Organic Acid-Catalyzed Hydrolysis of Magnesium Hydride for Generation of Hydrogen in a Batch System Hydrogen Reactor

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***Abstract*— Hydrogen generation from MgH_2 is of interest to the research community due to various alluring attributes of MgH_2 as a hydrogen generation substrate. In this study MgH_2 powder was utilized as a substrate in hydrolysis reaction catalyzed by acetic acid, an environmentally friendly and relatively cheap acid. The reaction was conducted in a hydrogen generation reactor operated in a batch mode. Three sample weights (0.4g, 0.8g and 1.2g) of the substrates were utilized for the experiment at 40, 50, 60 and 70 wt% acetic acid concentration at 50 °C for investigation of the roles of substrate weigh and catalyst concentration on hydrogen yield. The results indicated that MgH_2 powder weight influenced hydrogen generation more compared to the catalyst concentration. The highest hydrogen yield in the study was 0.048 L hydrogen gas from 0.4g MgH_2 powder (70 wt% acetic acid) while the highest hydrogen generation was reported when 1.2g substrate hydrolyzed in 50 wt% acetic acid.**

***Index Terms*— Hydrolysis, hydrogen generation, kinetics, magnesium hydride, thermodynamics.**

I. INTRODUCTION

ENERGY plays an important role in the day to day living of man [1]. The growth and sustained development of any economy and society has energy as one of the pivots. With the undeniable importance of energy to life comes the increase in demand for various reasons such as economic and population growths [2, 3]. The cost of energy is huge and unaffordable to some people. Furthermore, besides the relative high cost of energy generation and energy tariff in most part of the world, some of the main energy generating methods are contributing to environmental pollution through the emission of greenhouse gases majorly in the form of methane, carbon dioxide (CO_2) and nitrous oxide (NO_X) [3, 4]. Moreover, renewable energy is an environment friendly means of energy generation that have offers advantage in environmental preservation and health [5]. Although, the scale up of renewable energy technologies now have not reached a stage where it can totally replace the major nonrenewable energy methods such as coal, thermal energy generation systems, it can serve a complementary energy sources. Hydrogen storage in metal hydrides is an interesting solid state hydrogen storage technique with increasing research interests with potentials for on board vehicular applications [6].

In the past, researchers have conducted energy storage tests on these special group of materials [7-11]. Brockman and colleagues[12], conducted an hydrolysis based reaction for hydrogeneration using ammonia borane as a substrate in a ruthenium (Ru) accelerated reaction. The study reported impressive hydrogen yields and storage stability. Conversely, the production of ammonia as a product of hydrolysis of ammonia borane represent a potential draw back due to toxic nature of ammonia. Similarly, the catalysis of the reaction with Ru a rare transition metal catalyst increases the cost of the experiment. Furthermore, metal alanates are another group of light weight metals with high hydrogen contents [13]. Conversely, applications of these set of materials as veritable hydrogen storage media have been limited due to reversibility and synthesis process limitations. Moreover, the study conducted by Bogdanovic and Schwickardi [14] proved that synthesis metal alanates ($NaAlH_4$, Na_3AlH_6, $LiAlH_4$) can be obtained in a single process for hydrogen storage with the aid of transition metal catalysts. In the study [14], acceptable reversibility at moderate temperature was achieved in the metal alanates by doping them with titanium catalysts. However, the adsorption and desorption temperature of over 150 C reported is high, likewise the there is need for reduction of desorption pressure. Similarly, the relative high cost titanium catalysts employed in the study has a potential of increasing reaction cost and render the approach non-sustainable.

Among the metal hydrides being studied as energy storage substrates magnesium hydride have generated great interests lately due to its high gravimetric (about 7.6 weight %) and volumetric hydrogen concentrations [15]. Magnesium hydride has energy density of about (9MJ/Kg Mg), the highest among the reversible metal hydrides

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[16].Furthermore, other attributes that have endeared MgH_2 to researchers on light weight metal applications for onboard vehicular applications include relative low cost and low hydrogen desorption pressure [17, 18]. In addition, hydrogen generation from MgH_2 is a renewable and environment benign process. The products of the reaction are non-corrosive in nature [19]. Magnesium is also regarded as the twelfth most copious element in the world and the third most prevalent in seawater [20, 21]. This translate to about 0.13% prevalence in seawater and 2.76 wt% on the earth respectively [22], thus providing hope for the availability of the substrate. However, sustainable application of MgH_2 as hydrogen storage material and upscaling of the technology for onboard storage in vehicles is threatened by slow reaction kinetics and thermodynamic limitation requiring the use of high temperature above the ambient temperature and pressure for hydrogen desorption [22, 23] . The kinetic and thermodynamic limitations need to be improved if the MgH_2 is to achieve its potential as a sustainable solid state hydrogen storage medium. Catalysts of various types have reportedly been used in hydrogen generation studies to improve reaction kinetics and thermodynamics. For example, Uan et al. [24] catalyzed an hydrolysis reaction of low grade magnesium scraps with platinum coated titanium net in sodium solution. The study reported remarkable hydrogen yield from the magnesium scrap substrate particularly under grinding condition. Conversely, the high cost of catalysts employed in the reaction could potentially limit the scale up of the technology. In another study, Hong and fellow workers [25], investigated the impact of ball milling, additive applications on hydrogen generation in an hydrolysis reaction involving the use of aluminium (Al) , titanium hydride (TiH_2), magnesium (Mg), unmilled and ball milled MgH_2 and MgH_2 alloyed with 5% (magnesium oxide) MgO, as substrates. Among the groups of substrates, the alloy of milled MgH_2 and 5%MgO recorded the best performance in terms of hydrogen generation with 0.97g hydrogen yield in one hour. However, like most hydrogen generations studies from metal hydrides, the hydrogen yield from this study is also small.

If hydrogen generation from metal hydride will be successfully scaled up, there is need to increase hydrogen yield, improve on safety, enhance the reaction kinetics of substrates, and reduce the desorption temperature and pressure (thermodynamics properties), and reduction of reaction cost. In this study, we report the use of magnesium hydride powder as hydrogen storage substrates in hydrolysis reaction catalyzed by an environmental friendly and cheap organic acid – acetic acid for hydrogen generation in a hydrogen generation reactor. This work is different from our previous study on acetic catalysis of MgH_2 for hydrogen generation because of the form of the substrates used. The previous substrates were MgH_2 tablets while MgH_2 powder was employed in the present study.

II. EXPERIMENTAL DESIGN AND METHOD

i. Hydrogen generation reactor operation

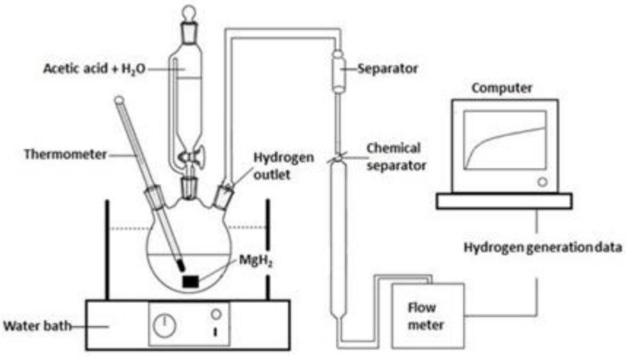

Fig. 1. Batch system hydrogen reactor experimental set up.

Fig 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), the moisture absorbent unit, the flowmeter (T1000, Fujikin) 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 datalogger connected to the flowmeter [26].

An organic acid catalyzed the experiment – acetic acid (99.8%, Labchem, SA (South Africa)). Magnesium hydride powder 99.8% purity (Rockwood Lithium, Germany) employed throughout the course of experiment as hydrogen storage media (substrate) was used as received from the supplier without further treatment with average particle size of 50 µm. The equation of reaction of magnesium hydride acetic acid catalyzed hydrolysis reaction can be seen in equation (1):

$$2\mathrm{M}g\mathrm{H}_2+2\mathrm{H}_2\mathrm{O}+2C\mathrm{H}_3C\mathrm{OOH}\rightarrow\mathrm{M}g\,(\mathrm{OH})_2+\mathrm{M}g\,(C\mathrm{H}_3C\mathrm{OO})_2+4\mathrm{H}_2+\Delta\mathrm{H}_{rxn}$$

The heat of reaction $(\Delta\mathrm{H}_{rxn})$ 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 (0.4g, 0.8g and 1.2g), except in 40 wt% acetic acid concentration where only 0.4g and 0.8g were utilized. Weighing of the substrate samples were carried out using BM-200 analytical balance with 0.0001g repeatability to enhance weighing uniformity. All experiments were carried out at 50 ºC external temperature.

Furthermore, the experiment was conducted using different catalyst concentrations (40 wt%, 50 wt%, 60 wt% and 70%).

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ii. Material characterization of reaction substrate (MgH_2) powder

Scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS) and X-ray-diffraction (XRD) analyses were conducted on the MgH2 powder for adequate material characterization. The SEM analysis of the MgH2 powder surface morphology was conducted using JSM 7600F Jeol ultra-high resolution field emission gun scanning electron microscope (FEG-SEM) equipped with EDS was utilized for the EDS analysis.

III. RESULTS AND DISCUSSION

i. 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 0.4g, 0.8g and 1.2g 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 Figures, 2, 3, 4 and 5.

Fig. 2. Present the result of hydrogen generation experiment at 40 wt % acetic acid concentration for 0.4g and 0.8g MgH_2 powder. From the results, it can be observed that higher hydrogen generation of 0.0098 L was obtained from the 0.8g MgH2 powder compared to maximum hydrogen generation of 0.005 L obtained in the 0.4g MgH_2 experiment.

From Fig.3. 0.4g MgH2 powder recorded the least hydrogen yield of about 0.0056 L, followed by maximum hydrogen generation of about 0.013 L at 0.8g while the highest hydrogen yield of 0.018 L obtained when 1.2g substrate was hydrolyzed in 50 wt% acetic acid.

Furthermore, the result of hydrogen generation experiment with 60 wt% acetic acid (Fig. 4.) indicated the least hydrogen yield of 0.005 L (0.4g MgH_2 powder), followed by 0.012 L and 0.013 L hydrogen at 0.8g and 1.2g MgH_2 powder respectively. Similarly, at 70 wt% acetic acid concentration, hydrogen generation increased with weight of substrate with 0.0048 L, 0.009 L, 0.013 L obtained from 0.4g, 0.8g and 1.2g substrate weight respectively.

From all the experiments conducted, hydrogen generation increased as a function of substrate concentration. Moreover, the least hydrogen yield was recorded from 0.4g MgH_2 at 70 wt% acetic acid concentration with a value of 0.0048L while the highest hydrogen generation of 0.018L was recorded at 1.2g 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 the substrate [26]. Thus, laying credence to the important role of substrate concentration to hydrogen yield in MgH_2 based hydrolysis experiment for hydrogen storage.

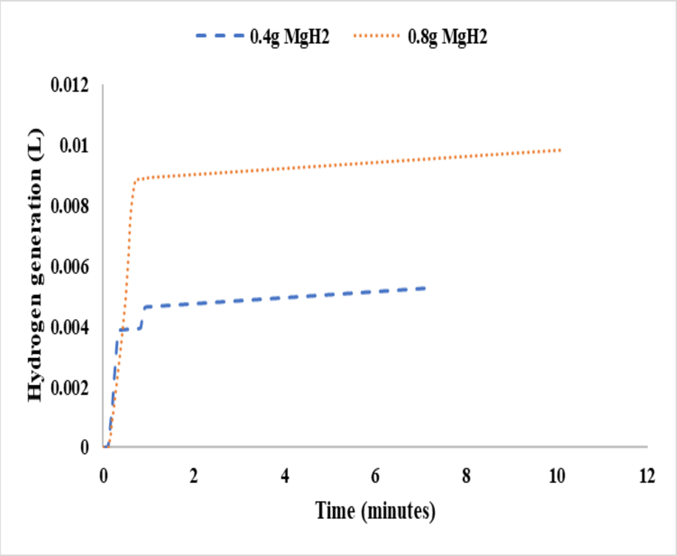

Fig. 2. Hydrogen generation at 40 wt % acetic acid concentration

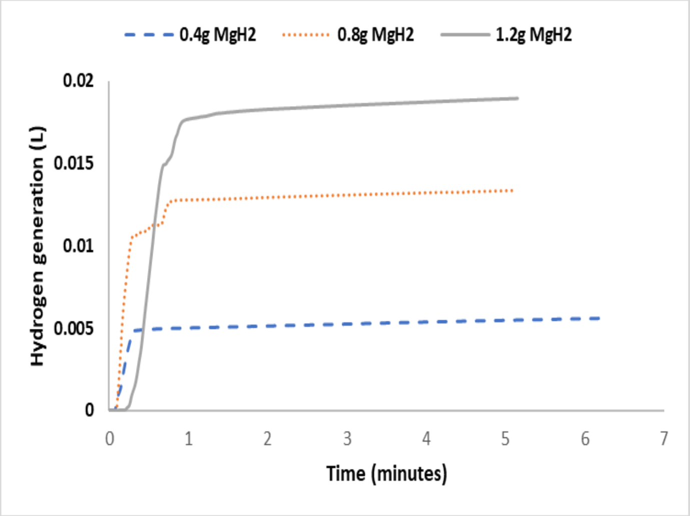

Fig. 3. Hydrogen generation at 50 wt% acetic acid concentration

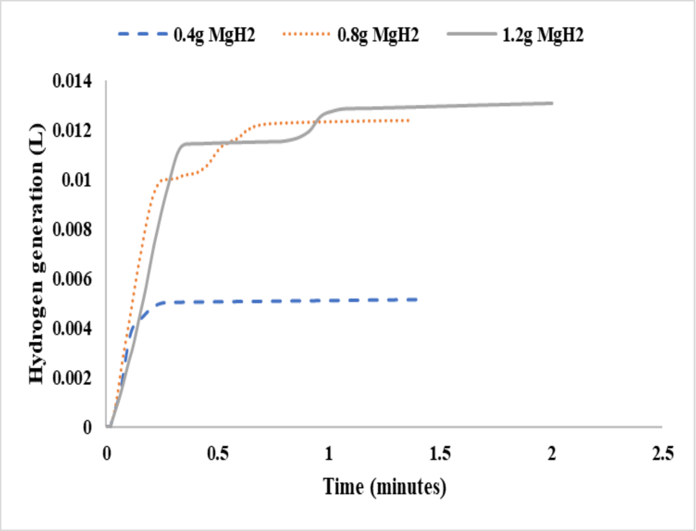

Fig. 4. Hydrogen generation at 60 wt% acetic acid concentration

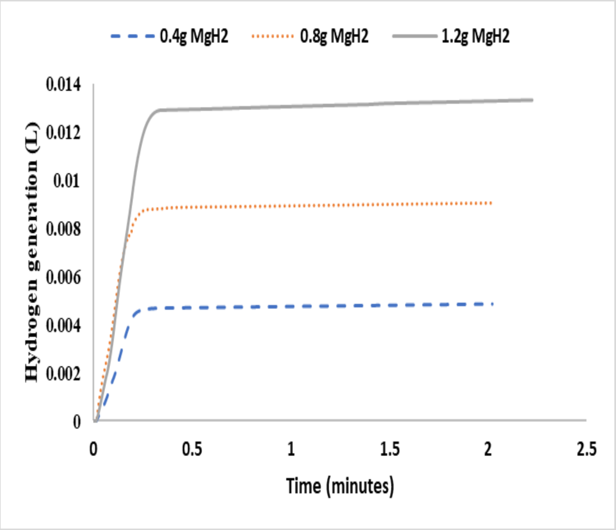

Fig. 5. Hydrogen generation at 70 wt% acetic acid concentration

ii. Scanning electron micrograph characterization of substrate

The SEM micrographs of the MgH_2 powder at different magnifications are indicated in Fig. 6 (a and 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 MgH_2 powder.

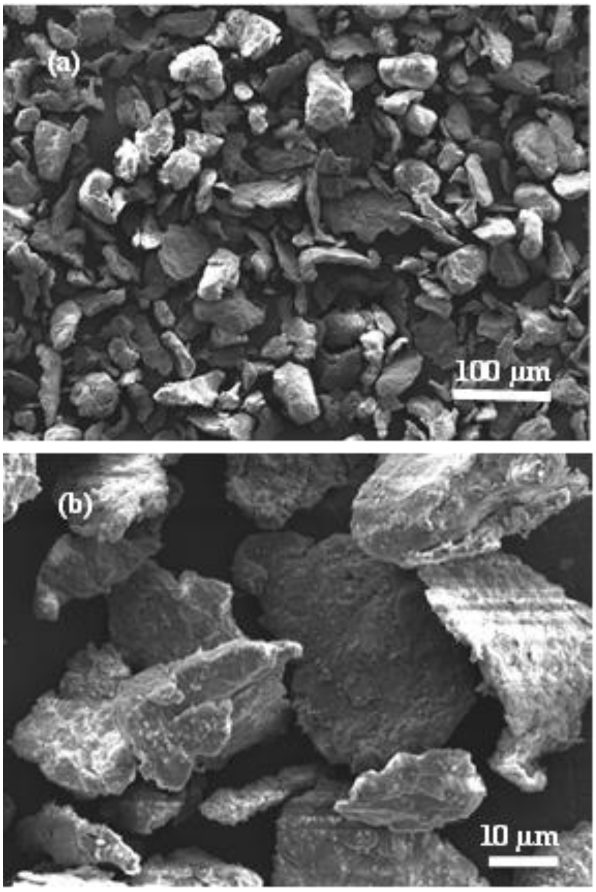

Fig 6. SEM micrograph of the MgH_2 powder as received from the supplier

iii. 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 I and Fig. 7, it can be observed 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.

TABLE I
ELEMENTAL COMPOSITION OF MgH_2 POWDER

Element	Weight (%)	Atomic(%)
O	5.81	8.97
Mg	88.88	90.35
Ir	5.31	0.68
Total	100	100

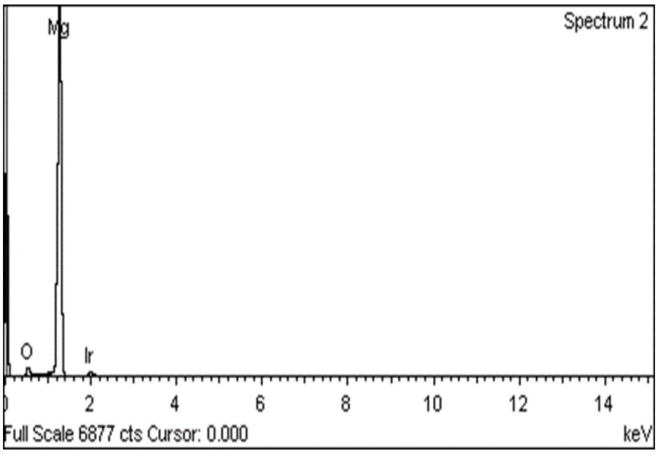

Fig. 7. EDS spectrum of the MgH_2 powder

IV. CONCLUSION

Hydrolysis of MgH_2 powder was catalyzed by an organic acid (acetic acid) using batch mode hydrogen reactor. The discovery of higher hydrogen yield at higher substrate concentration also open area of research on optimization parameters for hydrogen generation. Acetic acid being a cheap catalyst employed also reduce the reaction cost thereby potentially enhancing the scale up potential of the technology.

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