

The effect of Ni/Al₂O₃ catalyst mass variation and operation time on the CO₂ methanation process

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ARTICLE INFO	ABSTRACT
<i>Article history:</i> Received: 08-08-2025 Received in revised form: 14-10-2025 Accepted: 17-10-2025 <i>Keywords:</i> CO₂, CH₄, Ni/Al₂O₃ Catalyst, CO₂ Methanation, Fixed Bed Reactor	Carbon dioxide (CO₂) is one of the biggest contributors to the greenhouse effect. Based on data from the International Energy Agency (IEA), greenhouse gas (GHG) emissions continue to increase, reaching 37.8 billion tons in 2024. One way to reduce carbon dioxide (CO₂) is to convert carbon dioxide (CO₂) into methane (CH₄) through a methanation process using a Fixed Bed Reactor. This study was conducted by varying the mass of Ni/Al₂O₃ catalyst between 55 grams and 60 grams and the operating time between 90, 100, 110, 120, and 130 minutes, as well as adding 20 grams of Zn promoter to improve catalyst stability performance. A Multi Gas Detector Analyzer was used to analyze the methane (CH₄) gas produced. The results of this study showed that the highest percentage of methane gas (CH₄) produced was obtained in sample 10 with a Ni/Al₂O₃ catalyst mass of 60 grams and an operating time of 130 minutes, which was 58.35%.

1. Introduction

Carbon Dioxide (CO₂) is one of the most significant contributors to the greenhouse effect. Based on data from the International Energy Agency (IEA) (2024), greenhouse gas (GHG) emissions continue to increase, reaching 37.8 billion tons in 2024, with CO₂ contributions coming from the processing industry, power generation, and transportation sectors, which collectively accounted for more than 80% of the national total emissions [1]. One way to reduce carbon dioxide (CO₂) in the atmosphere is by converting carbon dioxide (CO₂) into methane (CH₄) through the process of carbon dioxide methanation.

Carbon dioxide methanation or hydrogenation of carbon dioxide to methane, also known as the Sabatier reaction, is an exothermic reaction where hydrogen and carbon dioxide react to form methane and water as byproducts [2]. This reaction is advantageous because it can be carried out at low temperatures between 25°C and 400°C, but hydrogenation of carbon dioxide can only be achieved with an effective catalyst [3].

The formation of CH₄ from CO₂ at low temperatures has become a significant breakthrough in understanding the role and use of CO₂, although the conversion is still very low [4]. Various types and variations of catalysts have been extensively researched and applied in the CO₂ methanation process. Nickel, rhodium, and ruthenium catalysts are among the most commonly used. Various combinations of catalysts consisting of Al₂O₃, MgO, SiO₂, CeO₂, ZrO₂, TiO₂, Nb₂O₅, and other Components have been proposed and studied as catalyst support materials.

Nickel catalysts were chosen because they can absorb hydrogen and are highly selective for methane formation [5]. Ni catalysts can maintain good activity for a long reaction time

by producing high CH₄. However, it is difficult to achieve high CO₂ conversion at low temperatures because it requires high activation energy [6].

Liza et al. [7] researched methane gas production from carbon dioxide using the Ni-Fe/Al₂O₃ catalyst and analysed the effect of variations in operation time and catalyst mass. The research results show that variations in the amounts of Ni, Al, and Fe catalysts of 3 g, 2 g, and 1 g, with an operation time of 60 minutes, resulted in 10.07%.

Putri et al., [8] conducting research on methane gas production from carbon dioxide by analysing the effect of varying amounts of Fe promoter and operation time. The research results show that the variation in the amount of Fe promoter used is 5 grams with an operation time of 60 minutes, which is 12.54%.

Saputra et al., [9] conducting research on methane gas production from carbon dioxide by analysing the effect of varying the mass of the Ni/Al₂O₃ catalyst and temperature. The percentage of the research results shows that the most methane gas is produced in situ with a Ni/Al₂O₃ catalyst mass of 15 grams at a production temperature of 150°C, which is 25.71%.

Several studies above conclude that the use of Ni/Al₂O₃ catalysts in CO₂ methanation shows good potential, but the results obtained are still not optimal. To address the existing issues and improve the yield of methane gas products, this study analyses the effect of varying the mass of the Ni/Al₂O₃ catalyst and the operating time using a Fixed Bed Reactor.

2. Materials and Methods

2.1. Tools

A set of Fixed Bed Reactor tools, analytical balance, 250 ml measuring flask, 250 ml beaker, 500 ml Buchner flask, spatula, stirring rod, watch glass, measuring pipette, rubber

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ball, filter paper, and gas sampling bag.

2.2. Materials

Carbon dioxide (CO_2), $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, Zn powder, NaOH, aquadest, deionised water, silica gel.

2.3. Research procedures

2.3.1. Preparation of sodium hydroxide (NaOH) solution

Weigh 40 grams of Sodium Hydroxide (NaOH) solution with a concentration of 4 M. Then add distilled water and transfer it into a 250 ml volumetric flask up to the mark.

2.3.2. Activation of $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst

Weigh 55 grams and 60 grams of $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, then slowly add 4 M NaOH solution in a 250 ml Erlenmeyer flask, then heat at 110°C for 2 hours over a water bath. After heating, the catalyst precipitate was washed with deionized water and dried using a vacuum. The activated catalyst was then furnace-dried at 600°C for 4 hours.

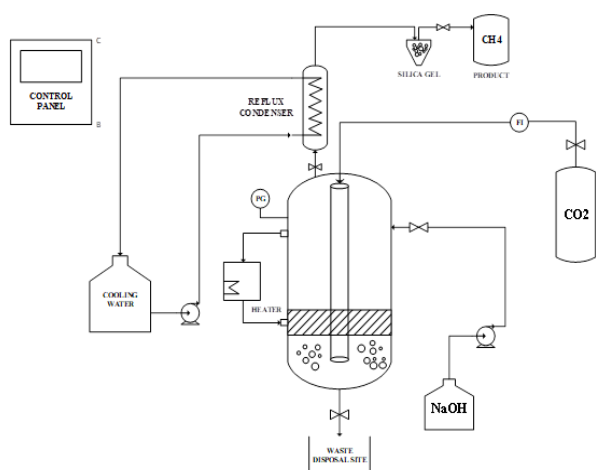


Fig. 1. CO_2 Methanation Process Scheme

2.3.3. CO_2 methanation unit operating procedure

Prepare all the tools and materials that will be used in the methanation process, then connect the tools to the power supply. Ensure that all hoses and valves are tightly connected and that none are loose. Once all the tools are ready for use, the next step is to add the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst according to the variation and 20 grams of Zn metal to the reactor. Prepare a 4 M NaOH solution in a 250 ml beaker. Turn up the fuse until the indicator light turns on. Set the temperature to 200°C . Then turn on the NaOH solution flow pump by setting the flow rate to 0.05 L/minute. Next, vary the catalyst mass between 55 g and 60 g, and the operating time between 90, 100, 110, 120, and 130 minutes. After the NaOH solution is added, flow CO_2 gas by setting the flow rate to 0.05 L/minute and the pressure in the reactor tube to 1 bar. During this process, when the NaOH solution reaches its boiling point, it will evaporate. The resulting vapor then comes into contact with a cooling device (reflux condenser), which functions to condense the vapor back into liquid and keep the system stable. The system is allowed to circulate in the reactor until the product container

is full according to the specified operating time. The CH_4 gas produced is distributed to the product tube, after which it is analyzed.

2.4 Analysis of experimental results using a multi-gas detector analyser

The analysis method uses a Multi Gas Detector Analyser that can measure the type and content of compounds in a sample both qualitatively and quantitatively. This tool can directly analyse the content present in the results of the CO_2 methanation process, with the analysis results being the volume percentage (% volume). The gas contents that the gas analyser can analyse include non-hazardous substances such as CO_2 , CH_4 , H_2O , N_2 , and hazardous substances such as CO , HC , NOX , H_2S , etc.

3. Results and Discussion

3.1. Research result

From the analysis results using the Multi Gas Detector Analyzer, three main gas components were identified, namely carbon dioxide (CO_2), hydrogen (H_2), and methane (CH_4). The CO_2 and H_2 gases that were still detected indicate the presence of reactants that have not fully reacted to form CH_4 . The percentage of each gas component can be seen in Table 1.

Table 1. Gas Analysis Results

Mass of $\text{Ni}/\text{Al}_2\text{O}_3$ Catalyst (grams)	Operating Time (minutes)	Analysis Results (% Volume)		
		CH_4	CO_2	H_2
55	90	35.33	61.44	1.92
	100	38.45	58.47	1.85
	110	41.55	55.53	1.75
	120	43.15	54.01	1.71
	130	45.35	51.92	1.64
60	90	44.22	52.99	1.67
	100	48.77	48.67	1.54
	110	52.23	45.38	1.43
	120	55.64	42.14	1.33
	130	58.35	39.57	1.25

3.2. Discussion

3.2.1. The effect of varying $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst mass and operating time on methane (CH_4) gas yield

In this CO_2 methanation reaction, two variations were used: a $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst mass of 55 grams and 60 grams, and an operation time of 90, 100, 110, 120, and 130 minutes with the addition of a Zn promoter of 20 grams. After conducting research and sample testing, it was observed that the more $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst mass and the longer the operation time, the more methane gas produced and the higher the percentage. This occurs because the greater the catalyst mass, the larger the surface area for the reaction to take place, making the formation of methane gas more optimal. Additionally, with a longer operation time, there is more complete contact between CO_2

and H₂ gas, resulting in more methane gas production. It can be seen in Figure 2 that the methane gas (CH₄) produced is directly proportional and continues to increase.

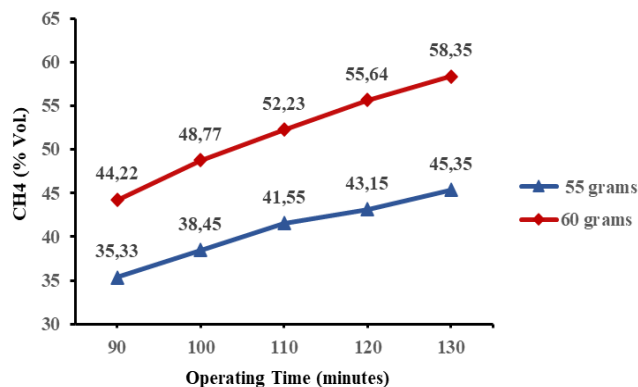


Fig. 2. The effect of varying Ni/Al₂O₃ catalyst mass and operating time on methane (CH₄) gas yield

The effect of varying the mass of the Ni/Al₂O₃ catalyst and the operating time significantly affects the yield of methane gas, resulting in a yield of 58.35% with a Ni/Al₂O₃ catalyst mass of 60 grams and an operating time of 130 minutes. This result indicates a much higher conversion achievement compared to several previous studies. The research conducted by Liza et al. [7] studied the production of methane gas from carbon dioxide using the Ni-Fe/Al₂O₃ catalyst with variations in operating time and catalyst mass. In the variation of the amounts of Ni, Al, and Fe catalysts at 3 g, 2 g, and 1 g with an operating time of 60 minutes, the yield was 10.07%. Based on the research by Putri et al. [8], which studied the CO₂ methanation process with variations in Fe promoter mass and operating times of 30, 45, and 60 minutes. At an operating time of 60 minutes and an Fe mass of 5 grams, the methane produced was 12.54%. Additionally, the research by Saputra et al. [9] involved variations in Ni/Al₂O₃ catalyst mass of 5, 10, and 15 grams and operating temperatures of 100°C, 120°C, and 150°C. At a Ni/Al₂O₃ catalyst mass of 15 grams and an operating temperature of 150°C, the highest methane yield was 25.71%.

3.2.2 The effect of varying Ni/Al₂O₃ catalyst mass and operating time on carbon dioxide (CO₂) gas residual

The increase in the mass of the Ni/Al₂O₃ catalyst from 55 grams to 60 grams and the operation time from 90 to 130 minutes decreased the volume of unreacted CO₂ gas. This can be seen in Figure 3, where this decrease indicates that the larger the mass of the catalyst and the longer the reaction time, the more CO₂ is successfully converted into other products such as methane (CH₄).

The reduction of CO₂ gas from 52.99% to 39.57% at a Ni/Al₂O₃ catalyst mass of 60 grams and an operating time of 90 to 130 minutes indicates that the methanation reaction proceeds more efficiently with a higher catalyst mass. This is due to the increased active surface area and the number of active sites on the catalyst, allowing more CO₂ molecules to

interact with hydrogen and be converted into methane (CH₄). Meanwhile, at a Ni/Al₂O₃ catalyst mass of 55 grams and an operating time of 90 to 130 minutes, the reduction of CO₂ gas from 61.44% to 51.92% still occurs, but at a slower rate.

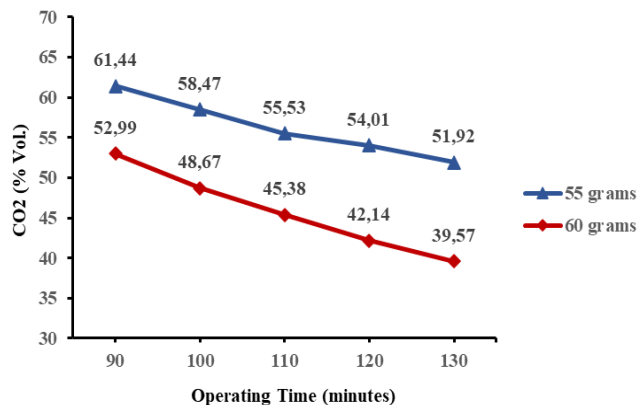


Fig. 3. The effect of varying Ni/Al₂O₃ catalyst mass and operating time on carbon dioxide (CO₂) gas residual

3.2.3 The effect of varying Ni/Al₂O₃ catalyst mass and operating time on hydrogen (H₂) gas formation

Figure 4 shows a decrease in the volume of H₂ gas with the increase in operation time from 90 minutes to 130 minutes using 55 grams and 60 grams of Ni/Al₂O₃ catalyst. This decrease in H₂ gas volume indicates that a reaction is occurring inside the reactor tube, forming H₂ gas, but the formed H₂ gas does not react due to insufficient adsorption of H₂ gas by Ni nanoparticles [10].

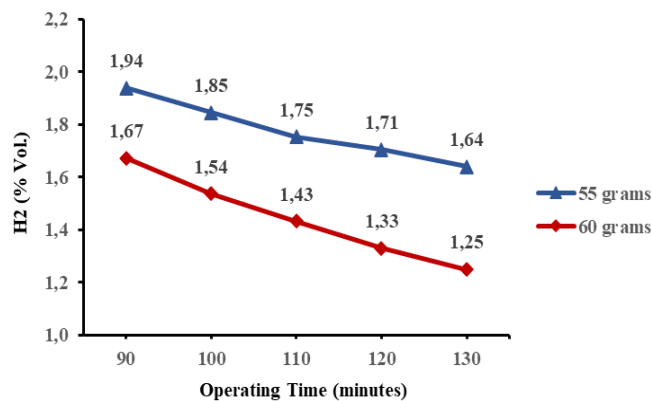


Fig. 4. The effect of varying Ni/Al₂O₃ catalyst mass and operating time on hydrogen (H₂) gas formation

Based on previous research by Putri et al. [8], a study was conducted on the methanation process of CO₂ with variations in the mass of the Fe promoter and operation times of 30, 45, and 60 minutes. The longer the operation time, the lower the yield of H₂ gas obtained; for the 60-minute operation time, H₂ gas decreased from 5.36% to 4.57%. This is consistent with the research conducted, where with operation times of 90 to 130 minutes and a Ni/Al₂O₃ catalyst mass of 60 grams, the formed H₂ gas decreased from 1.67% to 1.25%, resulting in a difference of 3.22% from the previous study. This indicates that a longer operation time in the methanation process leads to a decrease in the amount of H₂ gas formed. Based on the research

conducted by Zhong et al. [10], it is stated that the longer the operation time of CO₂ methanation, the longer the contact process of CO₂ gas with the formed H₂, resulting in a decrease in the unformed H₂ gas.

3.2.4 Methanation reaction mechanism and the contribution of Ni and Zn to the active catalyst sites

The mechanism of CO₂ methanation occurs through a gradual reduction and hydrogenation process that takes place on the surface of a metal catalyst, where CO₂ is reduced to CH₄ with the help of H₂ gas. This reaction is known as the Sabatier reaction with the equation $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$, which is exothermic and greatly influenced by the properties and number of active sites on the catalyst.

Ni (nickel)-based catalysts play a major role as active sites for the adsorption and activation of H₂ molecules, where H atoms are dissociated and act as electron donors to reduce CO₂ into intermediate molecules such as CO*, HCO*, and finally CH₄.

Meanwhile, Zn (zinc) metal support enhances catalyst performance in two ways: first, Zn can interact with Ni to form a Ni–ZnO surface that improves Ni dispersion and expands the number of metal active sites; second, ZnO acts as a promoter that aids CO₂ adsorption through the formation of carbonate or formate groups that are more easily hydrogenated into methane. The combination of Ni and Zn in the Ni/Zn–Al₂O₃ catalyst produces a synergistic effect that increases activity and selectivity towards CH₄, reduces activation energy, and suppresses the formation of by-products such as CO. Thus, the presence of Ni as the active center of hydrogenation and Zn as a structural and electronic promoter is key to accelerating the CO₂ methanation mechanism efficiently.

4. Conclusion

Based on the research results, the highest percentage of methane gas (CH₄) produced was obtained from sample 10, which had a Ni/Al₂O₃ catalyst mass of 60 grams and an operation time of 130 minutes, which was 58.35%. The more mass of the Ni/Al₂O₃ catalyst and the longer the operating time, the more methane gas (CH₄) is produced. This is because the addition of Ni/Al₂O₃ catalyst mass and the longer operating time can increase the number of active surface sites, allowing for more prolonged contact between the reactants and the catalyst in the CO₂ methanation reaction, resulting in more optimal methane gas (CH₄) production.

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