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Hydrogen Gas Production using Electro-activated Carbon Catalyst from Coconut Shells

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Abstract. The synthesis of heterogeneous carbon catalyst using electro-activation method has been carried out to assess the effect of temperature on surface morphology of hydrogen production and the surface area of the carbon catalyst as well as characterization of hydrogen production that was resulted. The electrolyte solution of NaOH with a concentration of 2.7 M which was produced from 2 grams of carbon and 25 ml of distilled water was used for electro-activation process. The activation process was taken place with a current of 3 A for 120 minutes and the variation of carbonization temperature of 1000, 1100 and 1200 $^{\circ}$C. The electrode system that was used in the process comprised a carbon cathode and copper anode. The results of carbon mass yield testing indicated that purification of charcoal applied at high temperature. The optimum amount of gas with an average rate of 9.19 ml/min/gr Al for a time of 1 hour was produced from carbonized catalyst at carbonization temperature of 1200 $^{\circ}$C. The SEM-EDS examination indicated that the reacted product consisted of a mixture of $Al(OH)_3$ and carbon catalysts which would be reprocessed through the re-electro-activation. The characterization of Brunauer-Emmet-Teller (BET) of the surface area of catalyzed carbon shown a value of 394.456 m^2/g; while the result test of Scanning Electron Microscope (SEM) shown that the morphology of surface layer tends to be more pores after carbon catalyzed was used with the concentration of NaOH electrolyte solution of 2.7 M. Results of Fourier Transform Infra-Red (FTIR) analysis also shown the formation of new carboxyl functional groups (O-H) in the wavelength range 464.41 cm^{-1}.

Keywords: Hydrogen, Electro-activated carbon, Catalyst, Coconut Shells

1. Introduction

Indonesia is one of countries which have a big number of coconut plantations in the world. The area is about 3.712 million hectares (for about 31.4% of the world's coconut plantation area) with coconut production of approximately 12.915 billion grains (24.4% of world's production). Coconut shell weight reaches 12% of the weight of coconuts as whole. With an average weight of a coconut for about 1.5 kg, the potential of Indonesia's coconut shell reaches 2324.7 million tons / year [1].

Coconut shell is a suitable material for charcoal or carbon, because it has high hardness, content of silica (SiO_2), a high carbon as well as low mineral ash. Coconut shell charcoal is the main product of the

coconut shell pyrolysis process which also contains volatile matters, water and ash [2]. Meanwhile, activated carbon was used as an absorbent material and purifiers, but small amounts of activated carbon can also be used as a catalyst [3].

A catalyst is a chemical compound that causes the reaction to be faster for reaching its equilibrium without experiencing chemical changes at the end of the reaction. Effective catalysts must have at least sufficient selectivity, activity and durability. It can also produce the desired product in not too extreme operating conditions. To produce an effective catalyst, the role of the buffer as a place for the spread of the active nucleus can increase the effectiveness of the entire catalyst. Thus, the catalyst support must have a structure that can disperse the active region, so that it can multiply the number of active areas on the surface of the catalyst. As the surface area of the active area increases, activity will increase, thus overall durability will also increase compared to the active region without support [4].

Carbon can electrochemically be activated and used in chemical reactions with water and fuel, such as aluminum, to produce hydrogen by electro-activation of carbon, where the by-products are the non-harmful aluminum oxide or aluminum hydroxide. Control the reaction temperature, and the amount of aluminum to carbon ratio and electro-activation process can provide amount of hydrogen according to the desired hydrogen rate [5,6]. Therefore, in this study a new approach of electro-activated carbon catalyst based on hydrolysis (water and aluminum reaction) with the aim of accelerating the production process of hydrogen with relatively abundant and inexpensive raw materials is proposed.

2. Experimental

In the present study, carbon was produced from coconut shells and carried out using electro-activation methods. In the electro-activation process, Natrium hydroxide (NaOH) with 2.7 M of concentration, 2 grams of carbon and 25 ml of distilled water was used as electrolyte. The electro-activation process was carried out for 2 hours with 3 amperes of DC current. The electro-activation system consists of a copper plate as a cathode and active graphite carbon from a waste battery as an anode. Carbon catalyst with a minimum temperature at 1000 ^{o}C and a maximum at 1200 ^{o}C were applied in the process of pyrolysis-carbonization. In the production produced hydrogen and by-product materials. The produced hydrogen was measured through an addition of the circumference of balloon for every 105 seconds or 1.75 minutes. The carbon catalyst surface was characterized and analyzed by using BET (Quantachrome Nova 4200e) and FTIR (Thermoscientific Nicolet iS-10). The sample of product was analyzed by scanning electron microscope SEM (Hitachi SU-3500) and with energy dispersive x-ray spectroscopy (EDX Horiba).

3. Results and Discussion

3.1 Carbonized catalyst production

The temperature of 1000 ^{o}C was chosen as the minimum temperature in the variation of the carbonization temperature. The carbonization process increased the carbon content of coconut shell, and opens the width of the pore surface of the carbon. It triggered more OH^{-} ions entering and binding to the carbon surface [7]. The process of carbonization powder was carried out for 1 hour under inert atmosphere with nitrogen gas was flowed during the process. Nitrogen gas was utilized to prevent the air entering the pyrolysis system as well as a carrier of the molecules that were evaporated and decomposed during heating process not accumulated on the furnace.

**Table 1.** Carbon yield of coconut shell after carbonization at 1000, 1100 and 1200 ^{o}C

Holding Temperature (^{o}C)	Coconut Shell Mass (gram)	Carbon Mass (gram)	Reduction Mass (gram)	% Reduction Mass	Carbon Yield (wt.%)
1000	19.53	4.57	14.96	76.60010241	23.3999
1000	18.44	4.39	14.05	76.19305857	23.8069
1100	22.83	5.421	17.409	76.25492773	23.7451

1100	11.95	2.74	9.21	77.07112971	22.9289
1200	11.56	2.83	8.73	75.51903114	24.481
1200	11.71	2.69	9.02	77.02818104	22.9718

Table 1 shows that the carbon powder which was produced after the carbonization process had experienced mass reduction. It was caused by the process of material decomposition occurring during the carbonization process. The result indicated that the highest carbon yield was obtained on carbonization process with a temperature of 1200 ºC which was as much as 24.48 wt%. This shows the level of purity of carbon at high temperatures to remove other minerals from the previous stage.

3.2 Surface Coconut Shell Carbon Area Before and After Catalysis (Electro-Activation)

The surface area of the carbon catalyst support is an important aspect in the function of carbon as a buffer for OH^- reacting ions. Carbon catalyst with a high surface area is a potential adsorbent for its use in the OH^- ion adsorption process. The surface area of the carbon catalyst in this study was measured by the BET method (Brunauer-Emmett-Teller). The graph of adsorption and desorption of N_2 gas isotherm is shown in Figure 1.
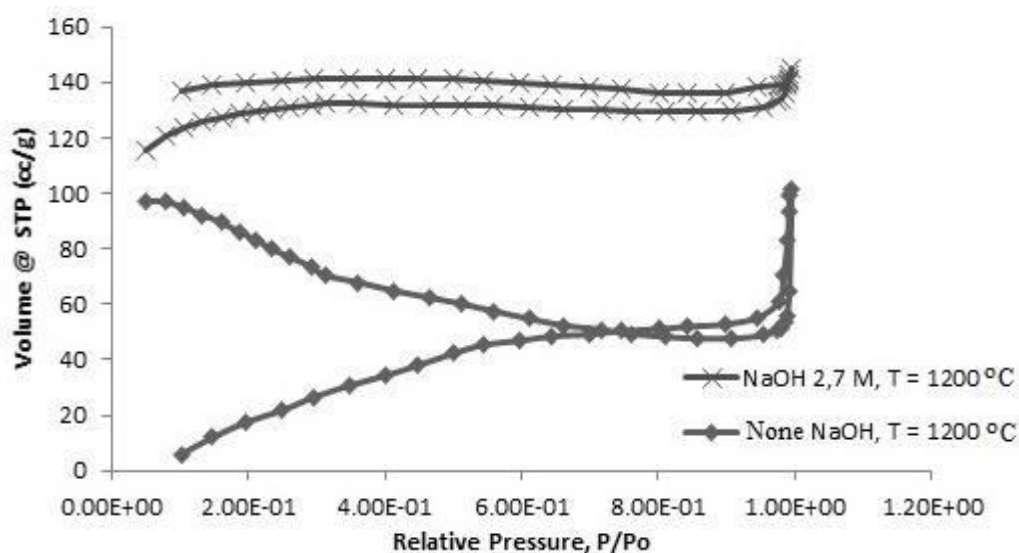

Figure 1. Adsorption and desorption of isotherm N_2 gas on carbon before catalysis and carbonized at 1200 ºC (without NaOH) and after catalysis (with NaOH 2.7 M).

Figure 1 shows the volume of N_2 gas adsorption in the highest isotherm condition on the electro-activated carbon. It was caused by a large surface area so that more N_2 gas is absorbed. According to the definition by IUPAC, the adsorbent pores are classified into three groups: micropore (diameter < 2 nm), mesopore (2–50 nm), and macropore (>50 nm). In general, micropores usually account for over 95% of the total surface area for common activated carbons [8]. Thus, Electro-activated carbons using NaOH are considered to be microporous solids with a relatively small external area. The surface area and pore diameter for the two types of carbons above is shown in the following Table 2.

**Table 2.** Surface area and average pore diameter of carbon catalyst

Carbon Condition	Surface Area (m²/g)	Average pore diameter (Å)
Before Catalysis	206.669	15.2
After Catalysis	394.456	21. 9

Table 2 shows that the surface area with electro-activation of NaOH was higher compared to before electro-activation of NaOH where the surface area after catalysis was 394.456 m^2/g. With the addition of NaOH, it will oxidize and erode the surface walls of the carbon to form more pores and increase the carbon surface area [9]. After the electro-activation process was complete, activated carbon was then filtered by using filter paper. It was found that carbon results from electro-activation were lesser than before electro-activation. This is because of a reduction in carbon yield. The decrease in the yield for activated carbon was most probably due to the dehydrating reagent (NaOH), which provided elimination and dehydration reactions; thus breaking the C–O–C and C–C bonds of the raw material [10]. Tseng and co-workers [11] reported that the activation mechanism with NaOH could be described according to the following reaction:

$$6NaOH + 2C \rightleftharpoons 2Na + 2Na_2CO_3 + 3H_2 \tag{1}$$
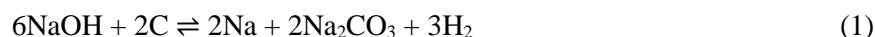
3.3   Hydrogen gas production

Data collecting of the produced hydrogen gas had been done by measuring the circumference of the balloon by a piece of threads taking at every 105 seconds (1.75 minute) measurement. The results shown on the following graphs.
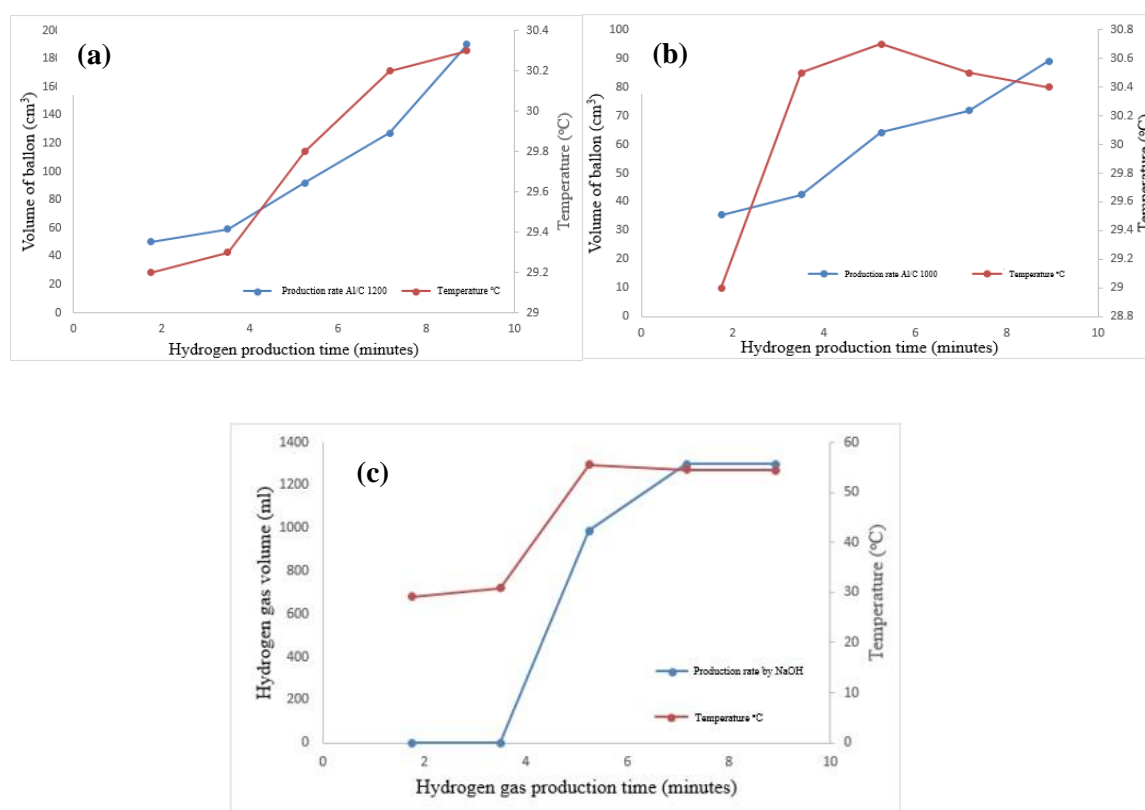
Figure 2. Hydrogen production of Al-water reaction with catalyst of (a) C carbonized at 1000 ºC, (b) Carbonized at 1200 ºC, and (c) NaOH.

3.3.1   Reaction time or induction time or delay time

In the production of hydrogen gas using a carbonized catalyst, it seems did not require such induction time (the delay time of the reaction to be started). Since the beginning of the reaction until the circumference of the balloon circle, it had perfectly been measured only at 1.75 minutes, as indicated in Figure 2(a) and 2(b). While, the hydrogen production process by using NaOH catalyst, the reaction needed more than 3 minutes to start producing hydrogen gas as shown in Figure 2(c).

The induction time did not occur in the reaction using carbon catalyst since the carbon catalyst directly works by splitting the hydrogen atoms from water molecules. While, in the reaction by using a catalyst of NaOH, it required time to be able to directly contact with aluminum until OH $^-$ ions to finish

bonding with aluminate that covered aluminum called the corrosion process of aluminum. Deng et al [7] speculated that the pressure difference between hydrogen bubbles trapped with the environment caused failure of the hydrated oxide layer, so that water can contact aluminum instead of the alumina layer. The method of producing hydrogen gas using a NaOH catalyst only relies on aluminum corrosion methods, so that it takes a long time for water to directly penetrate and contact aluminum.

Carbon catalysts contact directly with water molecules and attract positively charged the hydrogen atoms since the surface of carbon becomes negatively charged after the electro-activation process. It is similar to the mirror charge produced on parallel capacitor plates. The potential of produced electricity is homogeneous for all carbon surfaces, since carbon is a conductor. As part of a water molecule, a hydrogen atom (which some electrons are depleted because of O^{2-} ion that binds to carbon and forms CO and CO_2 as gases, and has a positive single-proton nucleus) will be attracted to the negative carbon surface. The reaction between hydrogen and carbon will help carbon attracting hydrogen atoms from water molecules [12].

As an experiment conducted by Lee [14] using $Al(OH)_3$, precursor of $Al(NO_3)_3$ and without the use of carbonized catalyst concluded that $Al(OH)_3$ effectively reacted with an oxide layer that envelops pure aluminum. The most optimum combination of Al, $Al(OH)_3$, and water to produce hydrogen to produce hydrogen were respectively 3, 15, and 50 with reaction temperature of 95 ^{o}C. However, the result of hydrogen production is almost 100% for 6 minutes with a specific volume of hydrogen of 1360 ml H_2 gr^{-1} Al. Whereas, the experiment conducted by Phillips [5] which used a wet carbon catalyst, the production of hydrogen gas was taken place at temperatures of around 65.6 to 87.8 ^{o}C. While our research indicated that the reaction in producing hydrogen gas was faster and taken place with lower temperature that was around 30.4 ^{o}C. It could be due to differences in the size of the catalyst used. Gai [13] revealed that the induction time of Al particles is mainly related to the H diffusion in bulk of Al and the critical gas pressure of H_2 bubbles at Al: Al_2O_3 interface. Moreover, our research used aluminum flakes and powder carbon. Accordingly, the activation energy increased with increasing the average size of carbon particles which probably originates from the fact that larger-size of Al having a wider particle size distribution. While, the small surface area of the carbon catalyst supported the function of carbon as a buffer for OH^- ions to react with H particle from the water or Al bulk.

3.3.2   Hydrogen yield

Hydrogen yield or produced hydrogen was obtained through the difference in the calculated volume of balloon subtracted by the initial calculated volume of balloon and divided by the total volume of measured hydrogen and multiplied by 100%, as described in equation (2).

$$Hydrogen\ Yield = \frac{Calculated\ volume - Initial\ calculated\ volume}{Calculated\ volume\ total} x 100\% \qquad (2)$$

The highest yield of hydrogen gas was obtained from the reaction using the result of carbon catalyze of 1200 ^{o}C, It had increased to 61.1% when left for 1 hour with volume was 489.1 ml and be predicted to continually increase for more than three days (based on preliminary research). However, it is because of the carbon content formed at 1200 ^{o}C in carbonization process was larger compared to the carbon content of 1000 ^{o}C. Increasing carbon content will cause more OH^- ion concentrations that can stick to the carbon surface [14].

3.3.3   The production rate of hydrogen gas

The rate of hydrogen gas production can be seen clearly in Figures 2 (a), 2(b) and 2(c). Figure 2(a) reveals a graph of the production rate of hydrogen gas that produced in the reaction of hydrogen production using carbon catalysts resulted from carbonization temperatures of 1200 ^{o}C. The production rate of hydrogen gas increased with increasing temperature; it was predicted to continually increase in certain time and temperature which indicated by the saturated of curve.

The obtained data indicated that there was a strong influence between the temperature and the rate of hydrogen gas production. As the temperature increases, it was also followed by increasing the production rate of hydrogen gas. Likewise, the production rate of hydrogen gas decreased as the reaction temperature decreased. Figure 2(b) shows the production rate of hydrogen gas using the carbonized

carbon at temperature of 1000 $^{\circ}$C decreased when it reached 7.17 minutes; while the production temperature decreased to 30.4 $^{\circ}$C however the volume was still experienced a little increasing. It also occurred in the reaction using a catalyst NaOH (Figure 2(c)) which indicated by the reaction only ended for about 1.75 minutes and temperatures starting to decline. The calculation model was done by Chen et al. [15] described that the reaction of aluminum and water should increase from room temperature to reach a temperature of 95 $^{\circ}$C, while in an experiment conducted by Gai [13] proved that the reaction could stop at 60 $^{\circ}$C.

3.4 By-product Analysis

Further evaluation was carried out in this study to understand the microstructure of aluminum hydroxide (Al(OH)$_3$) sample by using SEM/EDX micrograph analysis as shown in Figure 3. From the SEM observation, indeed some void still can be observed as shown in the surface top view. Figure 3 shows the morphology of mixture of Al(OH)$_3$ and carbon after the first hydrogen production between aluminum - water by using a carbon catalyst that was resulted in a carbonization temperature of 1200 $^{\circ}$C. Figure 3(a), 3(b) and 3(c) show the appearance of the reaction between aluminum that has reacted with water which then becomes Al(OH)$_3$ flakes (mark in red circle). Figure 3a shows that the content of Al(OH)$_3$ was still consist of carbon (mark in blue circle). The mixture of carbon and Al(OH)$_3$ was confirmed by the EDX test results, as indicated in Figure 5.

Figure 4 shows the morphology of Al(OH)$_3$ and carbon mixture from the test results of the second reaction of hydrogen production between aluminum - water using a carbon catalyst resulted from a carbonization temperature of 1200 $^{\circ}$C. When, it is compared with the SEM result of the first reaction (Figure 3), it is only Al(OH)$_3$ that was detected. Figure 4(b) and 4(c) shows the appearance of the reaction between aluminum used in conjunction with water which then becomes flakes of Al(OH)$_3$. At this condition, it can be seen that the content of Al(OH)$_3$ is indicated more compared with the previous result. Its by-product of carbon and Al(OH)$_3$ were also confirmed by EDX analysis, as shown in Figure 6.
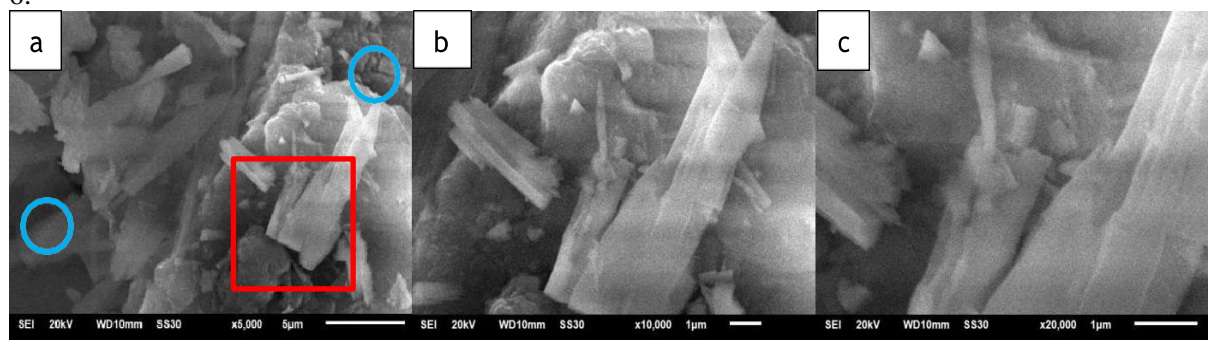
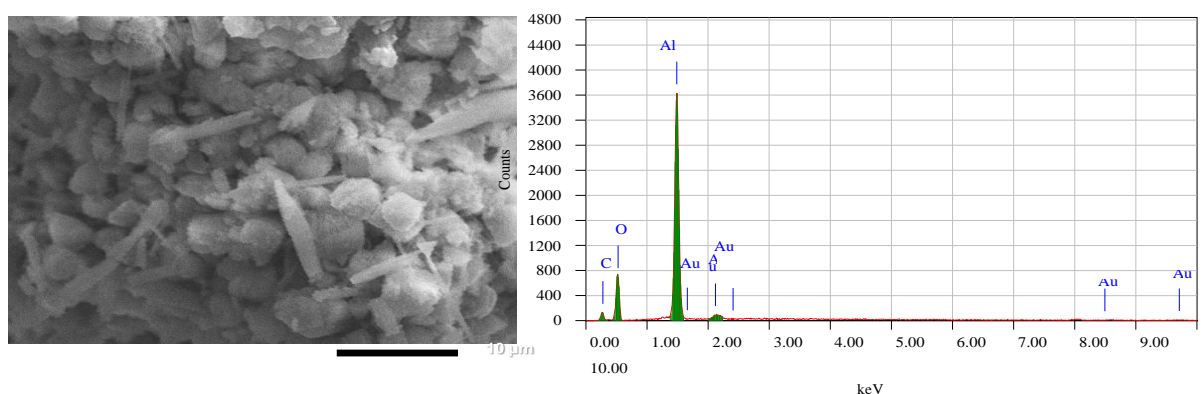**Figure 3.** Characterization result of Al(OH3) morphology mixture from first reaction, (a) 5.000x magnification, (b) 10.000x magnification, (c) 20.000x magnification.
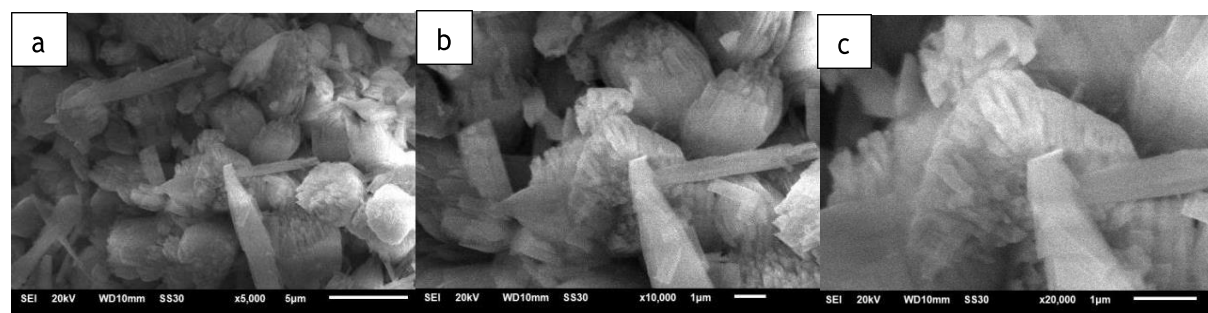
Figure 4. Characterization result of Al(OH3) morphology mixture from second reaction, (a) 5.000x magnification, (b) 10.000x magnification, (c)10.000x magnification.
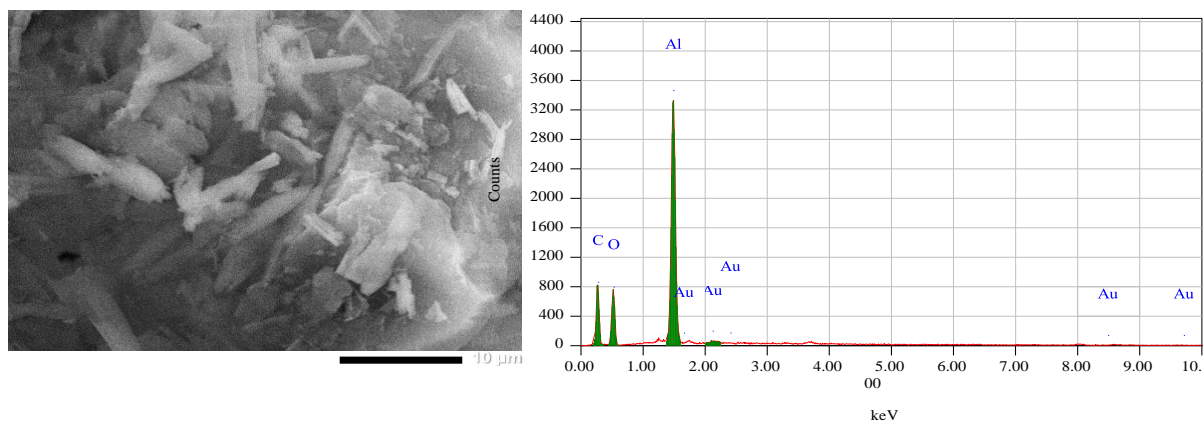
Figure 5. Characterization result of Al(OH3) mixture content from first reaction.

Figure 6. Characterization result of Al(OH3) mixture content from second reaction.

Figure 5 and 6 shows the location of EDX that shows a mixture of $Al(OH)_3$ and carbon in the sample. It also shows a graph based on the mass value of aluminum and oxygen detected from the EDX results. The comparison of the masses will be applied to determine the formula that can be calculated using Proust's law of mass comparison. Based on the results of calculations that can obtained by comparing with the result of EDX analysis. It is known that the phase of $Al(OH)_3$ consist of aluminum and oxygen with mass ratio of 23: 48.

4.   Conclusions

Based on the data analysis and discussion, it can be concluded that catalysts based on electro-activated carbon from coconut shell can be utilized to produce hydrogen gases from reaction between aluminum and water. The carbon catalyst that was used to produce hydrogen gas was produced in the reaction of aluminum and water using carbonization temperature of 1200 °C. FTIR analysis showed that carbon catalyst contained OH^- ions which entered the O-H functional group in the wavelength region of 464.41 cm^{-1}, 1035.36 cm^{-1}, and 3431.43 cm^{-1}. The production rate of hydrogen gas using carbon catalysts with carbonization results of 1200 °C was more stable with the average production rate of 9.19 ml/minute/gram. However, the rate of hydrogen gas production by using NaOH was much greater compared to previous one, but the reaction taken place for only 7.17 minutes and unstable.

5.   References

[1]   Wijaya Y 2012 *Dampak Teknologi Pirolisis Pembakaran Tertutup terhadap Kualitas Lingkungan dan Nilai Tambah Produk Tempurung Kelapa* (Lampung: Universitas Lampung)
[2]   Wang Q and Sarkar J 2018 *Int. J. of Energy Prod. & Mgmt.* **3** (1) 34

[3]   Cheremisinoff P N and Morresi A C 1978 *Carbon Adsorption Application,* In: Carbon Adsorption Handbook ed P N Cheremisinoff and F Ellerbusch (New York: An Arbor Science) p 1-53

[4]   Viswanathan B, Neel P I and Varadarajan T K 2009 *Methods of Activation and Specific Applications of Carbon Materials* (Chennai: Indian Institute of Technology Madras)

[5]   Phillips D H 2015 *Methods and Systems for Producing Hydrogen* US 9,102,529 B2 (United States: United States Patent)

[6]   Walther H J 1980 *Carbon Adsorption Handbook* ed P N Cheremisinoff and F Ellerbusch (New York: Ann Arbor Science Publishers)

[7]   Deng Z Y, Ferreira J M F and Sakka Y 2008 *J. Am. Ceram. Soc*. **91** (12) 3825

[8]   Chrysoula M, George G S, Costas P, 2008 *Bioresour. Technol*. **99** 6400–6408

[9]   Shofa 2012 *Pembuatan Karbon Aktif Berbahan Baku Ampas Tebu dengan Aktivasi Kalium Hidroksida* (Depok: Universitas Indonesia)

[10]   Basta A H, Fierro V, El-Saied H, and Celzard A 2009 *Bioresource Technology* **100** 3941–3947

[11]   Wu F C, Tseng R L, Juang R S 2005 *Sep. Purif. Technol.* **47** 10–19

[12]   Onda A, Ochi T and Yanagisawa K 2009 *Topic in Catalyst* **52** (6-7) 801

[13]   Gai W Z, Liu W H, Deng Z Y, and Zhou J G 2012 *Int. J. Hydrogen Energy* **37** 13132

[14]   Alfatah T 2015 *Pembuatan Karbon Aktif dari Tempurung Kelapa dengan Aktivator NaOH serta Aplikasi Adsorpsi Merkuri menggunakan Kolom Unggun Tetap.* (Aceh: Universitas Syiah Kuala)

[15]   Chen Y K, Teng HT, Lee TY, et al, 2014 *Int J Energy Environ Eng* **5** 87

Authorship Contribution

D S Khaerudini conceived and directed the project. D Junia and A Badruzzaman prepared and pre-treated the raw material, calcined and sintered sample. F D Dirgantara carried out XRD and SEM/EDS experiments and data analysis. D S Khaerudini and C E Rustana supervised and controlled the preparation of coconut shell into activated carbon/carbon catalyst material as a proper carbon source. F D Dirgantara carried out hydrogen gas production preparation and mass of balance calculations. D S Khaerudini and C E Rustana supervised, provided consultation and problem solving as well as help in analyzing data for the hydrogen gas production phenomena, XRD and SEM/EDS characterizations. C E Rustana, D Junia, and D S Khaerudini drafted and edited the manuscript (with the help of F D Dirgantara, A Badruzzaman, and V Marsya). All the authors discussed the data and contributed in the manuscript.