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The Use Of Aluminum And Coconut Shell Waste For Hydrogen Production

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Abstract

Renewable energy applications should be prioritized in order to implement clean and environmentally friendly energy, one of which is hydrogen gas. Hydrogen gas production can be obtained through metal hydrolysis process, using specifically, aluminum cans waste, which would help the effort of aluminum waste recycling. The waste recycling effort is also carried out by adding organic waste like coconut shells. Both of these materials were used in this research for hydrogen gas production. This study aims to analyze the effect of the differences in the composition ratio of aluminum and NaOH solution mass, and the effect of activated carbon catalysts presence to hydrogen production. The method used in this study is experimentation, where the data is obtained, processed and then analyzed by using statistic's descriptive techniques to determine the effectiveness of hydrogen production. The results showed that the optimal ratio of aluminum and NaOH solution mass of 1:5 (Al 16.67%w.t), and the additional of activated carbon catalysts can affect the increase on hydrogen production (volume, rate, and yield), even in the condition of room temperature and pressure. These results provide the opportunity to utilize domestic waste recycling approach in producing hydrogen as a source of clean energy for the environment.

Keywords: activated carbon, hydrogen gas, metal hydrolysis, renewable energy

Introduction

The use of renewable energy should be the main concern of the world government not only as an effort to reduce the use of fossil energy but also to implement clean and environmentally friendly energy[1]. One example of technology that is being developed in implementing the use of renewable energy is hydrogen gas.

Hydrogen, which is the most abundant element in the universe, is one of the promising sources of alternative energy. This is because the hydrogen combustion process only produces water and energy, so it is an environmentally friendly energy fuel[2]. Hydrogen is considered an effective and zero-emission alternative fuel. Several methods have been used to produce hydrogen, such as methanol reformation, water electrolysis, solar water distillation and natural gas formation [3].

Another method of producing hydrogen is to recycle metal waste, through the process of metal hydrolysis, especially aluminum metal waste in the form of used cans of beverage or food packaging, etc. The process of hydrolysis of metals, especially aluminum, is carried out with the help of catalysts. Aluminum is often used for energy production and energy storage.[4]. This is proven by the use of aluminum-based batteries, which is one of the examples of an implementation of a potential energy resource[5], and is one of the metals that have abundant resource because of its reproduction and its sustainability[6].

However, aluminum also accounts for the production of non-ferrous (non-iron) metal waste, currently. The production of aluminum metal waste is mostly obtained from packaging waste which accounts for about 60% of non-iron type metals[7]. This is due to the increasing consumption of aluminum metal every year, in all parts of the world. Based on data obtained from Mathilde Carlier and team, aluminum consumption globally continues to increase from 2016 at 58 million metric tons (equivalent to billion kilograms), to 62.5 million metric tons this year[8]. This number is predicted to continue to increase every year. One of the contributions of aluminum metal waste that can be found in everyday life is beverage cans.

Aluminum metal in beverage cans have been increasing the consumption of soft drinks such as soda and beer to a large extent, that it reaches 2×10^{11} cans annually[9]. If the mass of a can reaches about 300 grams, then the amount of waste mass of aluminum cans will reach about 6 billion kilograms every year. Nevertheless, such waste has significant value in the recycling cycle, especially metal waste.

In addition to recycling aluminum waste, recycling efforts are also carried out in organic waste or biomass, where biomass waste, produced particularly from agriculture, is considered a very important raw material because it is reusable and cheap in cost[10]. One example of biomass waste searched for recycling is coconut shell waste, where the waste can be used as an active carbon bio-fuel, which can be used a catalyst for the production process of hydrogen gas. In addition, activated carbon products produced from coconut shell waste have much more carbon content and less impurities, compared to other raw materials[11].

One way to reduce aluminum metal waste and coconut shells is to utilize both materials into clean energy technology namely hydrogen gas, that do not pollute the environment because they produce no waste at all. This clean energy is renewable energy.

In this study, the objective is to analyze the effect of differences in the composition of the ratio of aluminum and NaOH solution mass on hydrogen production through the process of hydrolysis and to analyze the effect of adding various different pre-treatment, varied by voltage and time in the activation process of carbon catalysts in the hydrogen production through the process of aluminum hydrolysis. This research is motivated by previous studies that have shown results of metal based hydrogen production through hydrolysis process with many different types of variations that affect its productivity, volume, and rate.

Methods

Review Stage

Fig 1 shows the flowchart of the experiment steps from the preparation of obtaining the electro-activated carbon, which undergoes these processes: pulverization, carbonization, and activation by electricity.

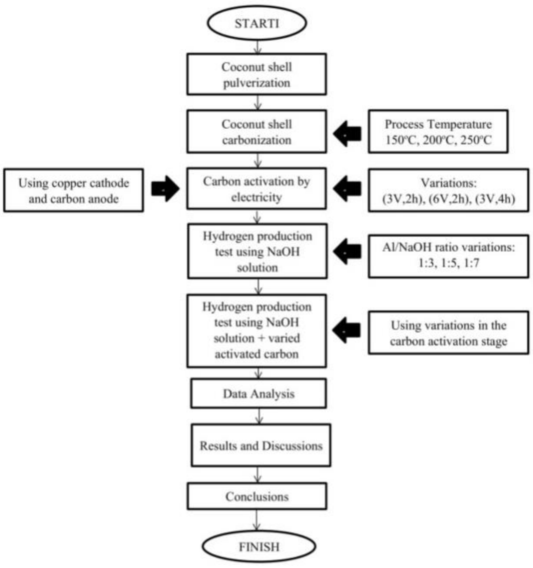


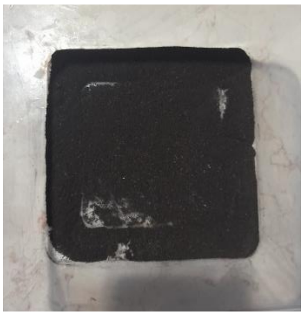
Fig1. Flow chart of the experimental steps for hydrogen production by hydrolysis process using catalysts and analysis.

The preparation started from cracking 1 kg of coconut shell waste using pestle and mortar into smaller pieces, and then the pieces were blanched in water for 3 hours. The blanching process was a preparation step before the pieces put into blender, in order to be pulverized without breaking the blender. Next, the wet and moist coconut shell pieces were pulverized using a blender for 3 minutes, so that the coconut shell is produced in the form of a very fine powder. After the process of refining by a blender, coconut shell powder was then dried for 1 day, and after that it was strained using sieve, so that the most refined coconut shell powder is obtained for use in the carbonization process. The pulverizing process of coconut shell pieces and the straining of coconut shell powder are to ensure even distribution in size and shape of the contact that occurs between temperature and the surface of the sample.

The powder was then heated up using direct heat from gas stove in 2 different stages of temperature (200°C and 250°C), so that it would transform into carbon material, and after that process, the powder was strained though sieve, once again, in order to set aside any impurities in the powder as a result of carbonization.

Fig2. Coconut shell powder after heating at (a) 150°C in the oven, (b) 200°C on a gas stove, (c) 250°C on a gas stove.

(a) **(b)**



(c)

Furthermore, using the carbon powder obtained, it was then activated using electro-activation method, which is electrolysis. This process required a carbon anode and copper cathode, with 15 mL of 1.5 M NaOH solution acting as the electrolyte solution. All of the equipment and material explained before were connected to DC power supply, with 3 treatment variations of activation method to the carbon powder.

For the hydrolysis process, it was divided into 2 different processes (without and with activated carbon). The hydrogen production without using activated carbon required 3 g of aluminum and 1.5 M NaOH solution poured inside an Erlenmeyer flask, and stirred until homogenous. This process used 3 different variations of solvent and aluminum mass ratio. The variations were 1:3 (Al 25%w.t.); 1:5 (Al 16.67%w.t.); 1:7 (Al 12.5%w.t.), which then the optimum ratio would be evaluated and used as a basis for the second hydrogen process using activated carbon. After that, the second hydrogen production process used the same basis from the result of the first process, and were added the electro-activated carbon, using the 3 different treatment variations, which after that the solution was stirred until homogenous, also. In the end, the hydrogen gas production duration, volume, and rate were then evaluated.

Results and Discussion

Carbonization Process

Fig2 shows the result of coconut shell powder carbonization, which started off by the drying process using oven at 150^{o}C, and then the pyrolysis process at 200^{o}C and continued at 250^{o}C on gas stove . The carbon produced after this process was then being analyzed for its mass reduction and carbon yield percentage. The mass reduction is calculated by subtracting the powder mass after from before, whereas the carbon yield percentage is calculated by comparing the coconut shell powder mass before and after the carbonization process.

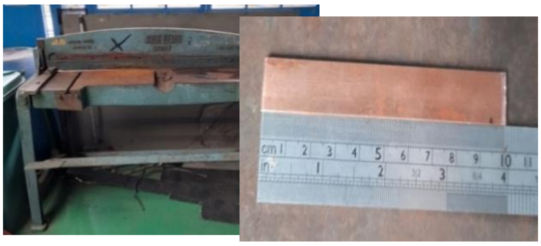
The carbonization process showed that substances like water, ash, and tar were mostly evaporated from the sample[12]. Moreover, this process helps to improve and increase the carbon content of the powder sample, in order to be used as a catalyst for the hydrolysis process.

TABLE I. Carbon yield data after carbonization process

Temp. (^{o}C)	Mass before (gram)	Mass after (gram)	Mass Loss (%)
150	45.1	43.4	3.77%
200	43.4	32.3	25.58%
250	32.3	30.2	6.50%

The Electro-activation Process

Before going through the electro-activation process, there were steps in the preparation required for the process, in order to obtain properly activated carbon material. At this stage, carbon rod was used as the anode, while copper bar was used as the cathode. The copper was first cut by manual plate-cutting tool, in order to obtain 10cm long copper bars. These electrodes were then connected to the power supply to provide electricity voltage and current, during the electro-activation process. This electro-activation process used electrolysis method, that utilize the redox (reduction-oxidation) chemical process and results[13], so that facilitates the OH^- ions diffuse (penetrate) more inside the pores on the surface of the carbon that has been added as a result of the electro-activation process. Water itself can be used for this process, however the addition of NaOH also helps on increasing the conductivity and also work as a de-foaming agent to help break the hydrogen bond[14].



(a) (b)

(c) (d)

Fig3. Preparation of electro-activation process; (a) Manual plate cutting machine, (b) Copper plate 3mm thick, 10 cm long, (c) Carbon cylinder rod 3mm in diameter, 10 cm long, (d) Circuit arrangement during electro-activation process.

In Fig3 above, displays the preparation required, the material and the equipment used for the carbon electro-activation process, which will be used as a catalyst for the hydrogen production using aluminum hydrolysis method.

Hydrogen Production without Activated Carbon

The hydrogen gas production process was done by reacting pieces of circular aluminum metal with a diameter of 1.8 mm from a used beverage can with a NaOH 1.5 M solution (NaOH + tap water), without using the activated carbon catalyst first. The composition of the solution can be seen in Table III below.

TABLE 3. Solution compositions in the hydrogen production without activated carbon

Water Volume (ml)	NaOH mass (gram)	Aluminum Mass (gram)	Ratio of Aluminum and NaOH solution mass
9	0.54	3	1 : 3 (Al 25%w.t.)

15	0.90	3	1 : 5 (Al 16.67%w.t.)
21	1.26	3	1 : 7 (Al 12.5%w.t.)

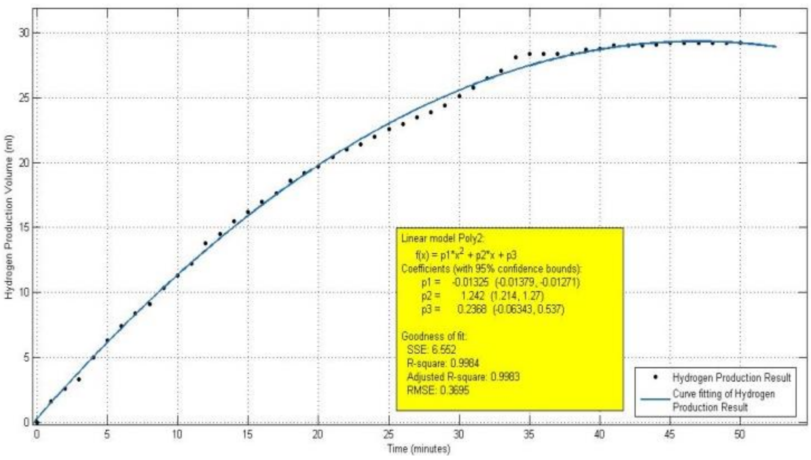
Once the hydrolysis reactor and other supporting tools are prepared and assembled as in Fig4, the aluminum hydrolysis process can be carried out. Hydrogen gas produced from hydrolysis, then channeled to water trapping to filter the water vapor carried along during the process. After that the volume of hydrogen gas will be accommodated into a container of water spilled due to the insistence of hydrogen gas where the volume will be measured. The method used to calculate the measurable volume of hydrogen gas is by the water displacement method.

Fig4. Preparation of hydrogen production without activated carbon process; (a) Hydrolysis reactor filled with aluminum pieces and NaOH solution, (b) The equipment set to run the hydrolysis process: (from left to right) the reactor, the water trapping bottle, and the water displacement set.

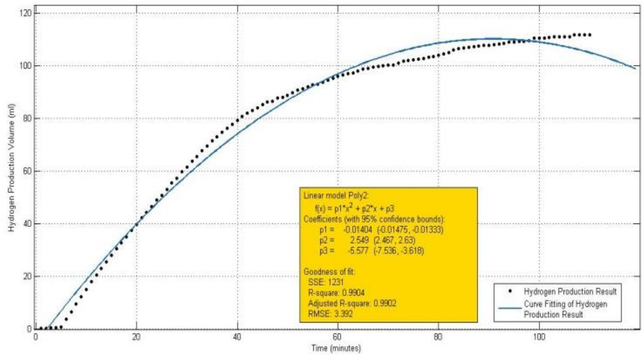
(a) **(b)**

The hydrogen gas production volume was measured using the volume of water spilled into a container where water is spilled every 1 minute. The calculation was stopped when there was no more drop of water dripping into the container. From there, the values of the calculated production volume were plotted in a volume vs. time graph.

Fig5. Hydrogen gas production result vs. time graph without carbon catalysts, with the composition of mass ratio of Al and solution mass NaOH (a) 1:3 (Al 25%w.t.), (b) 1:5 (Al 16.67%w.t.), (c) 1:7 (Al 12.5%w.t.).



(a)



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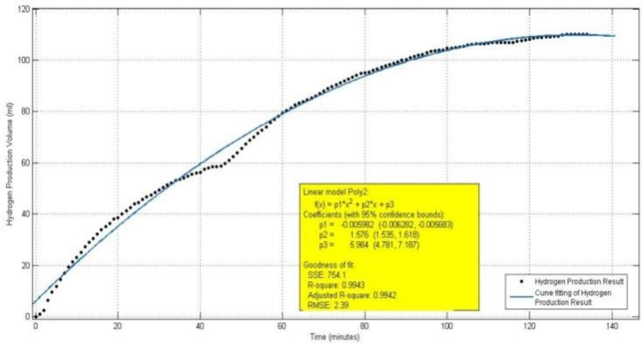

(c)

Based on the graphs in Fig5, The induction time of the hydrolysis reaction process occurs only in the reaction with a ratio of aluminum mass and a solution of NaOH 1:5 (Al 16.67%w.t.), which is for the first 5 minutes. Moreover based on the data recorded, the regression model used for curve fitting (represented in the blue line from each graph) that described the graph shape tendency is the quadratic regression model. This model explains almost all variations that occur between dependent variables (time) and independent variables (volume) and very strong interrelationship influences between each other, with values of coefficient determinant, $R^2 \approx 100\%$ in all variations in the of aluminum mass and solution ratio, which consecutively have a coefficient of determination value of 99.64% at a ratio of 1:3 (Al 25%w.t.), 99.04% at a ratio of 1:5 (Al 16.67%w.t.), and 99.43% at a ratio of 1:7 (Al 12.5%w.t.). This suggests that the relationship between the two variables, production volume and time, can be influenced by other factors as well, such as pressure or temperature during the experiment. Furthermore, the graphs showed that the hydrogen production in the process without using activated carbon was at a steady rate, since the production volume increased gradually, in which the result corresponded with one of the results from Hiraki et al. researches on aluminum hydrolysis process[15].

Hydrogen Production with Activated Carbon

This hydrogen gas production process was done by reacting pieces of circular aluminum metal with a diameter of 1.8 mm from a used beverage can with a NaOH 1.5 M solution (NaOH + tap water), also with the activated carbon catalyst being added, where the ratio of aluminum and activated carbon catalyst mass is 1:1. The process was done with 3 types of activated carbon treatment variations explained in Table 3.

TABLE 3. Treatment variations of carbon electro-activation

VARIATIONS	TREATMENT
1	Connected to 3V DC power supply for 2 hours
2	Connected to 6V DC power supply for 2 hours
3	Connected to 3V DC power supply for 4 hours

Fig6. Hydrogen production process with activated carbon process; (a) Electro-activated carbon result, (b) The hydrolysis reactor filled with aluminum pieces, NaOH solution and activated carbon

(a) **(b)**

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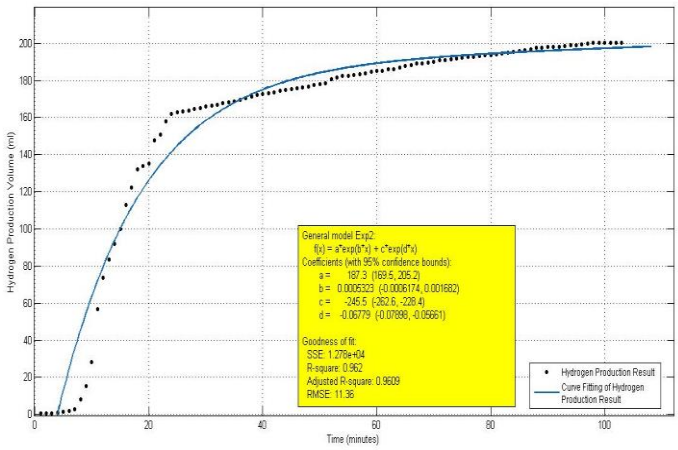
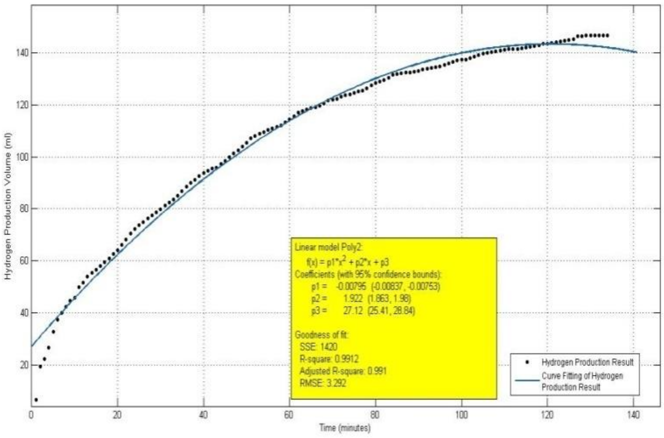
The hydrogen gas production process is carried out with the exact same set of equipment in Fig4(b), and the method of volume measurement was by using the volume of water spilled into a container where water is spilled every 1 minute. The calculation was stopped when there was no more drop of water dripping into the container. From there, the values of the calculated production volume were plotted in a volume vs. time graph.

Fig7. Hydrogen gas production result vs. time graph with carbon catalysts on (a) variation 1, (b) variation 2, (c) variation 3.



(a)



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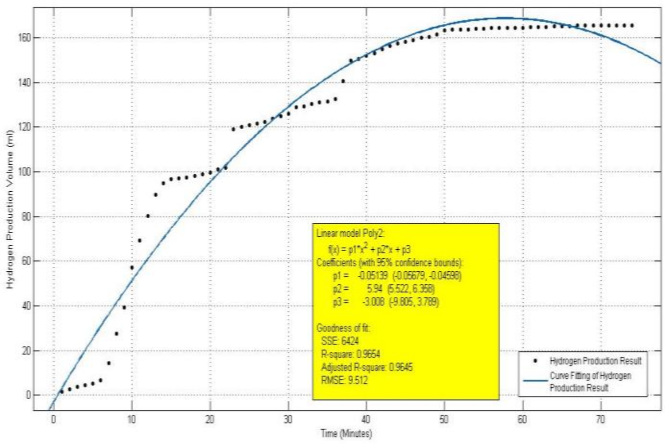
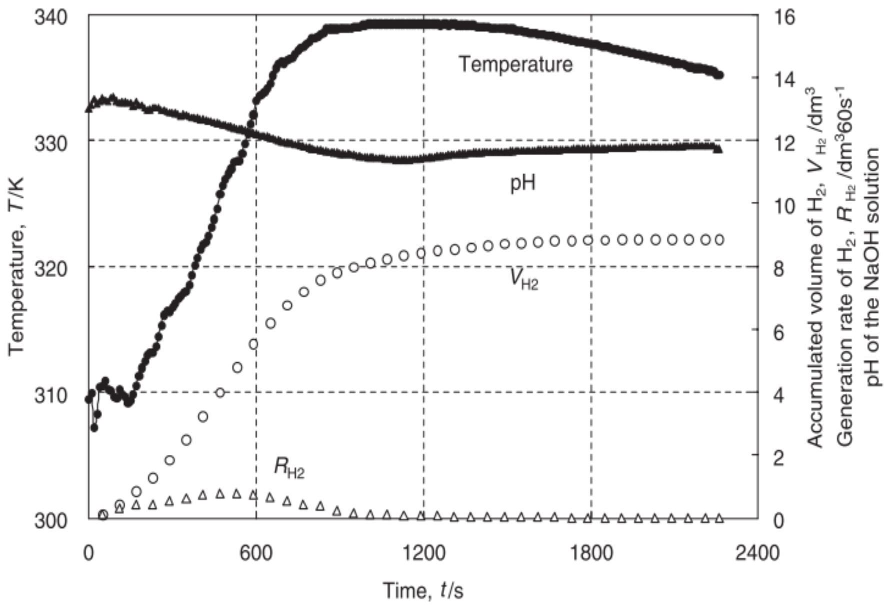


(c)

Based on the graphs in Fig7, The induction time of the hydrolysis reaction process occurs only in the variation 1 reaction, which is for the first 4 minutes. Moreover based on the data recorded, the regression model used for curve fitting (represented in the blue line from each graph) that described the graph shape tendency almost perfectly is the exponential regression model for variation 1, whereas variation 2 and 3 is best described using the quadratic regression model. This model explains almost all variations that occur between dependent variables (time) and independent variables (volume) and very strong interrelationship influences between each other, with values of coefficient determinant, $R^2 \approx 100\%$ in all variations in the of aluminum mass and solution ratio, which consecutively have a coefficient of determination value of 96.2% in variation 1, 99.1% in variation 2, and 96.5% in variation 3. This suggests that the relationship between the two variables, production volume and time, can be influenced by other factors as well, such as pressure or temperature during the experiment. Furthermore, just like in Fig5, the graphs in Fig7 showed that the hydrogen production in the process using activated carbon was at a steady rate, since the production volume increased gradually. In addition, the highest hydrogen yield value was obtained here in the hydrogen gas production process with activated carbon, specifically in variation 1, which was 22.3%, with 200.4 mL of hydrogen gas volume produced. This shows that with the help of activated carbon as catalyst, the OH¬ ions will easily stick on the activated carbon pores. Consequently, this helps the effort to release hydrogen gas bubbles easier, so that it will help the increase of volume production and production effectiveness from this particular method of hydrogen gas production, which is by aluminum hydrolysis process[16]. Also, it also proved that with the help of activated carbon as catalyst in this hydrogen gas production method, it will help increase its productivity and effectiveness even in the condition of room temperature and pressure[14].

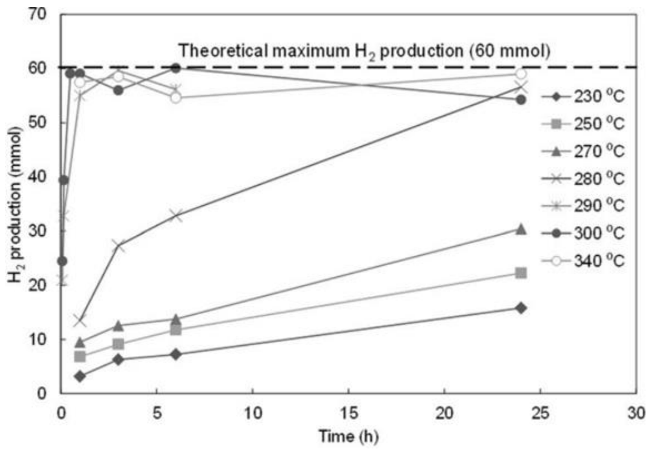
In the study from Hiraki et al., it was reported that there was an increase in the hydrogen production volume along with the increase of temperature in the hydrolysis reaction. The effect of temperature changes on the volume of hydrogen production can be seen in Fig8. The result of this hydrogen production is much more substantial and significant. Furthermore, in their research, they were able to react to all (100%) aluminum in hydrolysis reactions at a temperature of 333 K in less than 10 minutes [15].

Fig8. External temperature impact on pH, production volume and production rate of hydrogen through aluminum hydrolysis[15].



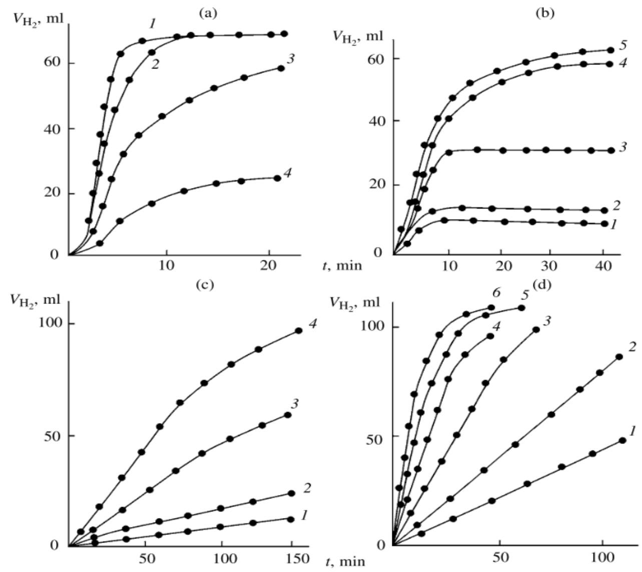
Next, based on research from Setiani et al., the hydrolysis process is carried out by an additional of extreme external temperature(> 200°C), thus affecting the pressure value in the reaction process as well. Fig9 is a graph of the relations between hydrogen production volume and the external temperature in the hydrolysis process over a period of 24 hours. Therefore, it is known that on hydrolysis reaction at 230°C, 250°C, 270°C, and 280°C, the hydrogen production volume increases in an almost linear trend. However, in reactions at 290°C, 300°C, and 340°C, the hydrogen production volume increases in exponential trend. Despite the differences in the graph trends, the production time of this particular hydrolysis process may last up to 24 hours or more[2].

Fig9. External temperature variations effect on hydrogen production volume graph[2].



Previously, this research has been conducted by Aleksandrov et al. (2003), which uses metal hydrolysis methods for the production of hydrogen gas with various variations, namely in the mass of aluminum, the concentration of NaOH solution, the surface area of aluminum, and the temperature during the reaction. Graphs of volume production obtained from research, can be seen in Fig10, which shows almost the same patterns and tendencies in each variation.

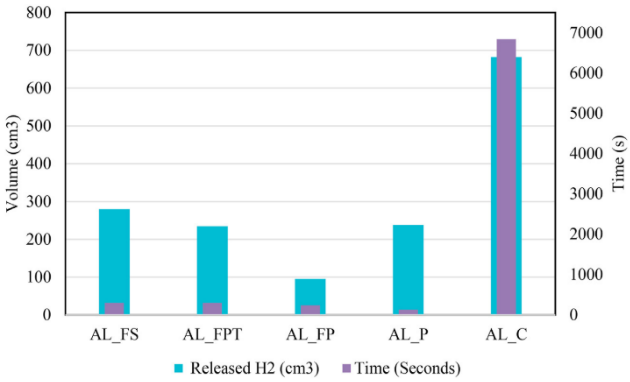
Fig10. Graph of hydrogen production volume by time with variations in (a) aluminum mass, (b) concentration of NaOH solution, (c) aluminum surface area, (d) reaction temperature[17].



Looking at Fig10, the variation in the mass of aluminum and in the concentration of NaOH has exponential trends on the graph, for the variations in aluminum surface area has linear and quadratic trends, and for the temperature variations quadratic and exponential trends. Also, it was found that in the process of experiments that were at 20°C, with a very small aluminum mass of 0.02 g, and a concentration of NaOH 0.1 M, the volume of hydrogen was produced at 102.5 mL[17].

Research into hydrogen production through aluminum hydrolysis method is then carried out with further modifications. Küp Aylikci, et al. did so using electrolysis methods assisted by solar panels, as well as hydrolysis reactors placed on stirrers and magnetic heaters, to add external temperature influence during the reaction. The results of hydrogen production obtained from this research method can be seen from the graph in Fig11 below.

Fig11. Hydrogen gas production yield reacting at 5 V [18].



The graph in Fig11, showed the production of hydrogen volume in aluminum hydrolysis of various types of materials, where aluminum obtained from small pieces of used cans is labeled "AL_C". The production obtained in hydrolysis with aluminum material is almost 700 mL, within 7000 seconds more, or close to 2 hours. Furthermore, during the electrolysis process, the NaOH solution is varied again in concentration, namely at 1 M and 2 M, where the result increased the maximum value of hydrogen gas production rate during the reaction from 200 mL/g.min to 250 mL/g.min. Therefore, with the help of electricity (electrolysis), as well as the addition of external temperature during the reaction could affect the increasing rate and yield of hydrogen production through this method of aluminum hydrolysis[18].

As such, compared with previous researches that were reviewed, based on their methods and results, this research and experiment used all tools and materials (except the hydrolysis reactor) that can be done outside the laboratory, and often used for everyday purposes at room temperature, without any assistance from the influence of external temperature. With this, the experiment did not need to factor the increasing pressure in the reactor, although it is still accompanied by a process of induction stage (Induction Stage) that is not quick, but this process could still produce a hydrogen production volume of 22.3%, with a relatively short time, because of the alkaline solution (NaOH) that accelerates the rate of reaction during the aluminum hydrolysis process[14], and the activated carbon catalyst that helps the process of releasing hydrogen gas bubbles, by becoming a buffer where the OH^- ions are formed during the hydrolysis process of aluminum metals[12], without the need for additional external influences be it temperature or pressure.

Conclusion

Based on the results of the data, analysis and discussion that have been explained, it can be concluded that:

1. The ratio between aluminum and NaOH solution mass used for the optimum result of this hydrolysis reaction is 1:5, or (Al 16.67%w.t.).

2. The addition of activated carbon catalyst to aluminum hydrolysis reaction helps reduce the induction stage of the reaction, also improve and optimize the production volume, the production yield, and the production rate, despite carrying out the experiment without any additional external factor contributing to its temperature and pressure of the reaction.

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