ARTICLES

The Future Energy Production from Aluminium and Water With Carbon Catalyst From Rice Husk

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Abstract. Hydrogen is an environmentally friendly fuel that is promoted as one of the most promising alternative energies to replace fossil fuels. The production of hydrogen through the hydrolysis reaction of aluminium is a solution to overcome the problems in the current hydrogen production method. The production of hydrogen through the hydrolysis of aluminium is an environmentally friendly process because this process produces hydrogen and AlOOH or $Al(OH)_3$ which are easily biodegradable in nature. However, this reaction has a low reaction rate so a catalyst is needed to increase the reaction rate. In this study, carbon catalyst from rice husk which was carbonated at a temperature of 800 °C and activated with 2 M sulfuric acid had been successfully synthesized by electrolysis method with 0.01; 0.1; 1 M NaOH solution. The morphological structure of the carbon catalyst produced has the same shape as activated carbon from rice husk, which is amorphous. The SEM-EDX results showed that the carbon catalyst electrolyzed with 0.01 M NaOH had the highest metal content of Na, which was 3.68 wt%. Meanwhile, 0.1 and 1 M have Na metal content of 2.17% and Na 2.54 wt%. The results of Thermal Gravimetric Analysis (TGA) show that the thermal stability of the carbon catalyst is higher than that of activated carbon. Surface area analysis by Brunauer-Emmett-Teller (BET) showed that the activated carbon and the synthesized carbon catalyst had microporous and mesoporous structures simultaneously. The electrolyzed carbon catalyst with 0.1 M NaOH has the largest surface area of 512,2 m^2/g. While the electrolyzed carbon catalyst with 0.01 M has the smallest surface area of 393,189 m^2/g. The effectiveness of the carbon catalyst is known from the amount of aluminium oxidized. The carbon catalyst electrolyzed with 0.01 M NaOH was found to be the most effective because it was able to oxidize 9.17% aluminium, while the carbon catalyst electrolyzed with 0.1 and 1 M NaOH was only able to oxidize 6.85 and 7.96% aluminium, respectively.

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Introduction

Hydrogen is an environmentally friendly fuel that is known as one of the most promising alternative energies so it has the potential to replace fossil fuels in the future. The successful transition of hydrogen to the future requires the development of better, sustainable, and economical production methods [1]. About 95% of the hydrogen available today is produced from fossil-based feedstocks. Hydrogen can be produced by several methods, such as electrolysis, biological, electrochemical, and thermochemical processes [2]. However, this method still needs further development due to the relatively low efficiency of the biological process, the high cost of the electrochemical process, and the production of carbon dioxide (CO_2) from the thermochemical process. Thus, there is a need for a hydrogen production process that is non-polluting, inexpensive, and efficient, such as in the production of hydrogen from aluminium and water [3-6].

Aluminium is an abundant metal and has little economic value. In theory, the reaction of aluminium and water can produce 1360 ml/g hydrogen at normal atmospheric pressure [7]. The widespread use of aluminium will produce waste that harms the environment. Aluminium waste can cause pollution to the environment because of its long decomposition process. Aluminium production in Indonesia reached 250,000-260,000 tons in 2017 and this number continues to increase every year [8] From these data, it can be seen that there is a lot of aluminium waste that can be used for hydrogen production. Production of hydrogen from aluminium and water is a friendly process environment. The products of this process are hydrogen and aluminium hydroxide $Al(OH)_3$ which can decompose easily in nature [5]. Since the reaction between aluminium and water is slow, a catalyst is needed to enhance the reaction rate. The catalysts commonly used are homogeneous catalysts. Shmelev, et al., in 2016 studied the effectiveness of alkaline solutions as a homogeneous catalyst in the production of hydrogen from the reaction of aluminium and water. The results showed that the most effective alkaline solutions were sodium hydroxide (NaOH) and potassium hydroxide (KOH). Due to it having the same phase as the reactants, this catalyst can only be used once. So that it requires relatively expensive costs, not to mention the use of homogeneous catalysts can produce chemical waste be-

cause these catalysts are difficult to be separated again after the reaction process [9]. Heterogeneous catalysts are needed solve this problem and maximize hydrogen production because the activity of heterogeneous catalysts is more active than homogeneous catalysts. Heterogeneous catalysts have an important role in chemical industrial production. This catalyst is prioritized because of its durability and low operating costs [10]. To maximize the reaction between aluminium and water, a homogeneous catalyst in the form of an alkaline solution can be converted into a heterogeneous catalyst by adding alkaline ions in the form of Na ions to a porous material such as activated carbon.

Activated carbon is a term used to express a material that is rich in carbon and has a good internal pore structure. The basic ingredient of activated carbon is a material that is rich in carbon. The production of activated carbon currently requires high costs, so a cost-effective synthesis of activated carbon is needed which can be obtained from biomass waste materials such as rice husk, oil palm shells, coir pith, palm fiber, and rice husks [10]. Therefore, in this study, heterogeneous catalysts in the form of carbon catalysts will be synthesized by adding Na ions into the pores of activated carbon from rice husks through electrolysis as a catalyst for hydrogen production by the reaction of aluminium with water. Variations in the concentration of NaOH solution were carried out to determine the effect of the concentration of the electrolyte solution on the electrolysis process on the effectiveness of the resulting catalyst

Experimental

In this study, 100 grams of rice husks were carbonized at 800 °C for 6 hours with a temperature increase of 10 °C every minute. After the carbonization process, the system is cooled to room temperature. The carbon produced from the carbonization process is then ground and sieved through a 150 mesh sieve. The carbon that escaped from the sieve was then activated with a 2 M sulfuric acid (H_2SO_4) solution. The composition of carbon and sulfuric acid used in the carbon activation process was 1:10 (w/v). The carbon activation process was carried out for 12 hours. After 12 hours, the mixture was filtered and washed with aquadest to neutral pH. The carbon was dried at 110 for 24 hours. The activated carbon was elec-

trolyzed with an electrical voltage of 12 V. This process used a ratio of 1:10 (w/v) between activated carbon and NaOH solution which was manipulated with the concentration of 1; 0.1; and 0.01 M. After electrolysis, the activated carbon was dried at 110 °C for 12 hours.

To determine the catalytic activity of a carbon catalyst, it was done by applying a carbon catalyst to the reaction of aluminium with water. In this reaction, the composition of aluminium, water, and catalyst is 1:50:1 wt%. These materials were put into a 100 ml Erlenmeyer then closed with a balloon. Reaction with a homogeneous catalyst 0.01 M NaOH solution was used as a comparison. The hydrogen production is marked by the inflating of the balloon on the Erlenmeyer. The effectiveness of carbon catalyst in hydrogen production from waste aluminium and water is calculated from the percentage of aluminium oxidized by the equation 1.

$$\% \; oxidized \; aluminum = \frac{m_1 - m_2}{m_1} \; x \; 100\% \qquad (1)$$

Where m_1 and m_1 are mass before and after reaction, respectively.

Results and Discussion

Synthesis of activated carbon

Activated carbon synthesis was initiated by carbonization of rice husk at 800°C for 6 hours. Weight measurement is carried out to determine the amount of material shrinkage in the activated carbon synthesis process. Table 1. shows the weight loss of the material before and after the carbonization and activation process. The carbonized rice husk weighs 100 grams. After the carbonization process becomes carbon black, the weight is reduced to 26.6 grams. This is caused by the loss of water content in rice husks during the carbonization process.

The next process is the activation of carbon with a 2 M H_2SO_4 solution. Before activation, the carbon is weighed as much as 15 g. After activation, the mixture of carbon and H_2SO_4 solution was separated with filter paper and then neutralized until the pH was neutral. The neutral carbon is dried and weighed. The weight of activated carbon resulting from the activation process has decreased from 1.1 grams to 13.9 grams.

Table 1. Weight loss during the carbonization and activation process

	Before carbon-ized	After carbon-ized	Before acti-vated	After acti-vated
Weight (g)	90	26,6	15	13,9

Synthesis of Carbon Catalysts

Carbon catalyst was synthesis by electrolysis method with 1; 0.1; and 0;01 M NaOH solution as electrolyte. This process uses a carbon rod electrode with a voltage of 12 V. The current that flows during electrolysis is 0.6 Ampere. The electrolysis process is controlled for 3 hours. This process made Na ions adsorb into the pores of the activated carbon perfectly.

After electrolysis, the carbon obtained was in an oven at a temperature of 110 °C for 12 hours and then weighed. Table 2. shows the weight of activated carbon before and after electrolysis. The weight of activated carbon before electrolysis was 4 g each. After electrolysis with different concentrations of NaOH, activated carbon experienced heavy shrinkage different too. Electrolyzed activated carbon with 1; 0.1: and 0.01 M NaOH decreased respectively by 1; 0.3; and 0.1 g.

Table 2. The weight loss of activated carbon during electrolysis

Concentration of NaOH (M)	1 M	0,1 M	0,01 M
The weight of carbon before electrolysis (g)	4	4	4
The weight of carbon after electrolysis (g)	3	3,7	3,9

Characteristics of Carbon Catalyst

The synthesized carbon catalyst was characterized by Scanning Electron Microscope (SEM), Thermo Gravimetry Analyzer (TGA) and N_2 adsorption-desorption.

Scanning Electron Microscope (SEM)

The surface morphology of the synthesized catalyst carbon can be determined from the Scanning Electron Microscope (SEM) results. This characterization is also to determine the effect of electrolysis on the morphology of activated car-

bon. SEM results are shown in Figure 1. From the figure, it is known that the activated carbon and carbon catalyst synthesized in this study have an amorphous form as reported by [11].

The morphology of carbon catalyst from rice husk (Figure 1 b, c and d) has the same morphology as activated carbon from rice husk (Figure 1a). The absence of morphological changes in the carbon catalyst indicated that the electrolysis process with NaOH solution did not change the morphology of the activated carbon. In Figures 1 b and d it can be seen that there are materials that fill the pores of the carbon catalyst. The material may be sodium metal (Na) which was deposited due to the electrolysis process.

SEM-EDX analysis was carried out to determine the amount of Na metal adsorbed on the carbon catalyst. The sodium metal adsorbed on the carbon catalyst is tabulated in table 3. The carbon catalyst electrolyzed with 0.01 M NaOH has the largest metallic Na content of 3.68%. The carbon catalyst electrolyzed with 0.1 and 1 M NaOH solution contained 2.17 and 2.54 wt% of metallic Na, respectively. Due to the low concentration of NaOH which contains few ions so the electric current flowing in the solution becomes slow and causes the electrolysis of Na metal to be more maximal.

Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) char-

acterization aims to determine the thermal stability and reduction of crystal weight due to the increase in temperature of the synthesized carbon catalyst. The decrease in mass that occurs shows the components that make up the carbon catalyst. The results of characterization with TGA are displayed in the form of a curve for the decrease in weight % of the compound in the sample (mg) with increasing temperature (°C). The characterization with TGA was heated to 800 °C and produced a thermogram curve. The samples tested for TGA were activated carbon and carbon catalyst with a NaOH concentration of 0.01 M. The TGA curve is shown in Graph 1.

Table 3. Composition of Na Weight Analysis Results With EDX

The Concentration of NaOH (M)	1 M	0,1 M	0,01 M
The Amount of Natrium (wt%)	2,54	2,17	3,68

Graph 1. shows there are 2 stages of mass reduction. The first stage of mass reduction in activated carbon and carbon catalyst occurs in the temperature range of 30 - 100 °C. This weight loss occurs due to the evaporation of water adsorbed on the surface of the material which has a boiling point of 100 °C. After that, the two samples did not experience a significant decrease in mass. A sharp decrease in the mass of activated carbon occurs in the temperature range of 450 − 700 °C. While on the carbon catalyst the sharp decrease
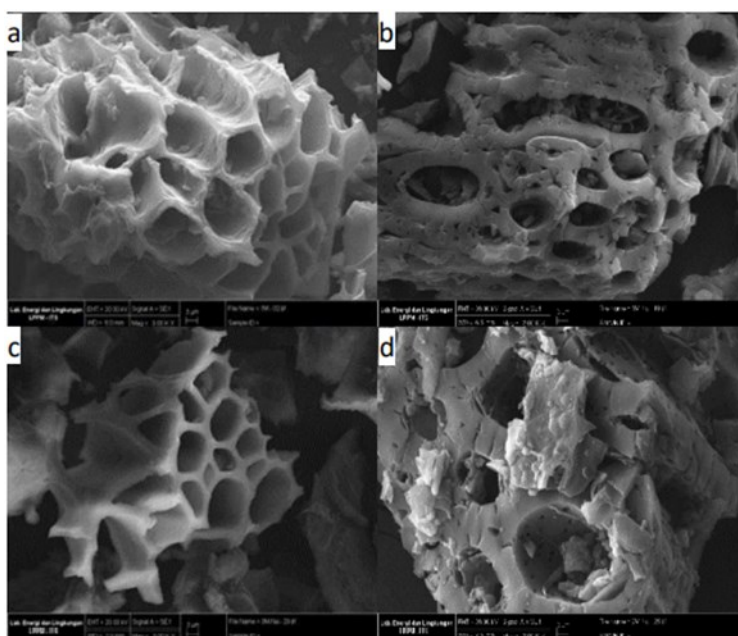

Figure 1. The morphology of activated carbon and carbon catalyst from rice husk (a) without electrolysis; (b) 1 M; (c) 0.1 M; (d) 0.01 M NaOH

occurred in the temperature range of 500 – 700 °C. This difference can be caused by the presence of metallic Na contained in the carbon catalyst. Metallic Na which has a boiling point of 828.9 °C causes an increase in the thermal stability of the carbon catalyst.

Surface Area (N2 Ads-Des, BET)

Nitrogen adsorption-desorption is used to measure the surface area and pore size distribution of a sample. The specific surface area was observed by the BET (SBET) method, while the pore size distribution was determined by the BJH and SF methods [12]. The analysis was carried out at -196 °C with a degassing temperature of 150 °C for 12 hours. The isothermal adsorption-desorption curve of nitrogen on carbon and car-

bon catalyst is shown in Graph 2.

The isothermal adsorption and desorption curve of nitrogen on activated carbon and carbon catalyst from rice husk as a whole shows the occurrence of adsorption activity of a certain amount of nitrogen in the monolayer layer on the pores of activated carbon and carbon catalyst at a relative pressure position of less than 0.2. Then when the relative pressure was increased there was no change in the amount of nitrogen adsorbed on the monolayer surface until the relative pressure reached 0.8. There was a significant increase in nitrogen adsorption again at a relative pressure of 0.9, this indicates the presence of nitrogen adsorption activity on the pore walls of the material. When the relative pressure is lowered, nitrogen gas desorption will occur. The hysteresis loop at a higher relative pressure is at P/P0 0.4-1 .
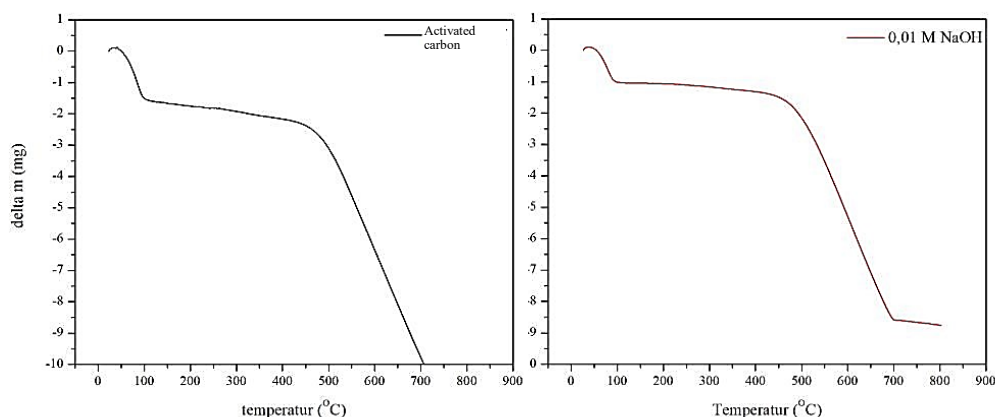
Graph 1. TG curve (a) activated carbon (b) 0.01 NaOH carbon catalyst
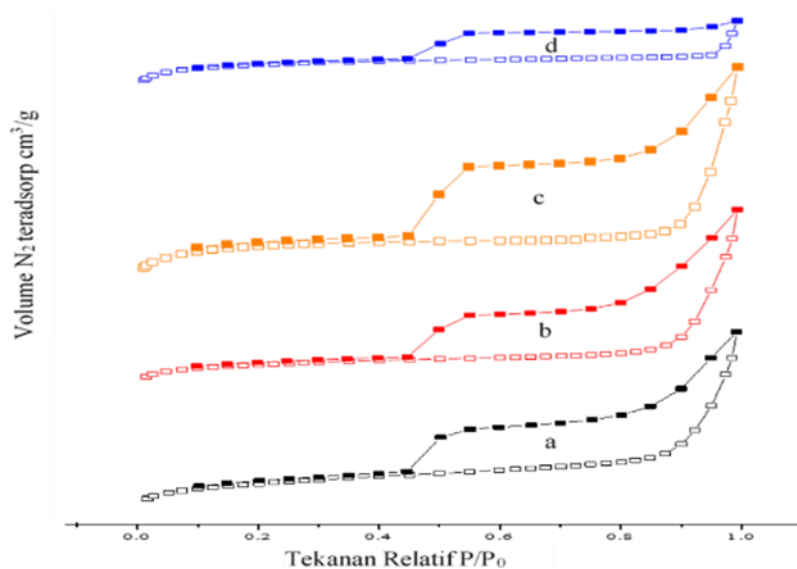
Graph 2. Isothermal adsorption and desorption curve of sample N_2 (a) activated carbon; (b) carbon 1 catalyst; (c) 0.1; (d) 0.01 M NaOH

According to IUPAC, the type of isotherm curve of the four materials is a mixture of type I and IV, which means this material has a micropore and mesoporous structure at the same time. Mesoporous carbon has a porosity in the mesoporous range, thereby significantly increasing the specific surface area. This large surface area can increase the catalytic activity of carbon catalysts from rice husks. A catalyst with a large surface area will provide more space for the reaction to occur to increase the reaction rate [13,14].

From the results of the N_2 Ads-Des analysis also obtained data on the surface area and pore volume of the tested material. The surface area and pore volume data obtained in this study are tabulated in Table 4. The carbon catalyst electrolyzed with 0.1 M NaOH has the largest surface area of 512,2 m^2/g. While the electrolyzed carbon catalyst with 0.01 M has the smallest surface area, which is 393.189 m^2/g. This can be caused by the Na metal being adsorbed in the pores of the carbon material.

Table 4. Pore characteristics of activated carbon and carbon catalyst from rice husk

Sample	Surface Area BET (m^2/g)	Pore Volume (cm^2/g)	Pore Diameter (nm)
Activated Carbon	408,449	0,394	3,823
Carbon Catalyst 0,01 M NaOH	393,189	0,392	3,815
Carbon Catalyst 0,1 M NaOH	512,200	0,319	3,812
Carbon Catalyst 1 M NaOH	407,303	0,202	3,825

Test of Carbon Catalyst Activity on Hydrogen Production Reaction from Aluminium

The effect of the concentration of NaOH solution on the electrolysis process on the effec-tiveness of the synthesized catalyst can be seen from the results of the catalyst test in the production of hydrogen from the reaction of aluminium and water. The production of hydrogen from the reaction of aluminium and water is carried out with an aluminium:water: catalyst ratio of 1:50:1 wt%. The reaction was carried out by putting all the reactants into an Erlenmeyer and then covering them with a balloon. The formation of hydrogen gas is indicated by the appearance of gas bubbles in the Erlenmeyer and the balloon expands. The hydrogen production process from the reaction of aluminium and water with a carbon catalyst is shown in Figure 2.

In the first minute, there is no inflated balloon on the four Erlenmeyer. But at the 15th minute, the balloon on the Erlenmeyer which was added with a carbon catalyst began to expand. This shows that the aluminium reaction process is faster when the heterogeneous catalyst is a carbon catalyst compared to the aluminium reacting with water using a homogeneous catalyst in the form of a NaOH solution. After two hours, the hydrolysis reaction was stopped, then the solution and solid were separated by the filtration method. The solids obtained were dried in an oven at 110 ° C for 12 hours. The carbon catalyst and residual aluminium were separated using a 150 mesh sieve, then the remaining aluminium was weighed and the effectiveness of the carbon catalyst was calculated using equation 1 to determine the effect of the concentration of NaOH solution on the electrolysis process on the effectiveness of the synthesized carbon catalyst. The results of the calculation of the effectiveness of the carbon catalyst are shown in Table 5.

From table 5. can be seen that the carbon catalyst synthesized in this study was more effective when compared to homogeneous catalysts, namely 0.01 M NaOH solution. Aluminium is a
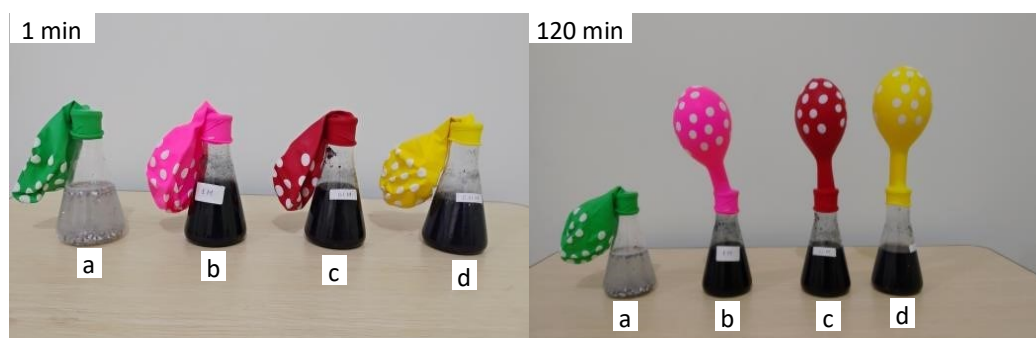

Figure 2. Hydrolysis reaction of Aluminium (a) with a catalyst solution of NaOH; (b) 1; (c) 0.1 and (d) 0.01 M NaOH

Table 5. Percentage of oxidized aluminium

Catalyst	Catalyst Carbon 1 M	Catalyst Carbon 0,1 M	Catalyst Carbon 0,01 M	Homogen Catalyst (NaOH 1 M)
Oxidized Alumunium (wt%)	7,96	6,85	9,17	1,02

metal that is stable at pH 5-9. Beyond this pH, the aluminium film will gradually dissolve in the water, causing the aluminium metal to corrode. Corrosion of aluminium at a pH close to neutral can increase when other metals are mixed with aluminium to form alloys [5]. In this study, the source of aluminium used was beverage can waste which is an aluminium alloy compound, it causes the hydrolysis reaction or aluminium corrosion to increase at a pH close to neutral, so the use of heterogeneous catalysts in the form of carbon catalysts is more effective than homogeneous catalysts in the form of NaOH solution 0, 01 M. Because the 0.01 M NaOH solution has a pH of 12, while the pH of a mixture of water and carbon catalyst with a NaOH concentration of 0.01; 0.1 and 1 M are 8, 9 and 9.5 respectively.

Table 5 also shows that the most effective carbon catalyst is a carbon catalyst electrolyzed with 0.01 M NaOH because it can oxidize 9.17% aluminium. While the electrolyzed carbon catalyst with 0.1 and 1 M NaOH can only oxidize aluminium at 6.85 and 7.96%, respectively. This can be caused by the amount of metal Na contained in the carbon catalyst.

Conclusion

The presence of Na metal in carbon catalysts reduces the surface area of carbon catalysts. The pore structure of the carbon catalyst produced in this study were micropore and mesopore at the same time. The thermal stability of a carbon catalyst is 50 °C higher than the activated carbon. The carbon catalyst is stable at a temperature of 500 °C. The results of the carbon catalyst activity test on the aluminium and water reaction showed that heterogeneous catalysts in the form of carbon catalysts could accelerate the aluminium and water reaction compared to homogeneous catalysts. Carbon catalyst which was electrolyzed with 0.01 M NaOH were more effective compared to carbon catalysts which were electrolyzed with 0.1 and 1 M NaOH because they could oxidize 9.17%

of the aluminium.

References

[1] Wang HZ, Leung DYC, Leung MKH., "A review on hydrogen production using aluminium and aluminium alloys", *Renew Sustain Energy Rev*, vol. 13, no. 4, pp. 845-53, 2009, DOI: 10.1016/j.rser.2008.02.009

[2] Vizcaino. A. J, A. Carrero, J. A. Calles, Activated Carbon Material Safety Data Sheet. Clear tech, Inc. 2014. Assisted potassium hydroxide induced palm shell activated carbon: Batch and column investigation.Int. J. Hydrogen Energy. Vol. 32, pp. 1450-1461, 2007.

[3] Anonymous, U.S. Department of energy, Office of fossil energy-hydrogen program plan, hydrogen from natural gas and coal: the road to a sustainable energy future, 2003, available online: www.hydrogen.energy.gov

[4] Yang, S. Jae, Haesol Jung, Taehoon Kim, Chong Rae P., "Recent advances in hydrogen storage technologies based on nano porous carbon materials", *Progress in Natural Science: Materials International,* vol. 22, no. 6, pp. 631- 638, 2012, DOI: 10.1016/j.pnsc.2012.11.006

[5] Czech E, T. Troczynski., "Hydrogen generation through massive corrosion of deformed aluminium in water", *International Journal of Hydrogen Energy*, 35(3):1029-1037, 2012, DOI: 10.1016/j.ijhydene.2009.11.085

[6] Shmelev, V., V. Nikolaev, J. H. Lee, C. Yim. Hydrogen production by reaction of aluminium with water. *International Journal of Hydrogen Energy*, 41(38):1-10, 2016, DOI: 10.1016/j.ijhydene.2016.05.159

[7] Jung C, Kundu A, Ku B, Gil J, Lee H, Jang J. Hydrogen from aluminum in a flow reactor for fuel cell applications, Journal of Power Sources 175(1):490-494, 2008, DOI: 10.1016/j.jpowsour.2007.09.064

[8] Anonymous, "Kemenperin Kejar Produksi

Aluminium Nasional 2 Juta Ton Tahun 2025", 2018, available online: www.kemenperin.go.id

[9] Shkolnikov E, Zhuk A, Vlaskin M., "Aluminum as energy carrier: feasibility analysis and current technologies overview", Renewable and Sustainable Energy Reviews, 15(9):4611–4623, (2011), DOI: 10.1016/j.rser.2011.07.091.

[10] Kumar JA, D. Joshua A, S. Sathish. Enhanced PAHs removal using pyrolysis-assisted potassium hydroxide induced palm shell activated carbon: Batch and column investigation. Journal of Molecular Liquids, 297:77-87, (2019) DOI: 10.1016/j.molliq.2019.01.121

[11] Schlapbach L., A. Züttel., "Hydrogen-storage materials for mobile applications", *Nature*, 414:353-358 (2001), DOI: 10.1038/35104634

[12] Mardhiah, H.H., Ong, H.C., Masjuki, H.H., Lim, S., Lee, H.V., "Latest Developments and Future Prospects of Heterogeneous Catalyst in Biodiesel Production From Non-edible Oils", Renewable and Suistanable Energy Reviews, (67):1225-1236 (2017), DOI: 10.1016/j.rser.2016.09.036

[13] Fan MQ, Xu F, Sun LX., "Studies on hydrogen generation characteristics of hydrolysis of the ball milling Al-based materials in pure water", International Journal of Hydrogen Energy, 32(14):2809-2815, (2007), DOI: 10.1016/j.ijhydene.2006.12.020

[14] Mahmoodi K, Alinejad B. Enhancement of hydrogen generation rate in reaction of aluminum with water. *International Journal of Hydrogen Energy*, 35(11):5227-5232, (2010), DOI: 10.1016/j.ijhydene.2010.03.016