19.1%| 3.5%| 0.4%| MGH 4%   |
| PW-HTPB-LAH4 | 46% | 27%  | 19.1%| 3.5%| 0.4%| LAH 4%   |
The fuel samples were subjected to controlled stress oscillatory sweep rheometry under two modes:

- **In-contact frequency varying amplitude mode:**
  Strain rate was varied from 0.01%–100% at a constant oscillatory frequency of 1 rad/s.

- **In-contact amplitude varying frequency mode:**
  Frequency was varied over the range of 0.1–50 rad/s at a constant strain of 1%.
  The viscoelastic properties of – viscosity ($\mu$), elastic/storage modulus ($G'$) and viscous/loss modulus ($G''$) were investigated as a function of temperature ($^\circ$C), strain rate ($\dot{\gamma}$) and oscillation frequency ($f$).

### 2.3. Thermal analysis

The thermal stability and decomposition behaviour of the prepared fuels were investigated by performing thermal characterisation on Shimadzu DTG-60 thermogravimetric analyser. The thermo-analytical analysis involving thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed over the temperature range of 20 to 500 $^\circ$C, under nitrogen (N$_2$) atmosphere. Fuel samples of weight 1.5 mg (approximately) were placed in a Platinum crucible for the experimentation. Heating rate of 10 $^\circ$C/min and a constant mass flow rate (N$_2$) of 50 ml/min was maintained during the tests.

### 2.4. Ballistic test

The ballistic performance of the developed fuels was investigated using static firing tests using gaseous oxygen (GOX) as the oxidiser. Major components of test setup included a lab-scale rocket motor, oxidiser-feed system, ignition system, live-feed camera and online data acquisition system (DAQ). The pictorial view of the hybrid rocket firing facility is shown in Figure 1. A graphite deLaval nozzle having semi-convergent and semi-divergent angles of 38.66$^\circ$ and 19.29$^\circ$, respectively was used with the hybrid motor. Axial/shower

![Figure 1. Hybrid rocket firing facility.](image-url)
oxidiser injection mechanism was employed during each test. Oxidiser injection pressure and mass flow rate ($m_\text{ox}$) were maintained at 300 psi and 30 gm/s, respectively. The ignition system comprised of a pyrotechnic igniter (AP/HTPB solid propellant of mass 5 gm), 34 SWG nichrome wire and 20 V DC supply (battery). The valves and ignition system were controlled from an automated system using LabVIEW. Four firing tests of duration 1 s each, were conducted for each fuel sample and the regression rate ($\dot{r}$) was determined using the mass-loss method over the interrupted firings.

3. Results and discussion

3.1. Viscosity

Viscosity is an important attribute of solid hybrid fuels as it significantly affects the entrainment-aided fuel regression behaviour.

3.1.1. Viscosity variation with strain rate ($\dot{\gamma}$)

The evolution of viscosity with the variation in strain rate from $10^{-4}$ to 1 s$^{-1}$ are presented in Figure 2(a,b). The PW-HPB-LAH4 fuel was tested over temperature range of 30–110 °C, while PW-HPB-MGH4 sample was tested over range of 30–70 °C. Flow curves were observed to be non-linear, representing non-Newtonian nature of the doped hybrid fuels. Both the fuels exhibited decrement in viscosity with elevation in temperature. This phenomenon can be largely attributed to the softening of HTPB gel as well as thermal degradation of the polymer cross-linkages in the fuel. The decrement was more pronounced in case of PW-HPB-MGH4 sample. Flow curves for temperature ≥ 60 °C became inconsistent and rheological response was difficult to be obtained, as can be seen in Figure 2(b). The developed fuels also exhibited shear thinning behaviour which resulted in reduced viscosity as a function of increased shear rate. Shear thinning in doped fuels was observed to be prominent at lower temperature levels.

Figure 2. Viscosity variation with strain rate.
3.1.2. Viscosity variation with temperature

Temperature dependence of viscosity in the doped hybrid fuels (presented in Figure 3), can be expressed mathematically by Arrhenius equation as:

$$\mu = \frac{E_A}{RT}$$

which can be rearranged logarithmically into:

$$\ln \mu = \ln \mu_\infty + \frac{E_A}{RT}$$

where, $\mu$ is dynamic viscosity (Pa·s), $\mu_\infty$ is pre-exponential viscosity at infinite temperature (Pa·s), $E_A$ is molar Arrhenius activation energy (J/mol), R is universal gas constant (8.314 J/mol·K), and T is temperature (K).

Regression analysis was performed to determine the Arrhenius parameters, as presented in Table 3. PW-HTPB-MGH4 fuel exhibited relatively lower pre-exponential viscosity as compared to the PW-HTPB-LAH4 counterpart. On the contrary, molar activation energy was observed to be relatively larger in case of PW-HTPB-MGH4 sample.

### 3.2. Storage and loss moduli

The dynamic spectra of $G'$ and $G''$ obtained from oscillatory tests is used to classify the fuel network structure as entangled or covalently cross-linked [28]. For a fuel to exhibit

### Table 3. Arrhenius parameters of the developed fuels.

| Fuel            | $\mu_\infty$ (Pa·s) | $E_A$ (J/mol) | Regression coefficient ($R^2$) |
|-----------------|---------------------|---------------|--------------------------------|
| PW-HTPB-MGH4    | $1.678 \times 10^{-5}$ | 41,303.95     | 0.878                          |
| PW-HTPB-LAH4    | $527.6 \times 10^{-5}$ | 27,244.97     | 0.933                          |

Figure 3. Temperature dependence of viscosity.
solid-like behaviour, $G' >> G''$ over the tested frequency regime, with $G'$ exhibiting a plateau extending over timescales of the order of several seconds [29]. Thus, the moduli provide insight into the stability of solid phase of the propellants prone to flight vibrations. In the present study, test samples were investigated over a temperature range of 30–50 °C, subjected to 1% strain over the oscillatory frequency sweep of 0–50 Hz. The variation of $G'$ and $G''$ as a function of frequency is presented in Figure 4.

![Figure 4. Storage and Loss moduli variation with frequency for PW-HTPB-LAH4 (left column) and PW-HTPB-MGH4 (right column).](image-url)
In case of PW-HPG-THPB-LAH4 fuel, the moduli ($G'$ and $G''$) exhibited depreciation in magnitude at elevated temperatures as seen in Figure 4(a–c), while in case of PW-HPG-THPB-MGH4 fuel, both the moduli remained nearly insensitive to temperature (Figure 4(d–f)). As the focus of this paper is nano-additives, for sake of brevity rheological data of undoped PW-HPG has not been presented. A detailed rheological investigation on PW-HPG formulation can be found in [30]. The decrement observed in the former case can be attributed to the weakening of covalent polymeric cross-linkages of the fuel. This curtails deformational energy storage capability of the fuel and renders it more susceptible to elongation, thereby subsequently reducing $G'$ and $G''$. Both the fuels exhibited a weak power law dependency of $G'$ and $G''$ on frequency, such that the moduli increased with frequency and the extent of increment stabilised at higher frequencies. The PW-HPG-THPB-LAH4 fuel lies in elastic region and exhibited solid-like behaviour as $G'$ dominated $G''$ over the tested frequency regime. Contrastingly, PW-HPG-THPB-MGH4 fuel lies in viscous region and exhibited liquid-like behaviour as $G''$ dominated $G'$ over the tested frequency regime.

3.3. Thermogravimetric analysis

The prepared hybrid fuels undergo three-step degradation as can be witnessed from the respective TGA thermograms presented in Figure 5(a). PW-HPG-THPB-MGH4 fuel is thermally more stable than the PW-HPG-THPB-LAH4 counterpart in the temperature range of 25–180 °C, as the latter exhibited 2.6 times thermal decomposition than the former. However, mass loss recorded by PW-HPG-THPB-MGH4 fuel was greater than PW-HPG-THPB-LAH4 over the remaining degradation phases, as summarised in Table 4. Residual masses obtained at the end of tests was observed to be 4.5 times greater in case of PW-HPG-THPB-LAH4 fuel, as compared to PW-HPG-THPB-MGH4. This can be attributed to the three-step degradation of LAH-additive, leading to formation of thermally stable compounds upon dehydrogenation.

3.4. Differential thermal analysis

The prepared hybrid fuels exhibited an initial melting point of $\sim$54 °C, marked by the corresponding endothermic peak on respective DTA thermograms presented in Figure 5(b).

Figure 5. Thermograms of the tested hybrid rocket fuels corresponding to: (a) TGA and (b) DTA.
This signifies endothermal melting of unbounded-PW present in the fuel matrix. The respective enthalpy values are provided in Table 5. DTA thermograms of both the fuels are marked by endothermal decomposition over the temperature range of 200–300 °C. This can be attributed to the dehydrogenation of nano-sized light metal hydride additives (Equations (7)–(9)), besides vaporisation of volatile products and poorly bounded PW, from the fuel matrix. Endothermal peak obtained at ~420 °C on PW-HTPB-LAH4 thermogram can be associated with the dehydrogenation of lithium hydride (LiH), as expressed in Equation (10). Furthermore, several endothermic peaks mapped at high temperature levels can be attributed to the melting of PW and/or HTPB microcrystalline moieties. This phenomenon highlights the multiple molecular packing or cross-linkages present in the PW-HTPB fuel matrix.

\[
\begin{align*}
\text{MgH}_2 + 2H_2O & \rightarrow 2H_2 + Mg(OH)_2 \\
3\text{LiAlH}_4 & \rightarrow \text{Li}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 \\
2\text{Li}_3\text{AlH}_6 & \rightarrow 6\text{LiH} + 2\text{Al} + 3\text{H}_2 \\
2\text{LiH} + 2\text{Al} & \rightarrow 2\text{LiAl} + \text{H}_2
\end{align*}
\]

### 3.5. Regression rate

The static ballistic firings of hybrid fuels were subjected to chamber pressure (\(P_c\)) ranging between 0.6 to 0.9 MPa and oxidiser mass flux (\(G_o\)) varied from 41.9 to 125.8 kg/m²s. The regression rates were determined over interrupted firings using mass-loss method [31], as presented in Figure 6. Ballistic firing of PW-HTPB-LAH4 fuel and PW-HTPB-MGH4 fuel are shown in Figure 7.

It was observed that doping of fuels resulted in enhancement of regression rate as compared to the PW-HTPB base fuel. This can be attributed to the production of nascent hydrogen gas upon dehydrogenation of metal hydrides (additives), which promoted pyrolysis of the solid grain thereby boosting fuel regression. The increment in regression

### Table 4. TGA data of the tested hybrid fuels.

| Fuel       | Start T (°C) | End T (°C) | Mass loss (%) |
|------------|--------------|------------|---------------|
| PW-HTPB-LAH4 | 25           | 180        | 9.89          |
|            | 180          | 440        | 44.49         |
|            | 440          | 500        | 13.16         |
| PW-HTPB-MGH4 | 26           | 180        | 3.83          |
|            | 180          | 440        | 64.76         |
|            | 440          | 500        | 24.19         |

### Table 5. DTA data of the tested hybrid fuels.

| Fuels      | On-set T (°C) | End-set T (°C) | Peaks T (°C) | \(\Delta H_{\text{endo}}\) (J) |
|------------|---------------|----------------|--------------|-------------------------------|
| PW-HTPB-LAH4 | 39.14         | 59.68          | 54.41        | 0.2014                        |
|            | 216.96        | 280.48         | 253.90       | 0.6228                        |
|            | 358.85        | 440.37         | 419.78       | 7.97                          |
| PW-HTPB-MGH4 | 48.71         | 59.64          | 54.57        | 0.1985                        |
|            | 201.54        | 270.42         | 257.50       | 0.8588                        |
|            | 305           | 443.37         | 396.06       | 4.23                          |
|            | 449.76        | 481.04         | 455.50       | 1.14                          |
rate was observed to be slightly greater for PW-HTPB-LAH4 fuel as compared to PW-HTPB-MGH4. This can be attributed to the production of Al-metal (during dehydrogenation of LAH), and increment in specific surface area which significantly enhances the radiant heat transfer to the regressing surface. During combustion, Al-metal undergoes exothermic thermo-oxidative reactions thereby, raising the flame temperature and contributing towards regression of the fuel. Regression rate of polymeric HTPB fuel is also plotted in Figure 6 for comparison. The prepared fuels exhibited significantly higher

![Figure 6. Regression rate ($\dot{r}$) – $G_o$ of the tested hybrid fuels.](image)

![Figure 7. Static ballistic firing of: PW-HTPB-LAH4 (top) and PW-HTPB-MGH4 (bottom).](image)
regression rates as compared to conventional HTPB fuel, due to the entrainment of PW (droplets) in the fuel matrix, thereby increasing the fuel mass flow rate. Thus, the regression results are in good agreement with the literature [11–13]. As expected, the regression rates of developed formulations are slightly retarded in comparison to the virgin PW fuel. This behaviour may be attributed to the addition of HTPB in the composition (0.27 %wt.). The relative regression rate enhancement with respect to the conventional polymeric HTPB fuel (at $Go = 110$ kg/m$^2$s) is summarised in Table 6.

The regression rate of the tested fuels can be expressed using the following power law:

$$\dot{r} = aG_o^n$$

(11)

where, $\dot{r}$ is regression rate, and $G_o$ is oxidiser mass flux. Regression-rate curve coefficient and exponential parameter are defined as ‘$a$’ and ‘$n$’, respectively. Table 6 summarises the experimentally obtained magnitudes of coefficient ‘$a$’ and exponent ‘$n$’, for all tested fuel samples.

### 4. Conclusions

A novel hybrid rocket fuel composition has been proposed which comprises of Paraffin wax and HTPB as base, blended with Lithium aluminium hydride (LiAlH$_4$) and Magnesium hydride (MgH$_2$) nanoparticles. A detailed investigation on rheological, thermal and ballistic characterisation of the paraffin-based hybrid rocket fuels had been carried out. It was observed that the Magnesium hydride doped hybrid fuels exhibit lower viscosity as compared to the Lithium aluminium hydride doped counterpart. It signifies comparatively greater entrainment-aided combustion phenomenon in the former case. LiAlH$_4$ doped hybrid fuels exhibit solid-like behaviour in contrast to the MgH$_2$ doped fuels. Thus, LiAlH$_4$ doped fuels are predicted to be comparatively more stable in the solid phase than the MgH$_2$ doped one. TGA/DTA data revealed that LiAlH$_4$ doped fuel is thermally more stable and produces relatively greater residual-mass as compared to the MgH$_2$ doped fuel. Static ballistic firing provided the regression behaviour of prepared fuels. It was obtained that regression rate is significantly enhanced by nanoparticle doping in comparison to the base fuel (PW-HPB). This can be attributed to the dehydrogenation of metal hydrides and production of metal nanoparticles (Al; in case of LiAlH$_4$) during combustion. Nascent hydrogen promotes pyrolysis of solid grain while metal nanoparticles undergo exothermic oxidation thereby enhancing heat transfer to the fuel surface. The enhancement in regression rate of all the prepared fuels was observed to be significantly higher (350%–475%) than the conventional HTPB hybrid fuel, as predicted in literature. A power law governing regression rate of the tested hybrid fuels was developed.

### Table 6. Coefficients and exponents for regression rate curves along with their respective rate law and relative regression rate enhancement (%) with respect to HTPB, for all the tested fuels.

| Fuels          | Coefficient ‘$a$’ | Exponent ‘$n$’ | Rate law               | $\dot{r}$ enhancement |
|----------------|-------------------|----------------|------------------------|------------------------|
| HTPB [26]      | 0.05              | 0.44           | $0.05 + G_o^{0.44}$    | –                      |
| PW [32]        | 0.22              | 0.52           | $0.22 + G_o^{0.52}$    | +540.9%                |
| PW-HTPB        | 1.3621            | 0.0582         | $1.3621 + G_o^{0.0582}$| +352.8%                |
| PW-HTPB-LAH4   | 0.5415            | 0.3055         | $0.5415 + G_o^{0.3055}$| +475.6%                |
| PW-HTPB-MGH4   | 0.6305            | 0.2717         | $0.6305 + G_o^{0.2717}$| +471.7%                |
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