

Production of H₂ from aluminium/water reaction and its potential for CO₂ methanation

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Abstract. Carbon dioxide (CO₂) is a natural gas that presents in excess in the atmosphere. Owing to its ability to cause global warming, capturing and conversion of CO₂ have attracted much attention worldwide. CO₂ methanation using hydrogen (H₂) is believed to be a promising route for CO₂ removal. In the present work, H₂ is produced using aluminum-water reaction and tested for its ability to convert CO₂ to methane (CH₄). Different type of water i.e. tap water, distilled water, deionized water and ultrapure water, concentration of sodium hydroxide (NaOH) (0.2 M to 1.0 M) and particle size of aluminum (45 m to 500 μm) were varied as parameter study. It was found that the highest yield of H₂ was obtained using distilled water, 1.0 M of NaOH and 45 μm particle size of aluminium. However, the highest yield of methane was achieved using a moderate and progressive H₂ production (distilled water, 0.6 M of NaOH and 45 μm particle size of aluminium) which allowed sufficient time for H₂ to react with CO₂. It was concluded that 1130 ml of H₂ can produce about 560 ppm of CH₄ within 25 min of batch reaction using nickel catalyst.

1. Introduction

The development of industrial revolution requires significant increase in energy supply. Fossil fuels play a vital role in supplying the demanded energy. However, huge consumption of fossil fuels has instigated serious environmental impact such as global warming due to greenhouse gases emissions i.e. carbon dioxide (CO₂), nitrous oxide, and methane (CH₄) [1]. Therefore, many scientists are currently focusing on the development of carbon-clean and alternate energy. According to Zhou et al. (2016), CO₂ capture and utilization is believed to be one of the reliable energy sources [2]. Among the methods for CO₂ utilization are CO₂ hydrogenation to methanol and CO₂ reforming to methane.

Methanation of CO₂, which is commonly known as Sabatier reaction is a reversible and extremely exothermic reaction [3]. The product of reaction, CH₄ is the major component of conventional natural gas which can be acquired from associated gas, stranded gas and shale gas [4]. Together with the renewable H₂, CH₄ can be the key for future energy turnaround strategy in countries such as Switzerland and Germany as it reduces CO₂ emission [5].

Hydrogen (H₂) is an essential molecule in CO₂ methanation reaction and has drawn much attentions over the decades [6, 7]. H₂ produces three times larger reaction energy than hydrocarbon fuels when it reacts with air [8]. Additionally, the combustion of H₂ produces zero carbon emission and is likely made through water electrolysis [9]. Nonetheless, the production cost is always the issue due to the



conventional method to produce H_2 (mainly water electrolysis) is neither economical nor sustainable [10]. Next, storage and transport of H_2 pose safety concern and has always been a challenge [9, 11]. Thus, a more simple, inexpensive and safe method to generate H_2 is preferred.

Aluminium-water reaction is considered as an alternative reaction method to produce H_2 as aluminium metal is abundant in Earth's crust and the by-product of reaction can be recycled [6, 12]. As reported by Teng et al., 1 g of aluminum can generate 1360mL of H_2 gas in complete reaction with water under ambient condition [13]. However, the restrictive properties of the protective alumina layer lower the reaction rate and H_2 production yield [12]. Therefore, aqueous alkaline solution is applied to remove the passive alumina layer to increase the yield of H_2 gas production [13]. Alkaline solutions such as sodium hydroxide (NaOH), potassium hydroxide (KOH), and calcium hydroxide ($Ca(OH)_2$) have been tested [7]. As reported by Huang et al., NaOH and KOH have been proven to improve the H_2 production rate [14].

Thus, in this study, a cheaper source of H_2 gas via aluminum-water reaction is tested for methanation process. The process will be utilized to replace the commercial H_2 gas. So far in the literature the usage of H_2 gas produced from aluminum-water reaction is yet to be tested for methanation. Moreover, a potential new route of CO_2 methanation to generate CH_4 will be explored. Through this way, an alternative and low cost H_2 gas can be generated and used a source of energy production via CO_2 methanation to CH_4 .

2. Materials and Method

2.1. Chemical reagents

Favorit distillation system (*W4L WaterStill*, Malaysia), Elga water purification system (*Micra*, Republic of Korea) and Human Corporation water purification system (*New Human UP 900*, United Kingdom) were used to produce distilled water (resistivity of $0.3\text{ M}\Omega\cdot\text{cm}$), deionized water (resistivity of $10\text{ M}\Omega\cdot\text{cm}$) and ultrapure water (resistivity of $18.3\text{ M}\Omega\cdot\text{cm}$) respectively. Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$), aluminium powder and sodium hydroxide (NaOH) were purchased from Sigma Aldrich, USA. Palm shell activated carbon (PSAC) were purchased from Nikom Global Marketing (M) Sdn. Bhd. Malaysia. Pure lab grade CO_2 and N_2 gas cylinders were purchased from Linde Sdn. Bhd. Malaysia. All these materials were used as received.

2.2. Preparation of catalyst

Catalyst for the methanation was prepared according to Younas *et al.* [15]. Palm shell activated carbon (PSAC) was used as a support to prepare nickel based catalyst. 15wt% of Ni on PSAC was prepared using incipient wetness impregnation method. Stoichiometric amount of nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$) was dissolved in distilled water and PSAC was added into the solution. The mixture was sonicated at $60\text{ }^\circ\text{C}$ for 5 hours. Then, the mixture was evaporated in a rotary evaporator under reduced pressure. After evaporation, samples was dried in the oven at $110\text{ }^\circ\text{C}$ overnight. The dried sample was then calcined in N_2 at $500\text{ }^\circ\text{C}$ for 3 hours in a tubular furnace.

2.3. Hydrogen Production via Water Displacement Apparatus

Figure 1 shows the experimental setup. A defined amount of NaOH solution and aluminum powder were added into a conical flask. A rubber stopper with plastic tubing at the neck was used to prevent the gas leakage and channel the gas produced to the measuring cylinder. A measuring cylinder was fully filled with water, inverted and was immersed into a basin of water. The generated H_2 gas occupied the space in the measuring cylinder, lowering the water level in the measuring cylinder. The occupied level in the measuring cylinder was recorded based on time. A range of parameter study i.e. type of water used for reaction (tap water, distilled water, ultrapure water and deionized water), NaOH concentration (0.2 M, 0.4 M, 0.6 M, 0.8 M, 1.0 M) and different particle sizes of aluminum powder ($45\text{ }\mu\text{m}$, $63\text{ }\mu\text{m}$, $300\text{ }\mu\text{m}$, $355\text{ }\mu\text{m}$, $500\text{ }\mu\text{m}$) were tested for H_2 production. Each test was repeated twice and an average value was reported.

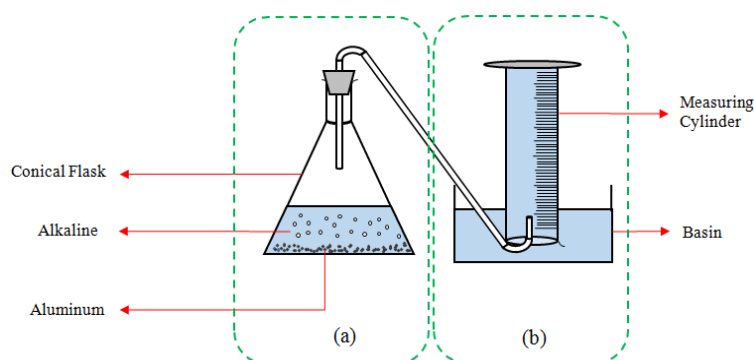


Figure 1. Schematic diagram of hydrogen production apparatus (a) and water displacement apparatus (b).

2.4. CO₂ methanation

0.5 g of nickel catalyst was used to initiate CO₂ methanation reaction at temperature 220 °C [4]. The produced H₂ gas and CO₂ were flowed through the CO₂ methanation apparatus until a stoichiometric ratio of H₂/CO₂ = 4 was achieved [16]. To achieve the ratio 20ml of CO₂ was purged every minute into the system. The outlet gases (CH₄ and CO₂) produced from the methanation reaction were collected into a gas sampling air bag every 5 min. The outlet gases were analysed using *MRU Air Emission Monitoring System (VARIOplus, Germany)*. Figure 2 shows the schematic diagram of CO₂ methanation apparatus. Methanation test was repeated five times for accuracy and an average value was reported.

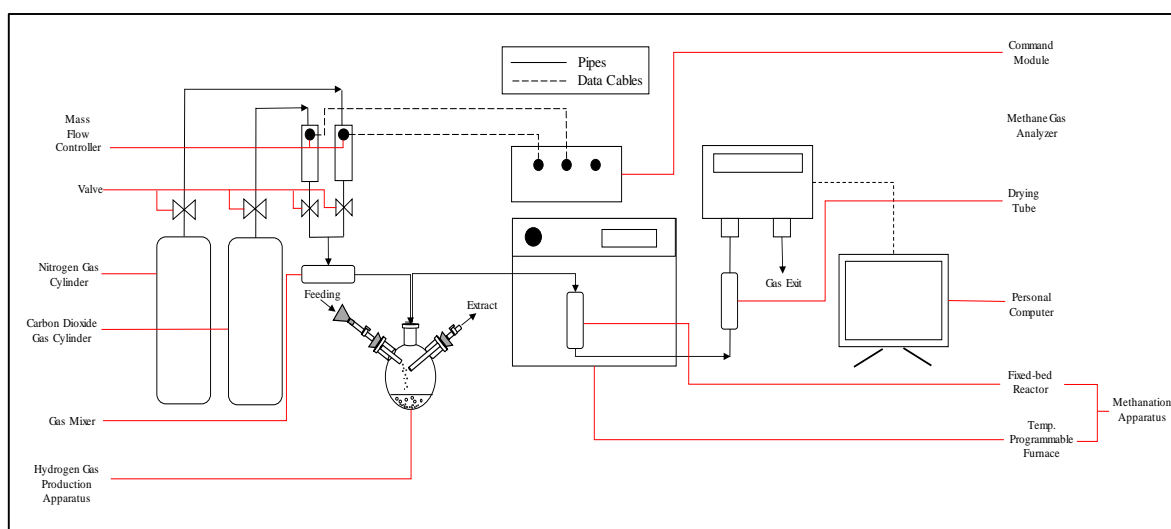


Figure 2. Schematic diagram of CO₂ methanation apparatus.

3. Results and Discussion

The effects of different type of water, concentration of NaOH and aluminum particle size were studied. H₂ solubility in water is very low, thus the volume of H₂ generated from the aluminium-water reaction was measured by the volume of water displaced with gas. The cumulative amount of H₂ produced from aluminum-water was measured and compared with the maximum theoretical yield of H₂ *i.e.* 1360 mL from 1 g of aluminium powder [13].

3.1. Effect of Water Type

200 mL of 1.0 M NaOH was prepared using distilled water, tap water, deionized water and ultrapure water respectively to examine the effect of type water for the H_2 generation. 1 g of 45 μm particle sized aluminum powder was used in this test. Figure 3 represents the amount of H_2 generated from aluminum-water reaction using different type of water.

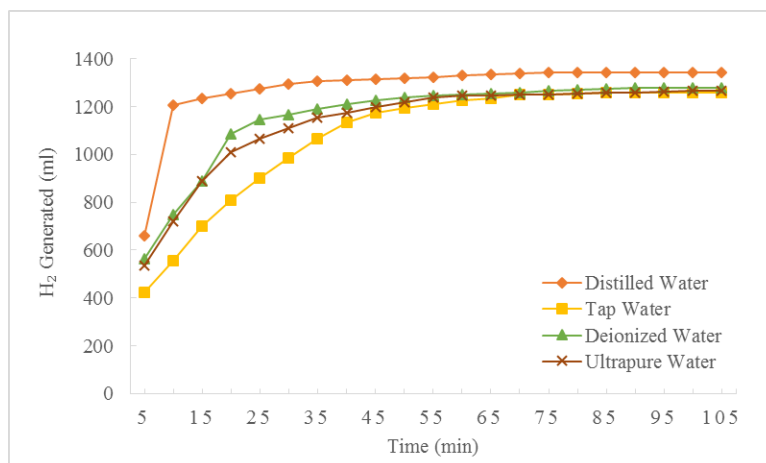


Figure 3. Hydrogen generated (ml) using different type of water.

Based on the data obtained, reaction using distilled water developed the fastest reaction rate. The reaction rate increased rapidly from the 1st min to the 7th min and reached stable condition after the 9th min. The maximum amount of H_2 generated was 1343 ml and was the highest amongst the others. Reaction using deionized and ultrapure water, produced slightly lower amount compared to distilled water. Moreover, the reaction rate was much slower compared to distilled water. It took about 20 min for deionized and ultrapure water to achieve about 1085 ml and 1010 ml respectively. Similar results was reported by Wang et al. [11]. It was known that salt content could help to activate aluminum surface and indirectly speed up the reaction of H_2 production. The more concentrated the salt content in the solution, the shorter the induction period of the reaction, the faster the reaction to reach production yield [17, 18].

Resistivity is a measurement of water quality as function of salt content (or ion) in water [19]. The resistivity of water is inversely proportional to the concentration of salt content. The resistivity of tap water, distilled water, deionized water and ultrapure water in this study were found to be as 0.0073, 0.3, 10.0 and 18.3 $\text{M}\Omega\cdot\text{cm}$ respectively. It is clearly seen that the ascending order of resistivity of the water was in line with the generation of H_2 . However, it was noticed that even though the resistivity of tap water was very low, the production of H_2 was still the least with a maximum yield of 1260 ml after 105 min of reaction. This was probably due to the impurities and chlorine content in the tap water. It is known that chlorination will cause significant loss in metallic aluminum and formation of aluminum chloride [20] which indirectly slows down the reaction. Therefore, the reaction rate of tap water was found to be the slowest.

3.2. Effect of NaOH concentration

To evaluate the effect of NaOH concentration on H_2 generation, a series of experiments were performed with different concentration of NaOH from 0.2 M to 1.0 M. 1 g of 45 μm aluminum powder was employed to react with 200 mL of NaOH solution in distilled water for this parameter study. Figure 4 describes the cumulative amount of H_2 generated from aluminum-water reaction at different concentration of NaOH.

As shown in figure 4, the higher the concentration of NaOH, the faster the rate of reaction for H_2 production. When the concentration of NaOH was 0.2 M, the rate of reaction was the slowest,

compared to reaction using higher concentration of NaOH. The fastest reaction was observed at 1.0 M, whereby within 10 min about 1200 ml of H_2 has been produced. At the same time, 0.2, 0.4, 0.6 and 0.8 M produced only about 175, 230, 445 and 725 ml of H_2 respectively. The highest yield was also obtained from 1.0 M i.e. 1342.5 ml. It was noticed that 0.6 and 0.4 M showed a trend of progressive and moderate reaction with almost a similar yield after 105 min of reaction. Similar results was reported other researchers [21, 22].

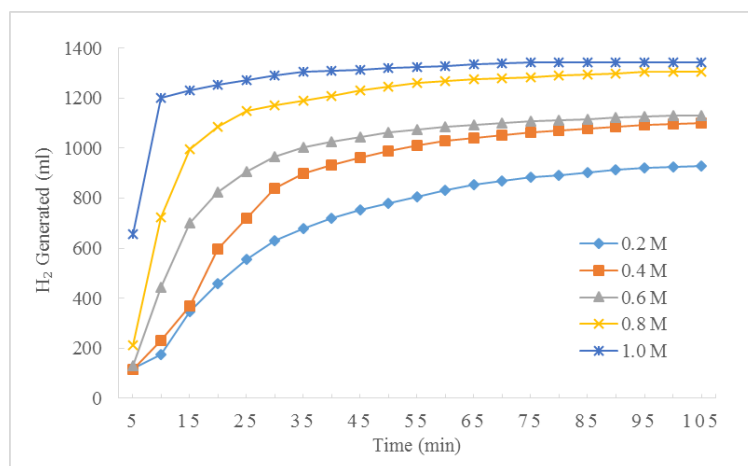


Figure 4. Hydrogen generated (ml) using different concentration of NaOH.

In general, the rate of reaction is faster when high concentration of alkaline is employed. This is because when the alkaline concentration is high, there are more hydroxide ion in the solution to dissolve the alumina film [14, 23]. The chemical attack progress results in more fresh aluminum surface which enhances the reaction with water to generate H_2 . Therefore, the initial rate of aluminum-water reaction was fast. As the hydroxide ion was consumed along the reaction, there were lesser hydroxide ion in the solution to dissolve the alumina film, leading to less reaction between fresh aluminum surface and water. Hence, the reaction rate dropped and the amount of H_2 generated correspondingly reduced.

3.3. Effect of aluminium particle size

Different particles sizes of aluminum, i.e. 45 μm , 63 μm , 300 μm , 355 μm and 500 μm were investigated with 200 mL of 1.0 M NaOH solution on H_2 production using distilled water. The experimental results were shown in figure 5. Figure 5 clearly shows that the smaller the particle size of aluminum, the more rapid the reaction rate and a shorter time is needed to achieve the maximum yield of H_2 . 45 μm exhibited the most rapid reaction rate with 1200 mL of H_2 generated within 10 min. After that, the reaction started to slow down until the 75th min. On the other hand, reaction with 300 μm showed a moderate reaction rate. The reaction was initiated with a fast rate within the first 10 min. Then, the reaction became stable and reached maximum yield of H_2 at the 90th min. For the reaction with 500 μm , only 355 mL of H_2 was generated within the first 5 min.

The rate of reaction increased gently after that until it reached a yield a maximum yield at the 75th min. A similar work was reported by Ilyukhina, Ilyukhin and Shkolnikov [24]. It is known that smaller size of particle has more surface area for reaction to happen. Smaller size also enhances the dissolution of alumina film [8, 25]. Thus, reaction with smaller aluminum particle size produces more amount of H_2 at a rapid rate [12]. At a point where hydroxide ion is used up in dissolving the alumina outer layer, there is no fresh aluminum to react hence, production is stopped. This shows that the system is stable and working well for H_2 production.

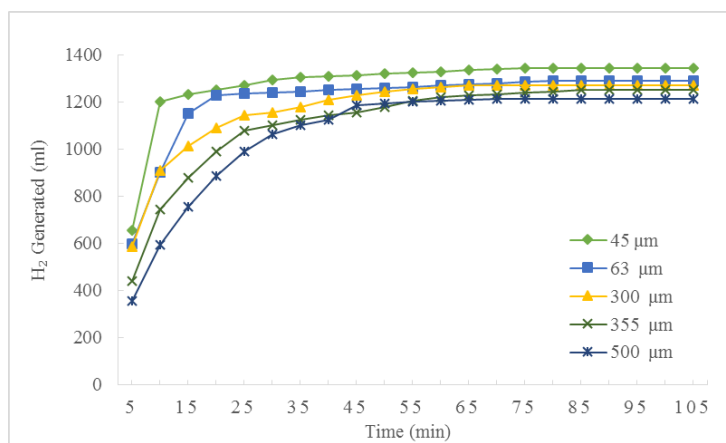


Figure 5. Hydrogen generated (ml) using different particle size of aluminum.

3.4. CO_2 methanation

CO_2 methanation was conducted using the optimized results of water type and aluminium particle size. The concentration of NaOH was varied to understand the difference in methanation if the production rate of H_2 is fast, moderate or slow. The reacted gas was collected every 5 min for a 35 min of continuous reaction. Figure 6 shows the methanation results. It was observed that a maximum of 25 min of reaction time was needed to produce CH_4 from a batch system. Reaction using 0.2 M and 1.0 M of NaOH obtained the lowest amount of CH_4 after 25 min of reaction as shown in Table 1. Interestingly 0.6 M showed the highest amount of methanation with about 229 ppm of CH_4 produced at the 20th min and a total of 560 ppm for a complete 25 min of reaction.

The rate of methanation in 1.0 M was low due to insufficient time for the reaction to happen between CO_2 and H_2 for CH_4 conversion. It was observed that at 1.0 M, H_2 was generated too fast with maximum yield within 10 min. It was suspected that most of the generated H_2 passed through the reactor without reaction as the analyser detected high concentrations of unused CO_2 in the outlet. A moderate and progressive reaction using 0.6 M of NaOH has shown the best conversion. Progressive or moderate production rate of H_2 allowed sufficient time for the reaction between H_2 and CO_2 and maintained the stoichiometric ratio between H_2 and CO_2 . Moreover, there was no CH_4 produced in the first 5 min of the reaction for all concentrations of NaOH. This was probably due to insufficient amount of H_2 produced which indirectly hindered the conversion. Thus, CH_4 was not produced. After 10 min of reaction, CH_4 was detected and the amount of CH_4 increased rapidly until the 20th min for 1.0 M. This was because there was sufficient amount of H_2 produced to convert CO_2 to CH_4 .

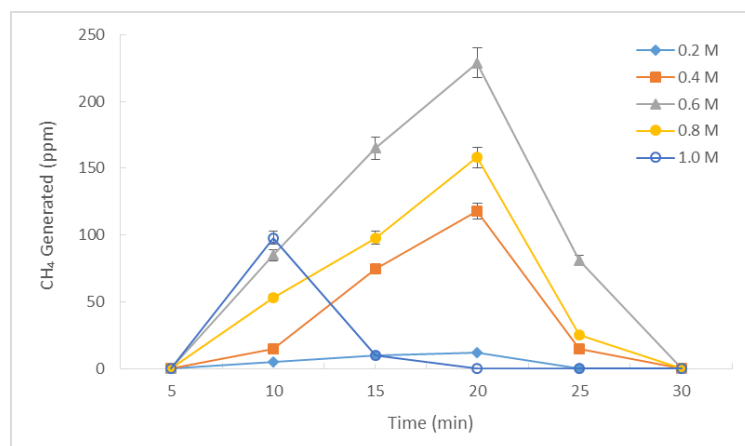


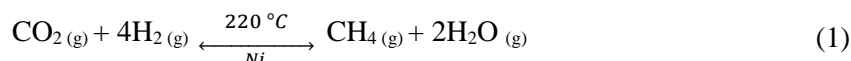
Figure 6. Methane generated (ppm) using different concentration of NaOH.

Table 1. Total amount of CH₄ produced after 25 min of reaction at different concentration of NaOH.

NaOH concentration (M)	CH ₄ produced (ppm)
0.2	27
0.4	223
0.6	560
0.8	334
1.0	108

After the 20th min, the reaction declined and stopped at the 30th min which identified the completion of the aluminum-water reaction. Hence, there was no H₂ produced for CO₂ methanation to take place.

Besides, reaction using 0.2 M of NaOH could not produce high amount of CH₄ due to low production rate and yield of H₂. To date, literature only focuses on catalyst performance of CO₂ methanation. For that reason, there is no similar data or report from literature to be compared. However, the batch CO₂ methanation reaction was expected to be similar to Sabatier reaction as shown in equation 1 below, where CO₂ reacts with H₂ and produces CH₄ at 220 °C in the presence of nickel catalyst.



4. Conclusion

In this study, H₂ gas was produced from aluminum-water reaction. The type of water, concentration of NaOH and particle size of aluminum powder were used as experimental parameter and has been optimized. In short, H₂ yield was directly proportional to the concentration of NaOH and was inversely proportional to resistivity of water and particle size of aluminum. Additionally, the optimum conditions of aluminum-water reaction investigated from these studies were 1.0 M of NaOH solution prepared by distilled water and 45 µm particle size of aluminum powder could yield a maximum of 1343 mL of H₂.

CO₂ methanation using H₂ produced from aluminium-water reaction could only last for 25 min of reaction. The maximum total yield of CH₄ for 25 min of reaction was 560 ppm and this amount could be only achieved using a moderate reaction rate of H₂ production using 0.6 M of NaOH. The results have proven that H₂ generated from aluminium-water reaction could be successfully used for CO₂ methanation in a batch study.

Acknowledgments

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