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# MATHEMATICAL MODELING OF HYDROGEN PRODUCTION FROM METALLIC ALUMINUM IN PILOT SCALE REACTOR

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**Abstract.** Fossil fuels are still the most used energy sources in the world, however many energy alternatives have been proposed to replace these fuels. As is common knowledge, these fuels contribute to the increase in the greenhouse effect and have their main sources in countries with great political instability, which makes the price of these derivatives very volatile. Among the fuels that can replace fossil fuels, hydrogen stands out. This fuel generates zero pollution, as its burning generates only water, not contributing to the generation of greenhouse gases and other pollutants. In addition, hydrogen can be used in fuel cells where efficiency can reach up to 70%. However, obtaining hydrogen is still economically unfeasible, as it requires electrolysis of water, a process that uses a lot of energy, or reforming of hydrocarbons that requires water vapor and generates greenhouse gases. In this context, hydrogen generation from metallic aluminum arises, where it does not require energy to generate hydrogen. In this hydrogen generation system, metallic aluminum reacts with sodium hydroxide and water to form sodium aluminate and hydrogen gas. Unlike other technologies, there is no need to add energy to the system as this reaction is highly exothermic, releasing a large amount of heat. However, this technology is still in its infancy and there is no commercial plant for generating hydrogen with this process. Thus, the objective of this work is to propose a mathematical model for the generation of hydrogen from metallic aluminum in pilot scale reactor. The model consisted of energy and mass conservation equations. The mathematical model was experimental validated in pilot scale 18 liters reactor. At the end of the work it is expected to obtain a model that can be used to design and optimize hydrogen generation systems from metallic aluminum in pilot scale reactors.

***Keywords:*** *hydrogen, pilot scale reactor, chemical kinetics, math model, aluminum*

## 1. INTRODUCTION

Fossil fuels are widely recognized for their abundance, vast reserves, and anticipated continued use for many years. However, it is crucial for scientific research and the policies implemented by various nations to focus on diversifying theenergy matrix with alternative sources. This approach aims to mitigate environmental impacts and preserve our ecosystem (Solarin et al, 2022; Feng and Zheng, 2022). Masnadi (2015) addresses the importance of replacing sources that release carbon dioxide into the atmosphere with renewable sources. Addressing the energy issue to change new matrices, in addition to seeking affordable energy solutions.

At the beginning of the 21st century, Dresselhaus and Thomas (2001) highlighted the urgency of developing innovative and environmentally sustainable technologies for future alternative energy sources, replacing conventional fossil fuels and nuclear power. More recently, Chen et al. (2018) reinforced the contemporary nature of this need and pointed that generating and storing renewable energy in a technically and economically viable manner are the main obstacles to overcome.

The aforementioned context includes various processes and technologies, such as hydrogen production, despite theirinherent limitations and challenges. Hydrogen can be utilized to generate energy in fuel cells through its reaction with oxygen. Moreover, the byproduct of this reaction is water ($H_2O$), which does not contribute to environmental degradationor temperature increases associated with the greenhouse effect (Bolt et al., 2020).

Hydrogen can be obtained through multiple processes and techniques, already extensively employed, involving biomass, water, and fossil fuels (Bakenne et al., 2016). Recently, a novel method of hydrogen production involving the use of aluminum has been investigated. This method utilizes aluminum to extract $H_2$ molecules from water molecules (Bolt et al., 2020). The authors also highlight that aluminum is the third most abundant element on Earth, constituting 8.1% of the Earth's crust. In this regard, aluminum waste, such as used beverage cans directed for recycling or disposal, can be utilized for hydrogen production. Consequently, the entire process can become more environmentally friendly, asit makes use of aluminum in its waste form. Given the extensive collection network for discarded aluminum, the availability of raw material for the process is not a concern.

The development of appropriate mathematical models plays a fundamental role in modern engineering projects. Thesemodels allow for the optimization of the system under study, aiming to achieve maximum performance with minimal energy or reagent consumption, while determining the optimal operating parameters for the proposed process. Mathematical models have the capability to simulate the process under any operating condition without the need for realexperiments. Incorporating mathematical modeling into the hydrogen production process from aluminum waste is of utmost importance to enhance the overall process. This integration enables gradual improvements in the technology's feasibility by reducing costs and increasing efficiency.

Several articles in the literature have already addressed the production of hydrogen from aluminum (Hurtubise et al.,2018; Setiani et al., 2018; Bolt et al., 2020; Noland et al., 2020; Haller et al., 2021). This article proposes the developmentof a mathematical model for a reactor designed to produce hydrogen from recyclable aluminum. The mathematical modelwas validated through experiments carried out in an 18-liter pilot-scale reactor, developed and produced by the authors of the study.

## 1. MATERIALS AND METHODS

A mathematical model, considering mass and energy balance, is introduced. A system of ordinary differential equations is conceived and solved using MATLAB. The model considers the kinetics of the chemical reaction of hydrogen generation from aluminum waste (Al) and sodium hydroxide (NaOH). For the present analysis, we considered a perfectly stirred reactor.

### 1.1 Pilot Scale Reactor

The 18-liter pilot-scale reactor was designed and manufactured, in partnership with the Maringa State University (UEM). Figure 1 shows a schematic and a photo of the hydrogen reactor.

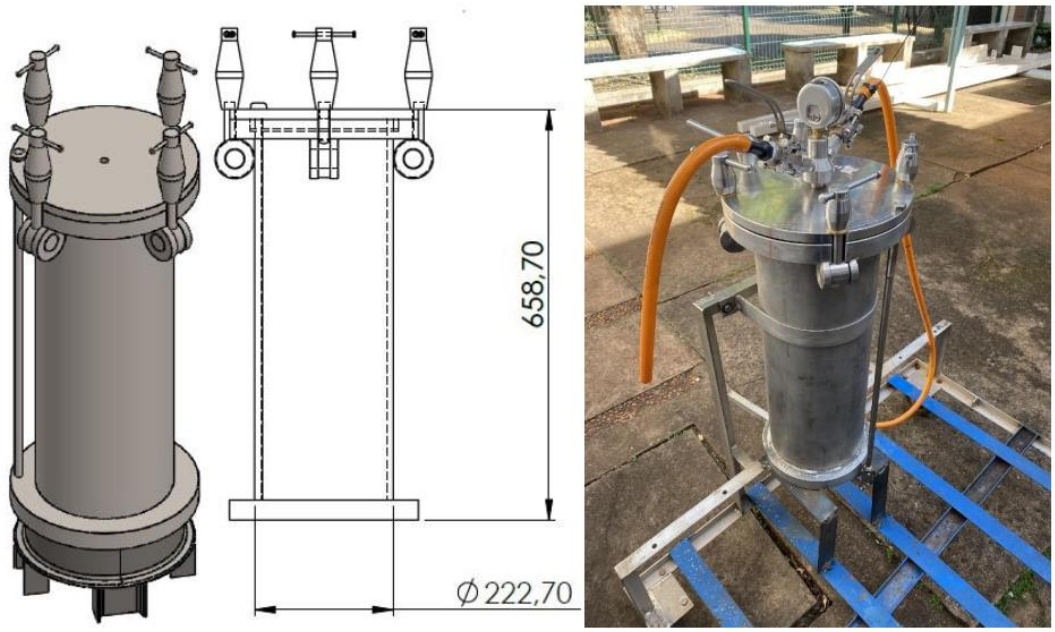


Figure 1. Pilot scale reactor used to perform the experiments and develop the mathematical model. Units in mm.

### 1.2 The hydrogen generator reactor mathematical model

The balanced chemical reaction of hydrogen generation in the presence of sodium hydroxide, according to Bolt et al., (2020), is described in Eq. (1):

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2 \tag{1}$$

According to Noland et al., the rate of the reaction is given by the Eq. (2):

$$r = k_0 S_{Al}^{bs} [NaOH]^{bc} \exp\left(\frac{E_a}{\bar{R}T_r}\right) \tag{2}$$

in which $k_0$ is the Arrhenius constant, $S_{Al}$ the particles total surface area, *[NaOH]* the mols of NaOH to mass of $H_2O$ ratio, $E_a$ the reaction activation energy, $R$ the universal gas constant, *bs* Al reaction order and *bc* the sodium hydroxide reaction order.

Aluminum consumption is proportional to the decrease in the particle radius, thus surface area. Therefore, the following equations allow for obtaining the mass and average particles radii of Al, mols of NaOH, mass of $H_2O$, the mols of NaOH to mass of $H_2O$ ratio and the hydrogen generation.

$$\frac{dm_{Al}}{dt} = -Y_{Al} r \ , \ R = R_0 \left( \frac{m_{Al}}{m_{Al,0}} \right)^{1/3} \tag{3}$$

$$\frac{dn_{NaOH}}{dt} = -Y_{NaOH} r \tag{4}$$

$$\frac{dm_{H2O}}{dt} = -Y_{H_2O} r \tag{5}$$

$$[NaOH] = \frac{n_{NaOH}}{m_{H2O}} \tag{6}$$

$$\frac{dn_{NaAlO2}}{dt} = Y_{NaALO2} r \tag{7}$$

$$\frac{dm_{H2}}{dt} = Y_{H2} r \tag{8}$$

In which, t is the time, $Y_{Al}$ = 7.93×10$^{-7}$ kg Al ml$^{-1}$H$_2$, $Y_{NaOH}$ = 2.93×10$^{-5}$ mol NaOH ml$^{-1}$H$_2$, $Y_{H_2O}$ = 5.28×10$^{-7}$ mol mol H$_2$O ml$^{-1}$H$_2$, $Y_{H_2}$ = 8.81×10$^{-5}$ mol H$_2$ ml$^{-1}$H$_2$ and $Y_{NaAlO_2}$ = 2.93×10$^{-5}$ mol NaAlO$_2$ ml$^{-1}$H$_2$.

The time dependent total aluminum particles surface area, $S_{Al}$, is estimated using the theory of monodisperse spheres as follows (Noland et al., 2020):

$$S = \frac{6 C_{Al} V_r}{\rho_{Al}} \tag{9}$$

in which, the theory assumes that the number of Al particles, $N_P$, remains constant during the entire reaction duration (Noland et al., 2020), so that $N_P = V_{T,Al,0}/V_{1p,Al,0} = (m_{Al,0}/\rho_{Al})/(4\pi R_0^3/3)$, with subscript 0 indicating conditions at t = 0 (start of the reaction), $C_{Al} = \rho_{Al} N_P 4\pi R^3/3/V_r$ is the aluminum mass concentration, kg m$^{-3}$, in the reactor at any instant t, $V_r$ the reactor volume and $\rho_{Al}$ the aluminum density.

The energy balance of the system can be observed in Eq. (10):

$$\frac{dT_r}{dt} = \frac{h_r r - UA(T_r - T_\infty)}{C} \tag{10}$$

The thermal capacity of the system can be defined as Eq. (10):

$$C = (c_{Al} m_{Al} + c_{NaOH} n_{NaOH} + c_{H2O} m_{H2O} + c_{H2} m_{H2} + c_{NaAlO2} n_{NaAlO2}) \tag{11}$$

### 1.3 Initial conditions used in the development of the mathematical model.

The initial parameters that were considered and used for the simulations through the mathematical model can be checked in Table 1:

Table 1. Initial parameters used in the development of the mathematical model.

| Parameter | Symbol | Value | Unit |
|---|---|---|---|
| Reaction order (Al) | bs | 1.0 | - |
| Reaction order (NaOH) | bc | 0.55 | - |
| Specific heat of water | $c_{H_2O}$ | 4180 | $J.kg^{-1}.K^{-1}$ |
| Specific heat of sodium hydroxide | $c_{NaOH}$ | 1.55 | $J.kg^{-1}.K^{-1}$ |
| Specific heat of hydrogen | $c_{H_2}$ | 14.4 | $J.kg^{-1}.K^{-1}$ |
| Specific heat of sodium aluminate | $c_{NaAlO_2}$ | 0.89 | $J.kg^{-1}.K^{-1}$ |
| Specific heat of aluminum | $c_{Al}$ | 0.89 | $J.kg^{-1}.K^{-1}$ |
| Reaction activation energy | $E_a$ | 65000.0 | $J.mol^{-1}$ |
| Reaction enthalpy | $h_r$ | 140000.0 | $J.kg^{-1}$ |
| Frequency factor | $k_0$ | $72004.9\times10^{6}$ | $mLH_2.s^{-1}.cm^{-2bs}mol\ NaOH^{-bc}kgH_2O^{bc}$ |
| Initial mass of $H_2O$ | $m_{H_2O}$ | 4.0 | kg |
| Initial mass of Al | $m_{Al,0}$ | 200.0 | g |
| Initial number of moles of NaOH | $n_{NaOH}$ | 8.0 | moles |
| Universal gas constant | R | 8.314 | $J.mol^{-1}.K^{-1}$ |
| Aluminum particle sphere radius | $R_0$ | $6.15\times10^{-6}$ | m |
| Ambient temperature | $T_\infty$ | 298.0 | K |
| Initial temperature reactor | $T_{r,0}$ | 335.0 | K |
| Thermal conductance | UA | 4725.0 | $W.K^{-1}$ |
| Reactor volume | $V_r$ | 0.02 | $m^3$ |
| Constant of stoichiometric proportionality | $Y_{Al}$ | $7.93\times10^{-4}$ | - |
| Constant of stoichiometric proportionality | $Y_{NaOH}$ | $2.93\times10^{-5}$ | - |
| Constant of stoichiometric proportionality | $Y_{H_2O}$ | $5.28\times10^{-7}$ | - |
| Constant of stoichiometric proportionality | $Y_{H_2}$ | $8.81\times10^{-5}$ | - |
| Constant of stoichiometric proportionality | $Y_{NaAlO_2}$ | $2.93\times10^{-5}$ | - |
| Aluminum density | $\rho_{Al}$ | 2700 | $Kg.m^{-3}$ |

## 2. RESULTS AND DISCUSSION

The Figure 2 presents the comparison between the theoretical and experimental hydrogen production of the reactor shown in the Fig. 1. The theoretical hydrogen production curve touches one point of the experimental data, closely matching the other points. The production of hydrogen in the reactor tends to reach the steady state (16 g) after 10 minutes of reaction.

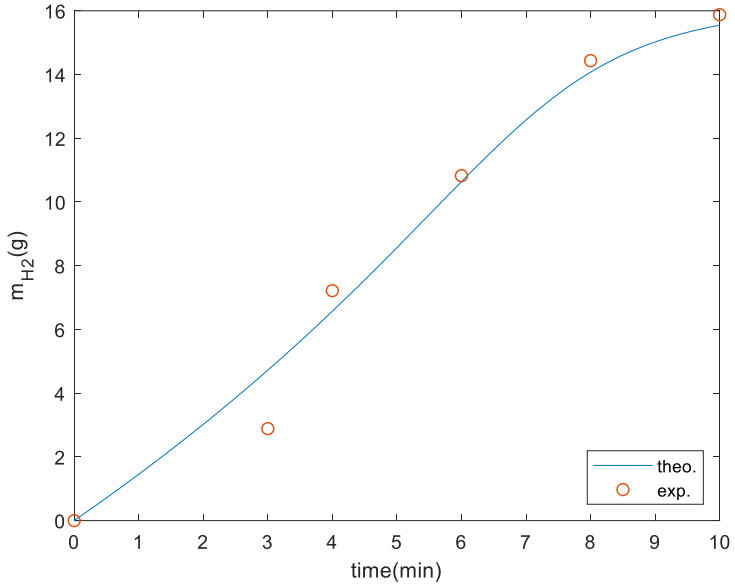


Figure 2. Experimental data and theoretical curve of the mathematical model of hydrogen production, in g, over time

Figure 3 demonstrates the consumption of aluminum to produce hydrogen by decreasing the mass of the metal particles. As the mass decreases, there is also a decrease in the total aluminum surface available for the reaction. After 10 minutes of reaction there is a decrease of approximately 75% of all aluminum in the reaction medium (150 grams).

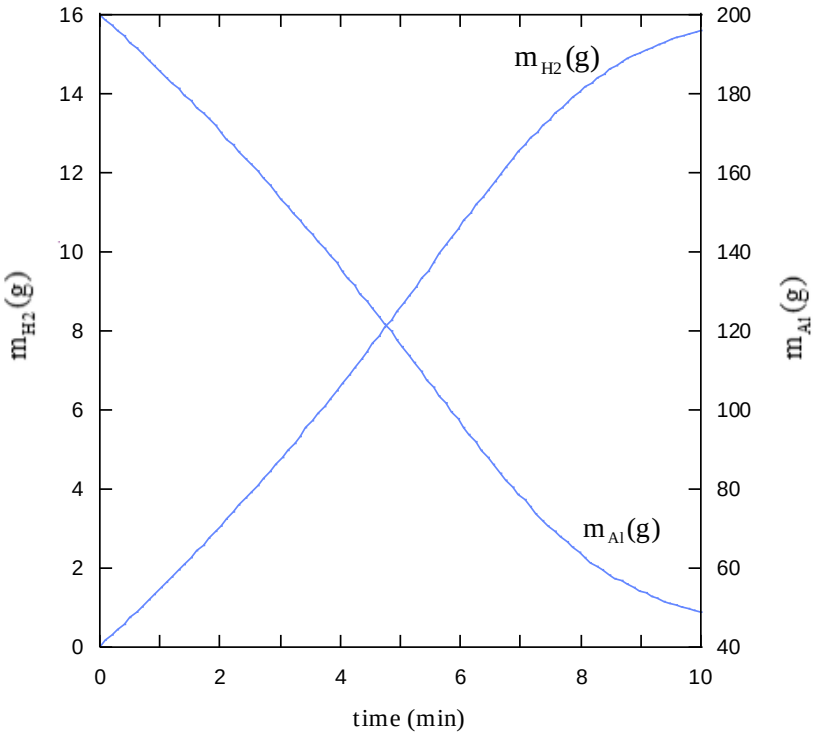


Figure 3. Theoretical curve of aluminum consumption (decreased mass) in the hydrogen production reaction over time

The sodium hydroxide consumption profile in the reaction occurs in a similar way. This information can be observed through the analysis of Figure 4. After approximately 10 minutes of reaction, the number of moles of sodium hydroxide is consumed from 8 to approximately 1.5; a reduction of 83 %.

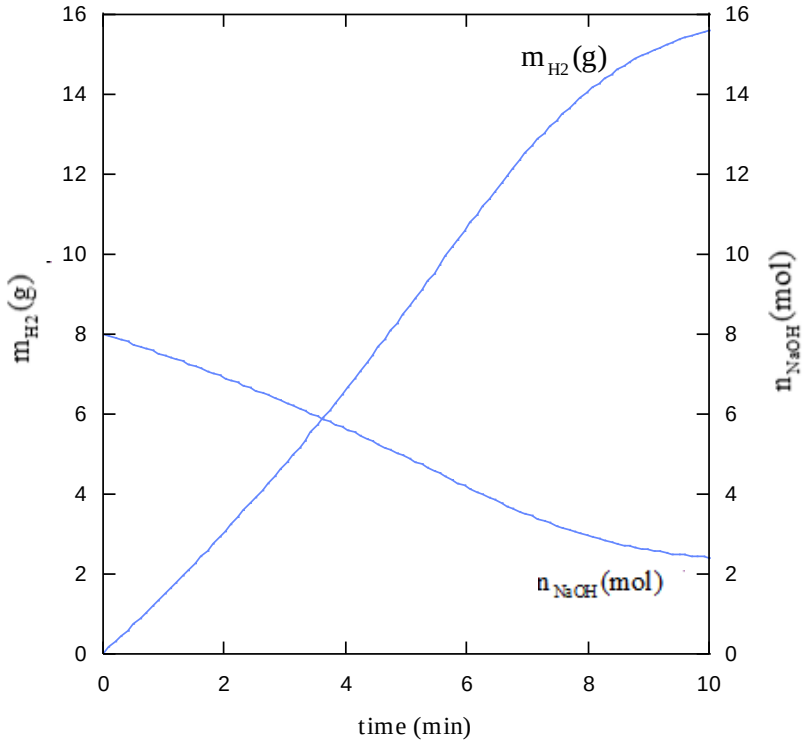


Figure 4. Theoretical curve of sodium hydroxide consumption, in moles, in the hydrogen production reaction over time

Figure. 5 depicts the consumption behavior of the water in the hydrogen production reaction. The water consumption profile is similar to aluminum and sodium hydroxide and, after 10 minutes of reaction, 0.1 kg of $H_2O$ is consumed (2.5%).

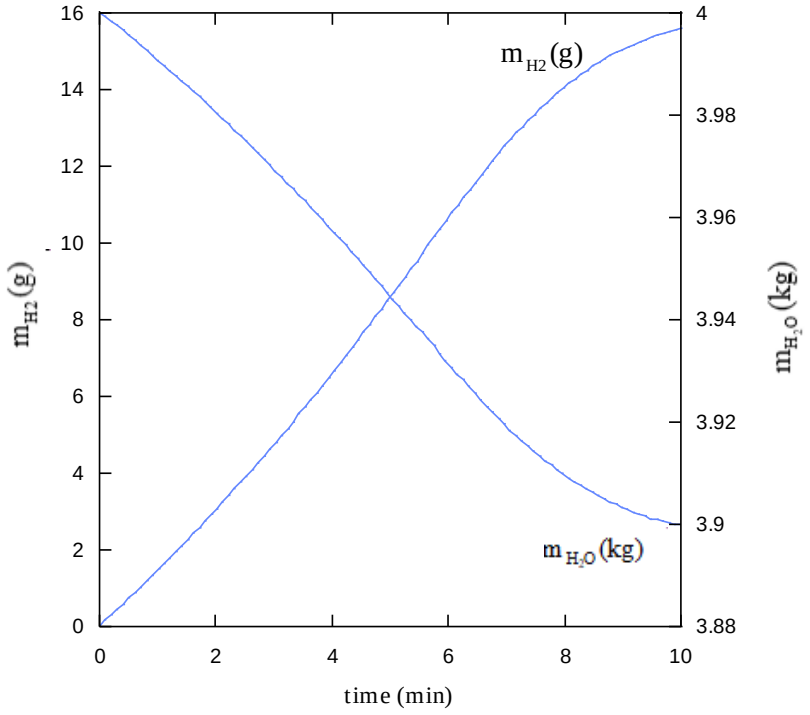


Figure 5. Theoretical curve of water consumption, in kg, in the hydrogen production reaction over time

Finally, Fig. 6 demonstrates the behavior of the last parameter modeled and considered in the hydrogen production: the temperature variation during the considered reaction time. In the seventh minute, the temperature peak occurs (355 K). From that moment on, there is a decrease in temperature, reaching approximately 339 K after 10 minutes of reaction. This is an indicative of the decrease in the reaction rate of hydrogen production.

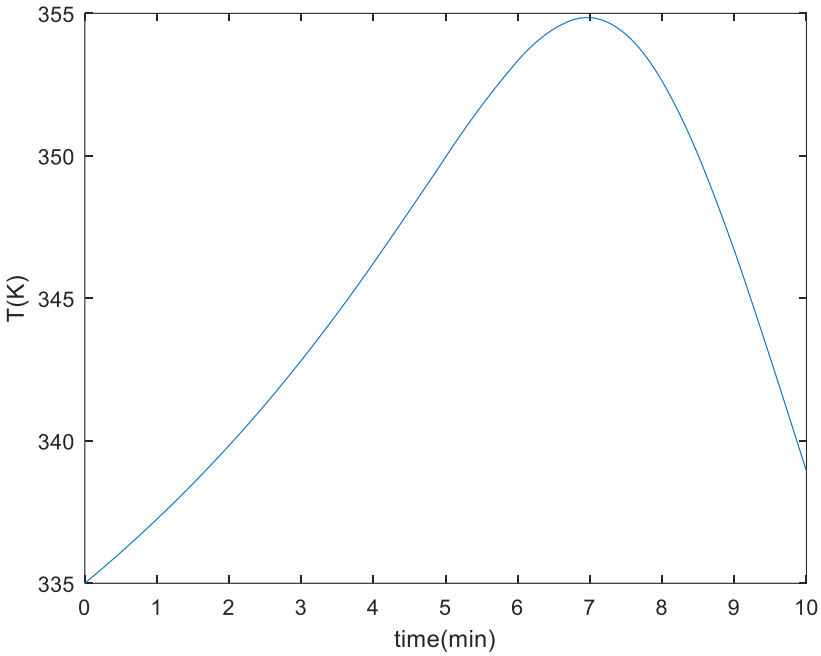


Figure 6. Theoretical curve of temperature variation, in K, in the hydrogen production reaction over time.

## 3. CONCLUSIONS

The objective of this article was to create a mathematical model that accurately describes the production of hydrogen from aluminum scrap. The proposed model successfully aligned with the experimental data, providing a comprehensive overview of the $H_2$ production process. Developing and refining mathematical models for this purpose is essential to ensure the viability and feasibility of the proposed technology. This will help enhance reaction performance while reducing energy costs, reagent usage, and time requirements. The subsequent stages of this research will involve incorporating additional variables associated with the process to further refine the model and improve the accuracy of hydrogen production predictions.

## 4. ACKNOWLEDGEMENTS

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