Annas ul Hassan Qureshi et al. Malaysian Journal of Microscopy Vol. 16, No. 1 (2020), Page 115-123

Conversion of CO_2-CH_4 Mixture into Carbon Nanomaterials via Chemical Vapour Deposition

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Abstract

One of the major factors for global warming is the increase in the concentration of CO2 in the atmosphere. There are several reserves of natural gas available in Malaysia that contain various other hydrocarbons; however, they are rendered useless due to the high concentration of CO2. There have been studies where CO2 is being utilized in the production of syngas, in which catalysts employed for the synthesis mainly consist of transition metals such as Fe, Ni, Al, Mg, and Mo. In this study, Fe and Ni hydrotalcites catalysts were prepared by co-precipitation method. Al_2NO_3, $MgNO_3$, and $NiNO_3$ were titrated dropwise against $Na_2CO_3.10H_20$ while maintaining the temperature and the pH of the solution at 70°C and pH 10, respectively. Similarly, for the iron catalyst, the $NiNO_3$ was replaced with $FeNO_3$ and the remaining chemicals were varied according to the stoichiometric parameters. The catalyst produced was then vacuum-filtered, dried at 80 °C and calcined at 650°C. The calcined catalyst was used in the reactor. The gases produced were analyzed using gas chromatography and showed that H_2 gas was being produced, finally after the reaction was completed the used catalyst was analyzed by Field Emission Scanning Electron Microscope (FESEM) to prove the growth of carbon nanomaterial.

Keywords: co-precipitation, carbon nanomaterials, chemical vapour deposition

Article Info

Received 13th November 2019
Accepted 21st February 2020
Published 1st April 2020
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ISSN: 1823-7010, eISSN: 2600-7444

Introduction

Currently, the greenhouse gases are responsible for the increase in Earth's temperature. These gases cause the radiation to reflect back to the surface of the Earth causing the surface temperature to rise. The key component of these greenhouse gases is CO_2 and by simply doubling the concentration of CO_2 the surface temperature can increase by 0.9°C. The radiation that leaves the surface is about 52%; however, to maintain Earth's equilibrium temperature this percentage has to increase [1, 2].

Greenhouse gases are composed of a variety of gases, where the most impactful gases are CO_2 and CH_4 as they contribute to about 80 – 85 % of the effect and throughout the last 20-30 years this percentage has not changed. The role of CH_4 in global warming is even more potent than CO_2 as exposure to high quantities of CH_4 can cause damage to vital organs such as the brain and the heart, as well as irritation to the eyes [3]. As the world's natural resources are being depleted every day to meet the daily requirements of people's lives, industries have to look for ways to utilize resources that are less feasible. In Malaysia, there are natural gas reserves that contain CO_2 concentrations as high as 87 % which renders the remaining useful composition impractical to extract. The reason CO_2 causes an issue is that it can cause corrosion in the equipment if moisture is present. Furthermore, CO_2 crystallizes during the cryogenic process and it cannot be readily used as fuel like other hydrocarbons such as methane, ethane, and propane. The CO_2 concentration of natural gas in Malaysia ranges from 28-87% and more than 13 trillion cubic feet of natural gas is not utilized as the high CO_2 concentration makes them economically unfeasible[4].

However, if the composition of high concentration CO_2 present in natural gas can be utilized and transformed into a valuable product such as carbon nanotubes (CNT), the extraction of the 13 trillion cubic feet of natural gas [5] can become economically feasible. At present, there is no large-scale production of CNT from high-concentration CO_2 and CH_4 as the carbon source. Nonetheless, if CNT could be economically manufactured from a mixture of these gases, it will ultimately result in a better procedure for the consumption of natural gas reserves rich in CO_2 concentration. Moreover, this will subsequently reduce CO_2 released into the atmosphere, thus lowering the carbon footprint throughout the world. Currently, the application of CNT is limited due to its price, as it ranges from $100 to $ 25,000 per kg of multi-walled CNT. The mass production of low-cost CNTs is anticipated to become a valuable asset for researchers as well as industries all over the world [6].

Chemical vapor deposition (CVD) technique was used for the synthesis of carbon nanomaterials. In CVD method, metal catalysts are used to decompose the molecules of a carbon source to synthesize carbon nanotubes, where the decomposition takes place at high temperature that ranges from 600 – 1000 °C. After heating, the sample is cooled down to room temperature in an inert environment to prevent unnecessary reaction of CNTs with oxygen, which will result in etching. CVD can use multiple types of carbon sources for the synthesis of CNT, and it has been effective for the synthesis of single-walled carbon nanotubes (SWCNTs). [7, 8].

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Materials and Methods

Materials

Nickel nitrate ($NaNO_3$), magnesium nitrate ($Mg(NO_3)_2$), iron nitrate ($Fe(NO_3)_2$), and sodium carbonate (Na_2CO_3) were purchased from Sigma Aldrich^{TM}, while sodium hydroxide (NaOH) and aluminum nitrate ($Al_2(NO_3)_3$) were purchased from Merck^{TM}. Nitrogen, Hydrogen, Methane, and Biogas (60% Methane and 40 % Carbon Dioxide) were purchased from Alpha Solution. All the chemicals were analytical grade and used without further purification. In this study, all solutions were prepared with deionized water.

Preparation of Nickel and Iron based hydrotalcites

The catalyst was synthesized using the methodology mentioned by Sikander et al. [9], by varying the molar concentration of the components utilized. The Ni-based hydrotalcite was prepared using solutions of $NaNO_3$, $Mg(NO_3)_2$ and $Al_2(NO_3)_3$ at molarity of 0.3 M, 0.75 M, and 0.75 M, respectively, where 0.5 M solution of Na_2CO_3 was used for CO_3^{2-} cation exchange reagent. NaOH at 1M was used to maintain the pH of the solution, while metal nitrates were mixed in different molar ratios and titrated dropwise against rigorously stirred Na_2CO_3 solution at 70 ^oC. The mother liquor was maintained at pH 10 by dropwise addition of 1M NaOH. Precipitates produced were washed with deionized water, separated using vacuum filtration and dried in the oven at 80^oC for 12 hours. The dried material was then crushed manually. The atomic weight percentage of nickel and iron was varied with respect to aluminum and magnesium, from 15 % to 60 % by manual calculations. The weight of iron present in 100 ml solution of $Fe(NO_3)_2$ was set as the base and the weight of aluminum and magnesium was varied to attain the required composition for iron based hydrotalcites. Similarly, this process was repeated for nickel hydrotalcites. Finally, the hydrotalcites were calcined at 650^oC for 6 hours. Iron based hydrotalcites were also synthesized using similar procedure however in this case nickel nitrate was replaced with iron nitrate.

Synthesis of Carbon nanomaterials

The procedure for the reaction was similar to the procedure mentioned by Pudokody et al. [10], however, the weight of the catalyst and the temperature of the reactor was varied. The calcined nickel and iron based catalyst were employed in a vertical fixed bed reactor. The temperature of the reactor was increased from 25^oC to 600°C with 1.5g catalyst placed within the reactor in the presence of nitrogen gas. The increase in temperature was done gradually in 90 min. The catalyst was then reduced in the presence of hydrogen gas at 600^oC for 60 min. Following the reduction, the temperature of the reactor was again increased from 600^oC to the varied temperature range from 700 to 900^oC in the presence of both pure CH_4 gas as well as a mixture containing 60% CH_4 and 40% CO_2. During the reaction, gas samples were collected in gas bags and analyzed using GC to determine the products being formed at specific intervals of time. After the reaction was completed the spent catalyst was analyzed using FESEM to determine the products formed.

Result and Discussion

The catalyst's morphology was examined by FESEM before and after the reaction had occurred. Furthermore, the gasses produced during the reaction were stored in gas bags after specific time intervals and analyzed using an offline GC analyzer.

Morphology and appearance of Nickel based Hydrotalcites

Figure 1 (a) and 1 (b) show the FESEM micrographs of Ni-based hydrotalcites, where the morphology in both cases is similar and shows that the catalyst has structures resembling porous coral. This type of morphology will be beneficial as the coral type structures will have a high surface area. These results are similar to the morphology of nickel based hydrotalcites observed by Sikander et al. [9].

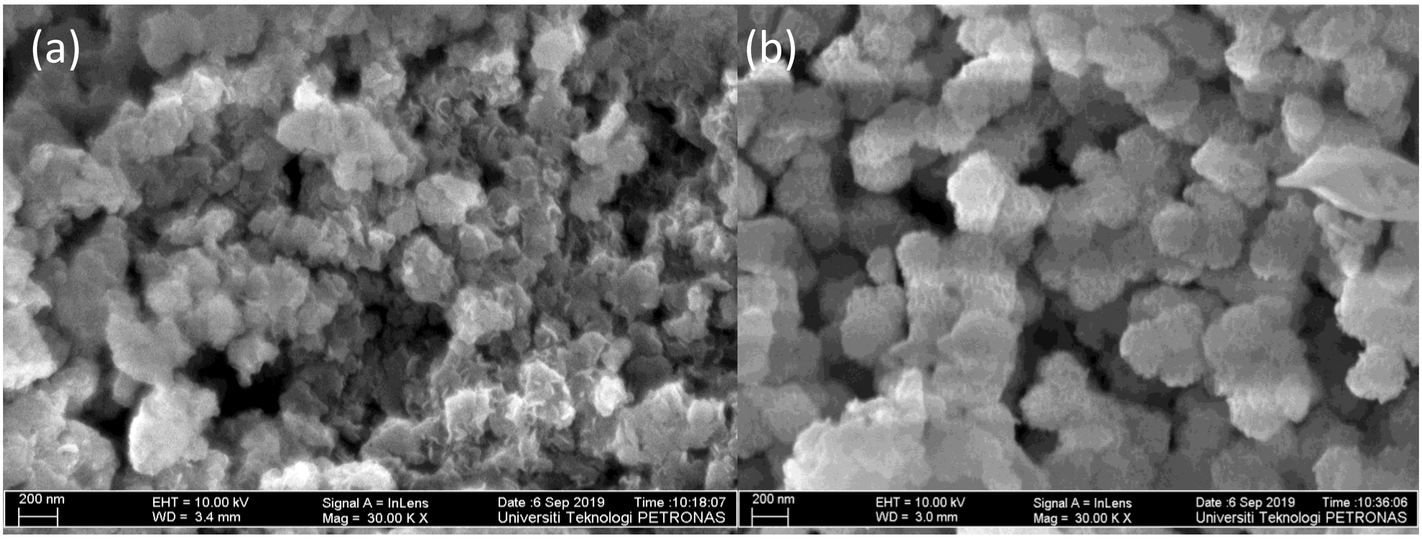

Figure 1 FESEM Nickel hydrotalcite with (a) 30 % Nickel (b) 40% Nickel

Morphology and appearance of spent catalyst

Finally, the spent catalyst was analyzed after the reaction had occurred. This was done in order to determine the growth of carbon nanomaterials and changes that took place during the reaction. Figure 2 (a) and 2 (b) display the catalyst used in the reaction for the formation of CNT and carbon nanofibers.

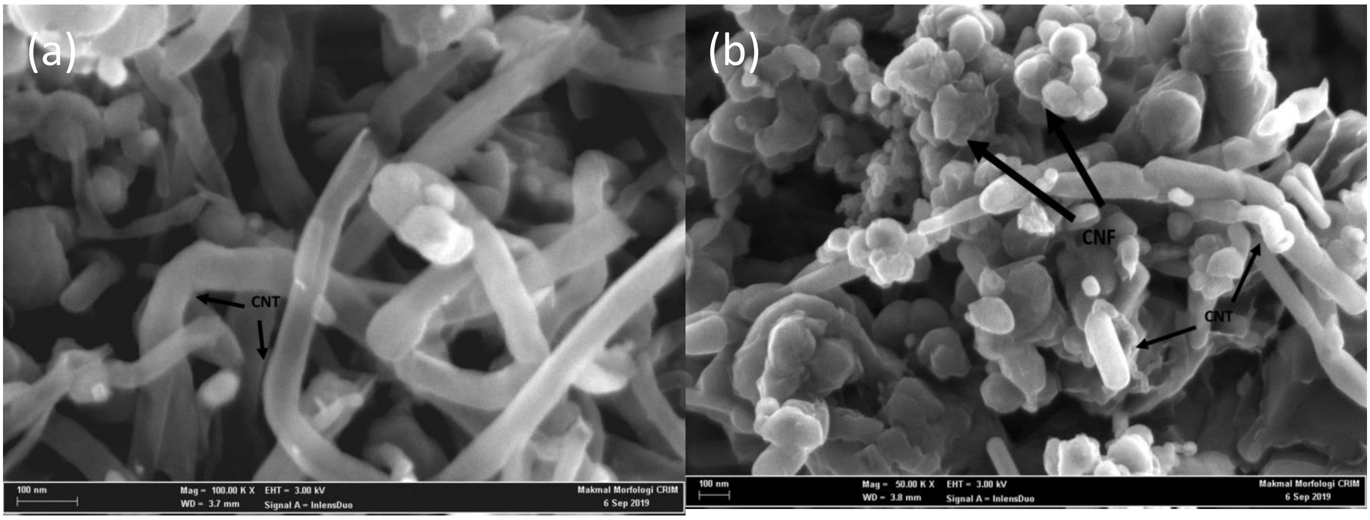

Figure 2: spent iron and nickel catalyst with carbon growth (a) FeHT15 (b) NiHT30

The catalyst had a coral-like structure before the reaction took place, whereas after reaction tube-like structures grown on the catalyst are clearly visible. The growth of CNTs can be either base growth or tip growth. The relatively thicker structures are CNF while the thinner tube-like structures are CNT. Figure 2 (a) contains the carbon nanofibers developed on the iron-based hydrotalcite where the concentration of iron, in this case, was kept to 15% Fe with respect to the other metals i.e. 43% magnesium and 42 % aluminum by weight, using manual calculation.

Figure 3(a) and Figure 3(b) show the spent nickel catalyst with nickel composition varied with magnesium and aluminum. The varied composition of nickel was 30%, 40%, and 60%, respectively with respect to the remaining metals of magnesium and aluminum. The CNTs and CNFs growth are similar to growth observed by Sikander et al. [9].

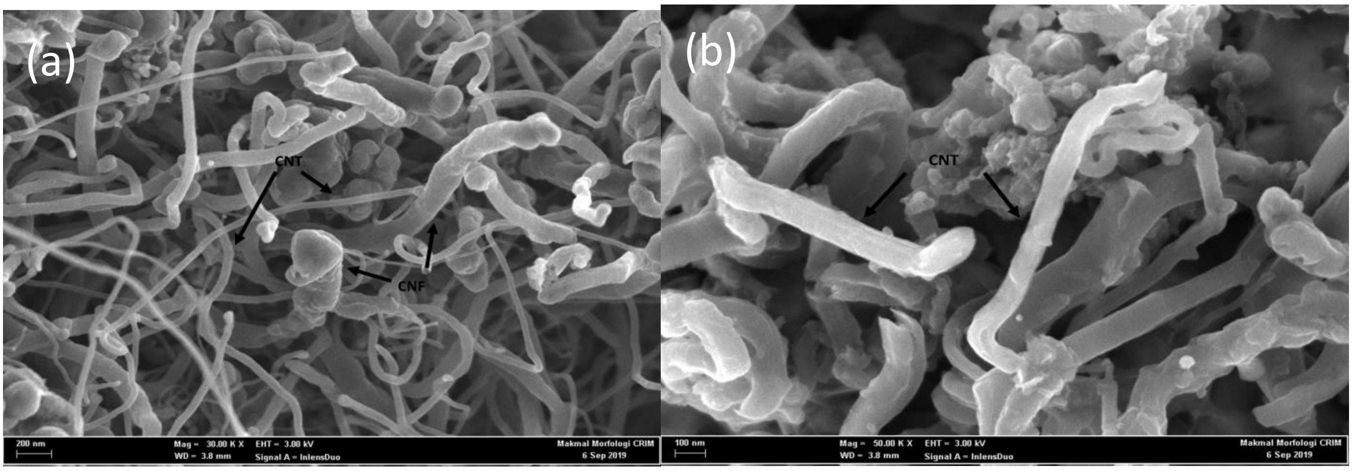

Figure 3: spent nickel catalyst with carbon growth (a) NiHT40 (b) NiHT60

GC Analysis

The GC analysis of the gases within the reactor shows that the NiHT 30 (nickel hydrotalcite) produces a maximum concentration of hydrogen gas as shown in Figure 4 and Figure 5, respectively. Figure 4 shows the intensity of hydrogen gas peak with a specific catalyst, Figure 5 compares the intensity of hydrogen peaks when pure methane is used and when a mixture of CH_4 and CO_2 is used with the same catalyst. The term NiHT 30 pure refers to the pure CH_4 gas used while the NiHT 30 refers to the mixture of CH_4 and CO_2 used. Finally, Figure 6 shows the concentration of various gasses within the reactor at a specific time when NiHT 30 (Nickel Hydrotalcite) used to convert pure CH_4 into CNF and CNT. The Ni-HT30 catalyst demonstrates a better performance as compared to the other catalyst as it produced more quantity of H_2 gas and carbon deposit while using the same quantity of catalyst. This can also be seen in Figure 4 where Ni-based hydrotalcite is more reactive compared to Fe-based hydrotalcite. The high performance of the Ni-based hydrotalcite is due to the lower size of nickel and the high stability of the support, as mentioned by Touhara [11]. Furthermore, it can also be seen in Figure 5 that when pure CH_4 has been used the production of H_2 is relatively more when the same catalyst is used for a mixture of CH_4 and CO_2 at the same temperature.

The NiHT30 catalyst shows a gradual increase in reactivity up until 60 minutes after which the reactivity of the catalyst starts to decrease which can be seen in Figure 6. This decrease in activity is most likely due to the deposition of carbon particles on the active sites of the catalyst hence rendering the catalyst site inactive and decreasing its reactivity, producing a similar trend as reported by Sikander et al. [9].

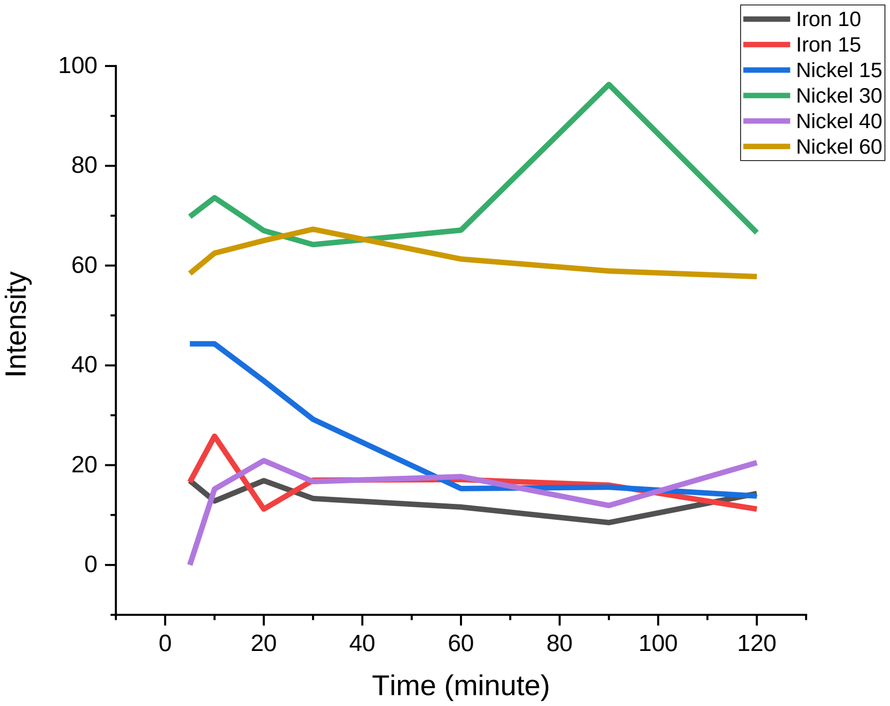

Figure 4: Intensity of hydrogen gas produced with different catalysts.

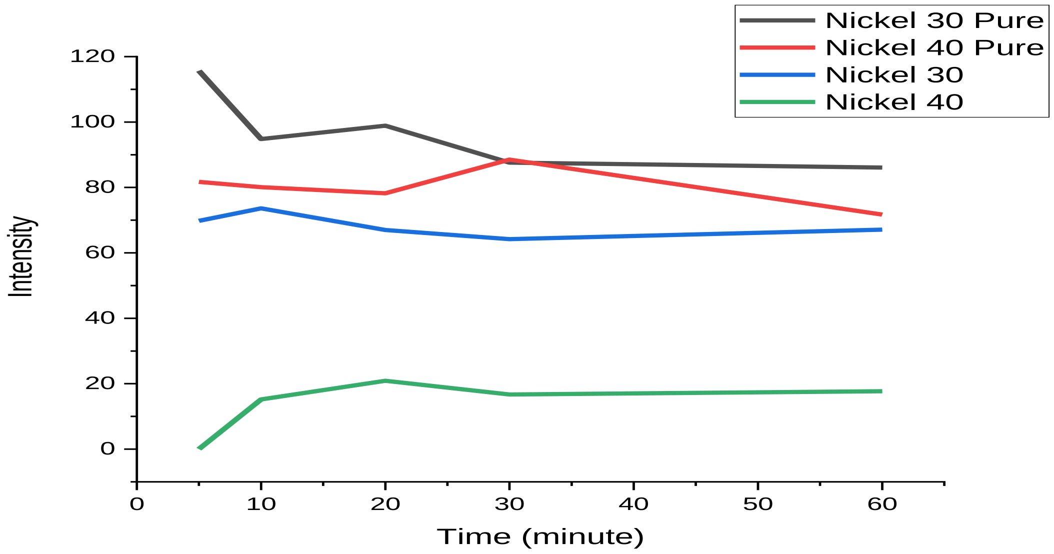

Figure 5: Comparison of intensity of Hydrogen produced using CH_4 (pure) and CH_4 and CO_2.

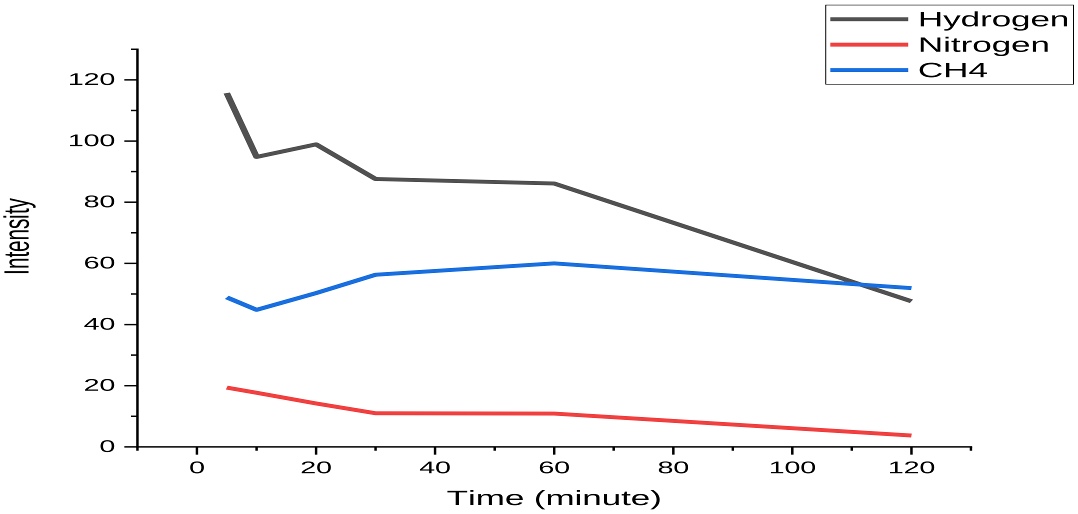

Figure 6: Intensity of gases produced using NiHT 30(nickel based hydrotalcite) in pure CH_4.

Conclusion

In summary, the synthesis of nickel based hydrotalcites with a varied composition of nickel was utilized to produce CNT and CNF from a mixture containing both CH_4 and CO_2. The results show that from the varied composition of nickel the most hydrogen gas and carbon deposited was from hydrotalcites containing 30 % concentration of nickel. The nickel based hydrotalcite produced the highest amount of carbon deposit from 1.5 g catalyst placed in the reactor. The GC analysis shows that more than 2.2 g carbon was deposited from the gas mixture showing high catalytic activity in the presence of a mixture of gases (60% CH_4 and 40% CO_2). Furthermore, the results from Figure 5 indicate that an increase in temperature and CH_4 composition results in an increase in carbon deposits as well as an increase in the production of hydrogen gas. Thus, nickel hydrotalcite can be effectively used in utilizing a gas mixture of CH_4 and CO_2.

Acknowledgment

The authors gratefully acknowledge the financial support from the YUTP grant (015LCO-037). A special thanks to the Department of Chemical Engineering Unversiti Kebangsaan Malaysia, and Department of Chemical Engineering, Universiti Teknologi PETRONAS, Malaysia for providing the lab facilities.

Author Contributions

The idea for this paper was proposed by S.Sufian; W.N.R. Isahak and Z. Yaakob provided the equipment and facilities for the experimentation in UKM. A.U.H Qureshi put together the literature review, performed the experiments and prepared the paper with guidance from S.Sufian; the funding for the experiments was contributed by M.Z.B Abdullah.

Disclosure of Conflict of Interest

The authors have declared that there is no conflict of interest.

Compliance with Ethical Standards

The experiments and research conducted were all in compliance with ethical standards

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