

Chapter 5

Temperature Optimized Hydrolysis of Acetic Acid Catalyzed Magnesium Hydride for Hydrogen Generation in a Batch System Hydrogen Reactor



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Abstract Interests in hydrogen storage in magnesium hydride (MgH_2) is on growing due to its high gravimetric and volumetric hydrogen concentration and less harmful environmental impact of its reaction. This study reports the usage of acetic acid as an accelerator in hydrogen generation experiment via hydrolysis, using a batch system hydrogen reactor. The study was conducted in two phases: investigation of role of substrate weight and catalyst concentration on hydrogen yield and optimization of temperature for hydrogen generation. The study investigated the roles of the organic acids in the reduction of the poor reaction kinetics limitation in MgH_2 through the catalytic characteristic of acetic acid. Three acetic acid concentrations were used in the study namely 40, 50 and 60 wt%. Similarly, three substrate weights (0.4, 0.8 and 1.2 g) were investigated for the role of substrate weight on hydrogen yield. Application of the acetic acid accelerated the hydrogen yield across board. Similarly, the hydrogen yield increased with MgH_2 weight in the study. The highest hydrogen yield of 0.0189 L was recorded from 1.2 g MgH_2 at 30 °C and 50 °C respectively and 50 wt% acetic acid. The lowest hydrogen yield in the study was 0.0048 L hydrogen gas from 0.4 g MgH_2 at 50 wt% acetic acid. The experiment conducted at ambient temperature (25 °C) revealed comparable hydrogen yield with higher temperatures.

Keywords Acetic acid · Hydrogen generation · Hydrolysis · Reaction kinetics
Temperature optimization · Thermodynamics

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5.1 Introduction

Hydrogen storage could be achieved through various means such liquid or cold hydrogen storage (cryogenic), pressure hydrogen storage, steam reform, biohydrogen storage such as hydrogen storage in wastewater, carbon nanotubes, solid state hydrogen storage in metal and complex metal hydrides [1–3]. Solid state hydrogen storage particularly metal hydrides have attracted attention due to its relative safe storage thus making it an alluring candidate for an on-board vehicular fuel applications. Furthermore, most metal hydrides have high specific hydrogen volumetric and gravimetric volumes [4]. Magnesium hydride (MgH_2) is one of the leading candidates among metal hydrides for solid state hydrogen storage purpose. The development is due to some of the endearing characteristics of the MgH_2 . For example, MgH_2 is relatively cheap compared to majority of the metal hydrides. In the same vein, magnesium (Mg) a major component of MgH_2 is abundant in earth crust. It is regarded as the eighth most abundant element in earth crust [5, 6]. Furthermore, other advantages of MgH_2 as a hydrogen storage substrate include its non-corrosive nature which makes it an environment benign hydrogen generation and storage material [7, 8]. Similarly, MgH_2 has high volumetric hydrogen storage capacity of about 7.6 wt%.

However, hydrogen storage in MgH_2 like most metal and complex metal hydrides is hampered by slow reaction kinetics and poor thermodynamics. The thermodynamic challenge being high reaction enthalpy and entropy. Consequently, high temperature is required to desorb the hydrogen embedded in the matrix of the MgH_2 . This application of heat leads to increase in reaction cost thereby limiting scale up of the hydrogen storage technology. Furthermore, different researchers have explored use of various materials or compounds as catalysts in a bid to lessen the poor reaction kinetics and unfavorable thermodynamics limitations to the utilization of MgH_2 as hydrogen storage medium. Noble metal catalysts such as platinum have been used and reported to catalyze hydrogen desorption or release in metal hydrides, but the major limitation of the intervention is the prohibitive cost of platinum metal to large scale hydrogen storage and generation [9]. Moreover, some of the reaction products of noble metal catalysis of hydrogen storage in metal and complex metal hydrides are toxic to the environment [8]. The use of ball milling technique with its attendant increase in reaction surface area due to reduction in crystalline sizes of the substrates have been reported to increase reaction kinetics and improve thermodynamic properties of hydrogen storage experiments. Moreover, fracturing of the metal hydrides crystals due to the milling process improves nucleation reaction which further enhances hydrogen desorption [10]. However, despite the successes recorded in hydrogen generation using ball milling, the quantity of hydrogen released is not enough for the use of the technology in large scale production. Organic acids have also been used as accelerators in for hydrogen release from metal hydrides. The advantages of this technique include relative cheap low cost of the organic acids and their nontoxic/environmental friendly nature. For example, in our laboratory we have reported highest hydrogen generation of 0.018 L from a reaction of 1.2 g MgH_2 powder with 50 wt% acetic acid [7]. In another study from the same research

group, it was observed that hydrogen generation increased with substrate weight and acetic acid concentration accelerated hydrogen release when the reaction of MgH_2 pills was catalyzed with acetic acid [11]. The study reported maximum hydrogen generation of about 1.285 L. Sustainable hydrogen generation is crucial to the scale up of the technology and cost reduction is an integral component of it. To ameliorate the challenges of unfavorable thermodynamic and slow reaction kinetics that have limited the scale up of hydrogen storage in metal hydrides, interventions of increased reaction temperature are among the interventionist approach employed. However, the application of heat to the experiments further add to the reaction cost because of the cost of powering the temperature regulators/water baths used for such purposes. Consequently, a successful elimination of need to raise reaction temperature above room temperature would reduce reaction cost, thus driving the hydrogen storage technique towards sustainability. Thus, optimization of reaction temperature will provide insight into hydrogen yield with regards to reaction temperature. In this study, optimum reaction temperature for hydrogen generation in the designed reactor was investigated. Furthermore, the role of substrate weight and acetic acid concentration on hydrogen yield were examined.

5.2 Experimental Design and Method

5.2.1 Hydrogen Generation Reactor Operation

Figure 5.1 indicates the experimental design for the hydrogen generation reactor employed in the study. The reactor is made up of a three-neck round bottom flask which serves as the reaction vessel, thermostatic regulated water bath [Julabo TW20, Julabo GmbH (Germany)], the moisture absorbent unit, the flowmeter [T1000, Fujikin (Japan)] and the data logger.

The hydrogen generation experiment is essentially a hydrolysis reaction. The substrate (MgH_2 powder) was poured inside round bottom flask wherein acetic acid of various concentrations was released through the soxhlet apparatus attached to the middle neck of the round bottom flask. The outer left and right neck of the reaction vessel was attached to the thermometer and the tube for harvesting the hydrogen generated from the experiment respectively. The moisture absorbent in the design trapped the moisture in hydrogen thus ensuring only hydrogen is recorded by the flowmeter. The hydrogen generation was recorded using the data logger connected to the flowmeter [11].

An organic acid catalyzed the experiment—acetic acid [99.8%, Labchem, South Africa (SA)]. Magnesium hydride powder 99.8% purity (Rockwood Lithium, Germany) employed throughout the course of experiment as hydrogen storage media (substrate) was used as received (AR) from the supplier without further treatment with average particle size of 50 μm . The equation for the reaction of magnesium hydride with acetic acid catalyzed hydrolysis reaction can be seen in Eq. (5.1):

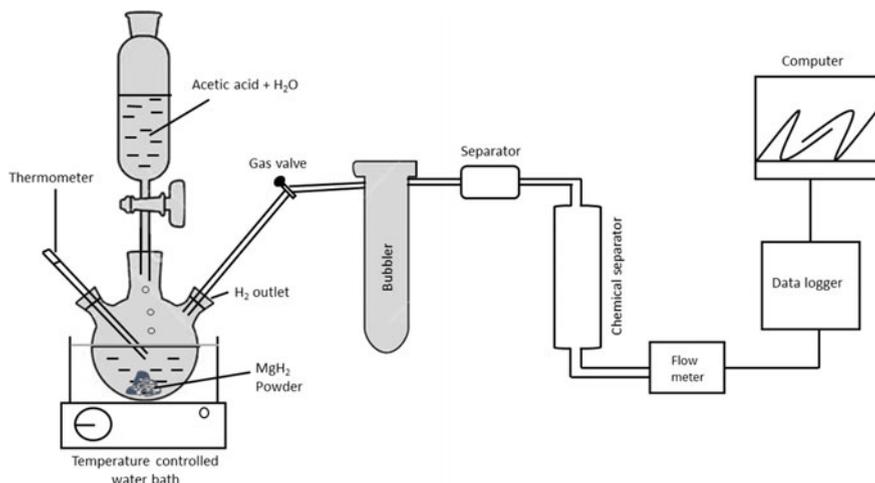
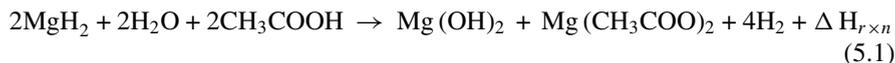


Fig. 5.1 Batch system hydrogen reactor experimental set up



The heat of reaction ($\Delta H_{r \times n}$) is approximately -277 kJ/mole.

The investigation of the impact of substrate weight on hydrogen yield was carried with three different MgH_2 powder weights (0.4, 0.8 and 1.2 g), except in 40 wt% acetic acid concentrations where only 0.4 and 0.8 g were utilized. Weighing of the substrate samples were carried out using BM-200 analytical balance (United Kingdom) with 0.0001 g repeatability to enhance weighing uniformity. The experiment was carried out at 25, 30, 50 and 60 °C external temperature. Furthermore, the experiment was conducted using different catalyst concentrations (40, 50, 60 and 70%).

5.2.2 Material Characterization of Reaction Substrate (MgH_2) Powder

Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) analysis was conducted on the MgH_2 powder for adequate material characterization. The SEM analysis of the MgH_2 powder surface morphology was conducted using JSM 7600F Jeol ultra-high-resolution field emission gun scanning electron microscope [(FEG-SEM), (USA)] equipped with EDS was utilized for the EDS analysis.

5.3 Results and Discussion

5.3.1 Role of Substrate Weight and Catalyst Concentration on Hydrogen Yield

In this study, the roles of substrate (MgH_2 powder) concentration and acetic acid concentration on hydrogen yield were examined to find the optimum parameters that can enhance hydrogen generation. Investigation of role of MgH_2 powder concentration on hydrogen generation was conducted using 0.4 g, 0.8 g and 1.2 g MgH_2 powders at various acetic acid concentrations namely 40 wt%, 50 wt%, 60 wt% and 70 wt% respectively. The results of the study are presented in Figs. 5.2, 5.3, 5.4 and 5.5.

Figure 5.2, Present the result of hydrogen generation experiment at 40 wt% acetic acid concentration for 0.4, 0.8 and 1.2 g MgH_2 powder. From the results, it can be observed that highest hydrogen generation of about 0.016 L was recorded from 1.2 g substrate while by 0.0098 L hydrogen yield from 0.8 g MgH_2 compared to maximum hydrogen generation of 0.005 L obtained in the 0.4 g MgH_2 experiment.

From Fig. 5.3, 0.4 g MgH_2 powder recorded the least hydrogen yield of about 0.0056 L, followed by maximum hydrogen generation of about 0.013 L at 0.8 g while the highest hydrogen yield of 0.018 L obtained when 1.2 g substrate was hydrolyzed in 50 wt% acetic acid.

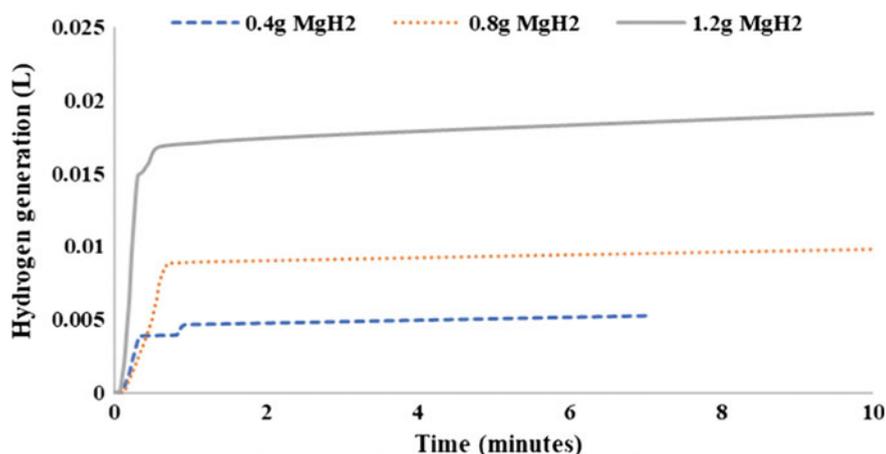


Fig. 5.2 Hydrogen generation at 40 wt% acetic acid concentration

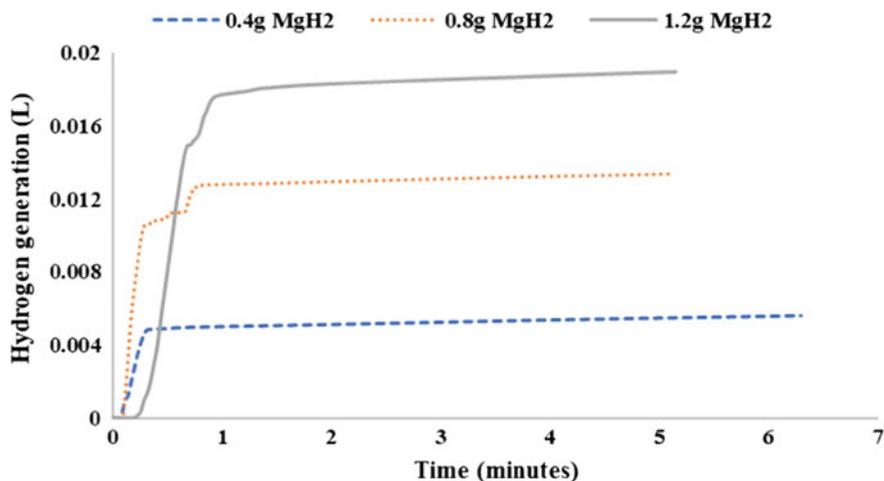


Fig. 5.3 Hydrogen generation at 50 wt% acetic acid concentration

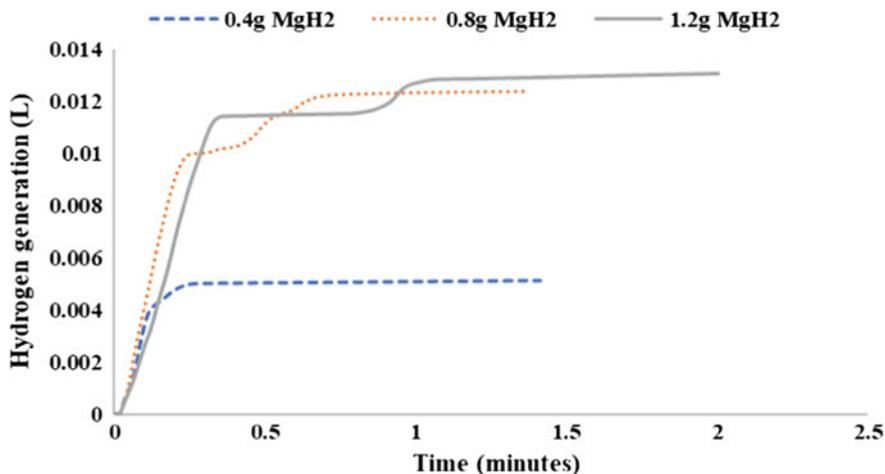


Fig. 5.4 Hydrogen generation at 60 wt% acetic acid concentration

Furthermore, the result of hydrogen generation experiment with 60 wt% acetic acid (Fig. 5.4) indicated the least hydrogen yield of 0.005 L (0.4 g MgH₂ powder), followed by 0.012 L and 0.013 L hydrogen at 0.8 g and 1.2 g MgH₂ powder respectively. Similarly, at 70 wt% acetic acid concentration (Fig. 5.5), hydrogen generation increased with weight of substrate with 0.0048 L, 0.009 L, 0.013 L obtained from 0.4 g, 0.8 g and 1.2 g substrate weight respectively.

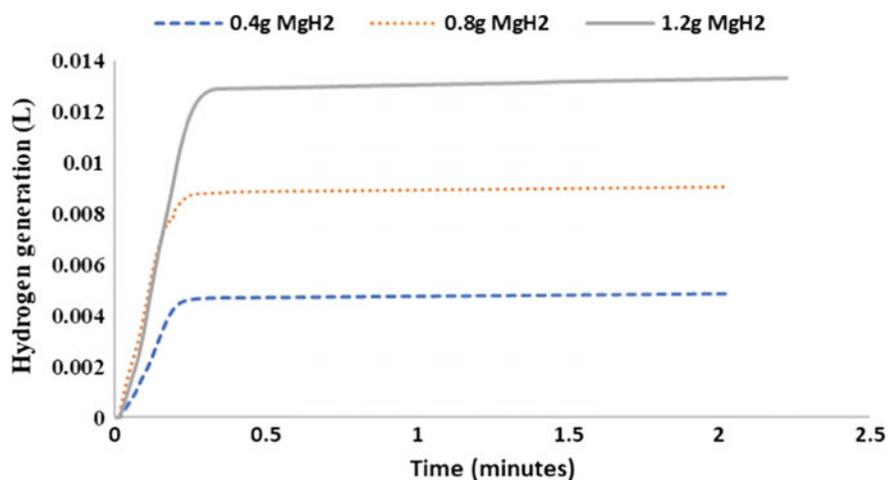


Fig. 5.5 Hydrogen generation at 70 wt% acetic acid concentration

5.3.2 Scanning Electron Micrograph Characterization of Substrate

The SEM micrographs of the MgH₂ powder at different magnifications are indicated in Fig. 5.6a, b. From the micrographs, it can be observed that the particles are of different orientations, some are flake like in nature, while some are rod like and debris particles could also be observed. This also reveals the hydrogen generation sites on the particle of the MgH₂ powder.

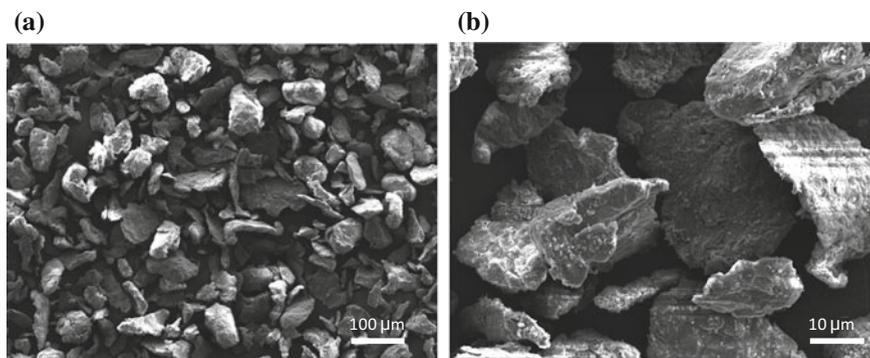


Fig. 5.6 SEM micrograph of the MgH₂ powder as received from the supplier

5.3.3 Substrate Elemental Composition Investigation

Composition/purity of the substrate is important to hydrogen yield. To ascertain the elemental composition of the MgH_2 sample, EDS analysis was conducted. From the EDS result in Table in 5.1 and Fig. 5.7, it can be revealed that three elements were observed in the MgH_2 powder namely magnesium (Mg), oxygen (O), and iridium (Ir). The Mg represent the major constituent as expected in the sample with weight and atomic compositions of 88.88 and 90.35% respectively. This composition is expected because Mg is the major composition of MgH_2 . The oxygen in the result could be attributed to oxidation process in the substrate while Ir is obtained from the coating material used in the preparation of the substrate for EDS analysis.

5.3.4 Temperature Optimization Effect on Hydrogen Yield

Temperature is believed to enhance reaction kinetics and thermodynamics in hydrogen storage in light weight metals. However, increasing reaction temperature also involves cost in terms of supply of heat throughout the duration of reaction which

Table 5.1 Elemental composition of MgH_2 powder

Element	Weight (%)	Atomic (%)
O	5.81	8.97
Mg	88.88	9.35
Ir	5.31	0.68
Total	100	100

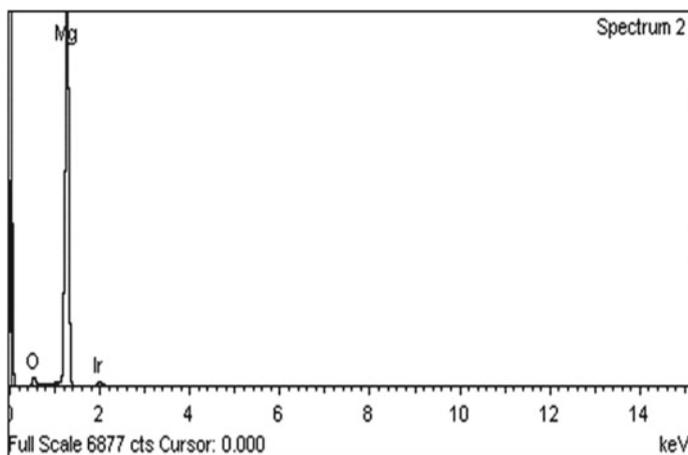


Fig. 5.7 EDS spectrum of MgH_2 powder

could be prohibitive to the sustainable scale of the technique of hydrogen storage in real time. It is important to examine the impact of external temperature supply on hydrogen yield to quantify its role. In this section three temperature parameters were examined in the addition to 50 °C wherein the first phase of experiments was conducted namely 25 °C, 30 °C and 60 °C respectively.

From the temperature optimization experiments (Figs. 5.3, 5.8, 5.9 and 5.10) it was observed that temperature change didn't have a significant impact on hydrogen yield. Interestingly, from Fig. 5.8, hydrogen yield at ambient temperature of 25 °C is comparable to what was obtained at higher temperatures in this study (Figs. 5.3, 5.9 and 5.10), this is a significant discovery as it proves that hydrogen release/desorption can take place at room temperature. Conversely, the test carried out at 25 °C recorded marginal difference in hydrogen generation from 0.8 g (0.139 L) and 1.2 g (0.015 L) MgH_2 respectively. While 0.0058 L hydrogen yield observed from the reaction of 0.4 g substrate was the third highest for all the 0.4 g MgH_2 reaction conducted in this study.

From all the experiments conducted, hydrogen generation increased as a function of substrate concentration. Moreover, the least hydrogen yield was recorded from 0.4 g MgH_2 at 70 wt% acetic acid (Fig. 5.5) with a value of 0.0048 L while the highest hydrogen generation of 0.018 L was recorded at 1.2 g MgH_2 (50 wt% acetic acid concentration). The results also followed the similar pattern to what was obtained in our previous study where MgH_2 pill was utilized as reaction substrate [11]. Thus, laying credence to the important role of substrate concentration to hydrogen yield in MgH_2 based hydrolysis experiment for hydrogen storage.

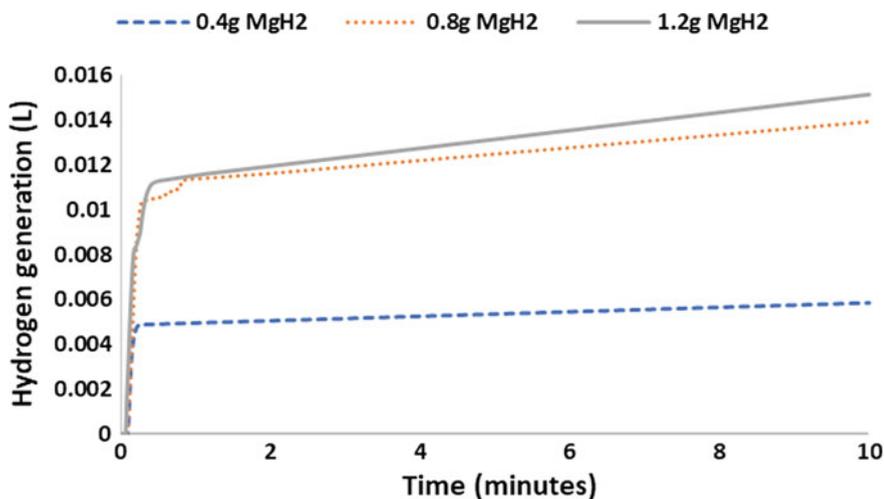


Fig. 5.8 Hydrogen generation at 25 °C, 50 wt% acetic acid concentration

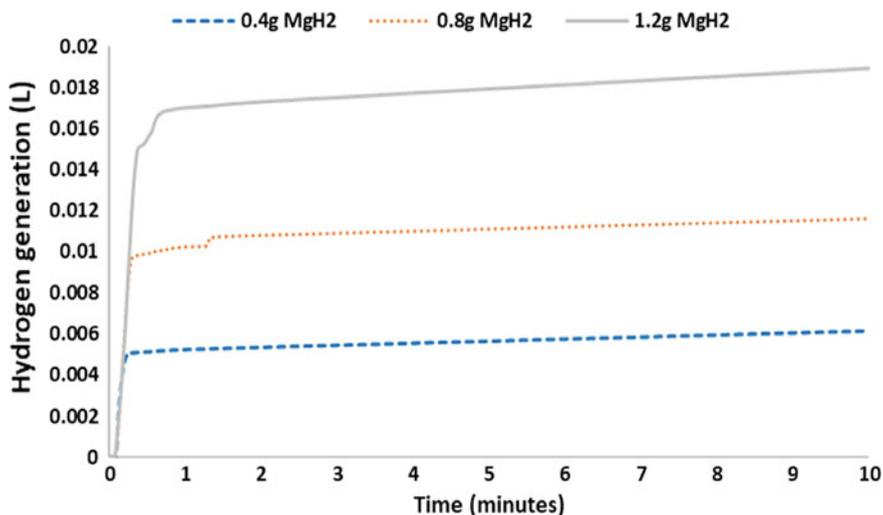


Fig. 5.9 Hydrogen generation at 30 °C, 50 wt% acetic acid concentration

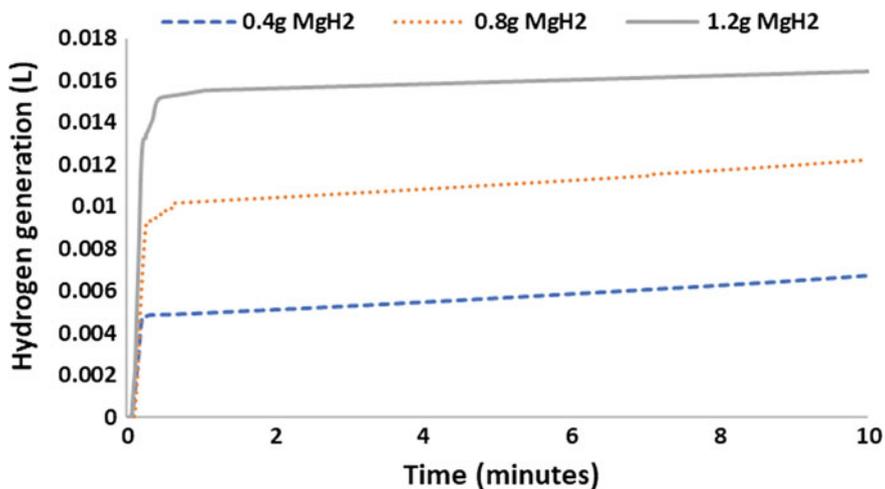


Fig. 5.10 Hydrogen generation at 60 °C, 50 wt% acetic acid concentration

5.4 Conclusion and Future Work

Hydrolysis of MgH₂ powder was catalyzed by an organic acid (acetic acid) using batch mode hydrogen reactor in this study. Acetic acid being a cheap catalyst employed also reduce the reaction cost thereby potentially enhancing the scale up potential of the technology. The observation that appreciable hydrogen can be generated at room temperature means experiment can be carried out without increasing

the reaction temperature thus eliminating the use of energy to supply heat which in turn reduce reaction cost. The cost reduction will further set the study in the path of sustainability drive necessary for the scale up of solid state hydrogen storage for on board vehicular application.

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