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Optimization of CO_2 methanation process using Ni-Fe/Al_2O_3 catalyst at low temperatures

Yurika D. S. Liza[1,*], Fadarina HC[1], A. Mediniariasty[1], R. Junaidi[1]

[1]Department of Chemical Engineering, *Politeknik Negeri Sriwijaya, Palembang - Indonesia*
**Email: yurikaliza07@gmail.com*

Abstract

Carbon dioxide is one of the major contributors to the greenhouse effect. According to IEA data, energy-related carbon dioxide emissions increased by 6 % in 2021 to 36.3 billion tonnes. Methanation of carbon dioxide, known as the Sabatier reaction, is an exothermic reaction in which hydrogen and carbon dioxide react to form methane and water as a by-product. Methane is a colorless, odorless, non-toxic but flammable and hazardous gas. Nickel, Rhodium, and Ruthenium catalysts are some of the most widely used active catalytic constituents in CO_2 methanation. Al_2O_3, SiO_2, CeO_2, ZrO_2, TiO_2, Nb_2O_5, and combinations of other constituents have been widely proposed and studied as catalyst supports. In this study, a Nickel catalyst was used with a combination of Al_2O_3 as a support and Fe as a promoter. The Nickel catalyst was chosen because it can absorb hydrogen, is cheap, and is very selective in methane formation. This study was conducted in situ, by reacting 1 gr, 2 gr, and 3 gr of Ni catalyst powder; 1 gr, 2 gr, and 3 gr of Al powder; Fe powder as much as 1 gr and 2 gr with 1 M NaOH solution which is heated while stirring at a speed of 100 rpm for 60 minutes. The highest methane gas yield was obtained in sample 10 with a mass of Ni, Al, and Fe respectively 3 gr, 1 gr, and 2 gr of 10.07 % with a CO_2 conversion of 2.70 %. The more Ni and Fe catalyst masses are used, the higher the temperature is and the more CH_4 is produced.

Keywords: Carbon Dioxide, Methanation, Methane, Ni-Fe/Al_2O_3

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1. INTRODUCTION

Carbon dioxide (CO_2) is one of the main contributors to the greenhouse effect. According to IEA data, energy-related carbon dioxide (CO_2) emissions increased by 6 % in 2021 to 36.3 billion tonnes. It is because the world economy is recovering from the Covid-19 crisis by relying on coal. CO_2 emissions from energy combustion and industrial processes contributed almost 89 % of the energy sector's greenhouse gas emissions in 2021, while CO_2 emissions from gas combustion contributed 0.7 %. One way to reduce CO_2 in the atmosphere is to convert CO_2 and utilize it into chemicals, for example, hydrogenation of CO_2 into methane.

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Hydrogenation of carbon dioxide to methane or methanation of carbon dioxide also known as the Sabatier reaction is an exothermic reaction in which hydrogen and carbon dioxide react to form methane and water as a by-product (Krisnandi et al., 2020). This reaction is advantageous because it can be used at low temperatures between 25 ℃ and 400 ℃, but carbon dioxide hydrogenation can only be achieved with an efficient catalyst (Fan & Tahir, 2021).

The formation of CH_4 from CO_2 at low temperatures is an important breakthrough in the knowledge of the role and use of CO_2, although the conversion is still lower (Martin et al., 2017). Catalysts applied in CO_2 methanation have been widely studied with various catalyst variations. Nickel, Rhodium, and Ruthenium catalysts are some of the most commonly used active catalytic constituents. Al_2O_3, SiO_2, CeO_2, ZrO_2, TiO_2, Nb_2O_5, and combinations of other constituents have been widely proposed and studied as catalyst supports.

Zhong et al., (2019) conducted a study on a novel and simple CO_2 to methane conversion method in water with an in situ synthesized Ni nanoparticle catalyst, in which water was used as the hydrogen source and earth-abundant metals (Zn or Fe) were used as regenerable reductants. Excellent methane yields of 98 % from either CO_2 or HCO_3 were obtained at 300 °C, and the in situ-formed Ni nanoparticle catalyst showed not only excellent catalytic activity but also stability. Mechanistic studies showed that methane formation from HCO_3 or CO_2 followed the pathway $HCO_3 \rightarrow CO_2 \rightarrow HCOOH \rightarrow CH_4$. This work demonstrates a simple approach for highly efficient CO_2 to methane conversion with earth-abundant materials.

Dias & Perez-Lopez, (2021) have conducted CO_2 to CH_4 conversion using Ni/SiO_2 catalysts promoted by Fe, Co, and Zn prepared by simple wet impregnation and evaluated. These characteristics have a positive influence on the methanation performance of the Fe and Co-promoted catalysts, which showed an increase in CO_2 conversion and CH_4 selectivity compared to the unpromoted catalysts. Ni-Co/SiO_2 gave the best results, reaching 73 % CO_2 conversion and 98.5 %CH_4 selectivity at 350 °C and high resistance to sintering. The Fe-promoted catalyst showed higher resistance to carbon formation, while promotion with Zn caused a strong decrease in selectivity for CH_4 and consequently increased selectivity for CO. These results suggest that the use of Fe and Co as promoters of Ni/SiO_2 catalysts has a high potential for CO_2 to CH_4 conversion.

In this study, Nickel catalyst was used with a combination of Al_2O_3 as support and Fe as promoter. Nickel catalyst was chosen because it can absorb hydrogen and is very selective in methane formation (Loder et al., 2020). Ni catalyst can maintain good activity over a long reaction time with high CH_4 selectivity (Chein & Wang, 2020).

2. MATERIALS AND METHODS

The research was carried out at the Chemical Engineering Laboratory of Sriwijaya State Polytechnic, Palembang.

2.1 Tools And Materials

The tools used in this study were beakers, magnetic stirrers, spatulas, glass stirring rods, measuring flasks, vacuum Erlenmeyer flasks, watch glasses, analytical balances, dropper pipes, thermoguns, ovens, hot plates, glass funnels, filter paper, RO pipes, plastic bags, plastic wrap, rubber, rubber stoppers, PVC pipes, CO_2 regulators, CO_2 tanks, cable ties, tape, and pH paper. The materials used were aluminum foil, distilled water, NaOH, Nickel, Fe, CO_2 gas, and deionized water. Aluminum powder was obtained after grinding the aluminum foil.

2.2 Treatment and Research Design

In this study, the fixed parameters used were the catalyst used Ni-Fe/Al_2O_3, NaOH concentration of 1 M, operating time of 60 minutes, and stirring speed of 100 rpm. The free parameters were the mass of Ni and Al with each variation of 1; 2; and 3 gr and the mass of Fe with variations of 1 and 2 gr.

2.3 Research Procedure

This research on methane gas production was conducted in an Erlenmeyer Vacuum with variations in the mass of Ni, Al, and Fe catalysts mixed using 1 M NaOH solution for 60 minutes with 100 rpm stirring and a CO_2 flow rate of 1 L/min. For more details, the design of a simple methanation device can be seen in Figure 1.

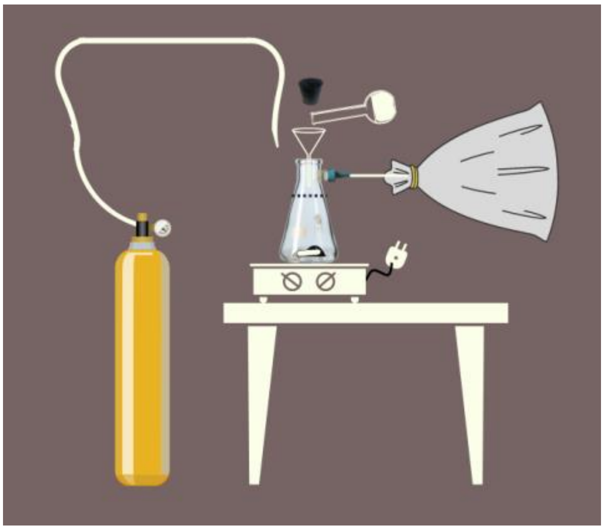


Figure 1. Methanation Tool Design

2.4 Analysis

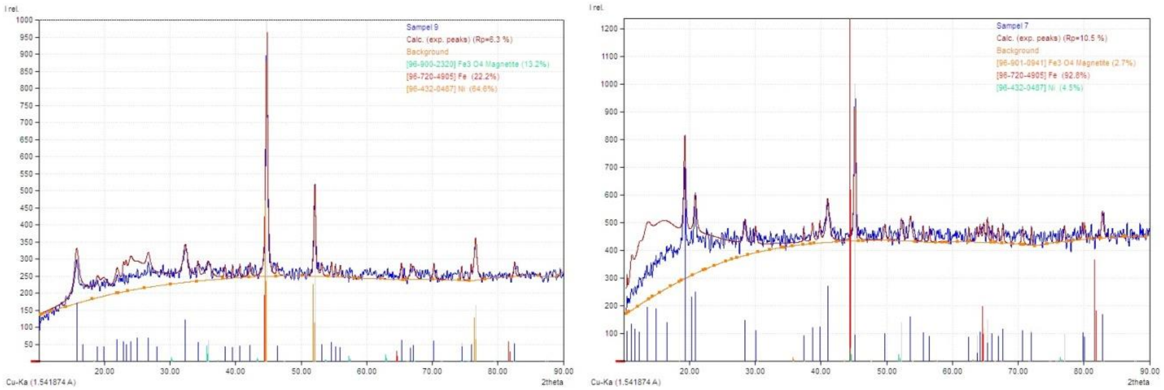
The analysis conducted in the study was an analysis of gas compound content and an analysis of compound content in sediment. The gas produced was analyzed using a Multi Gas Detector Analyzer that can measure the type and content of compounds in a gas sample. The sediment that had been filtered and dried was analyzed using X-ray diffraction (XRD).

3. RESULTS AND DISCUSSION

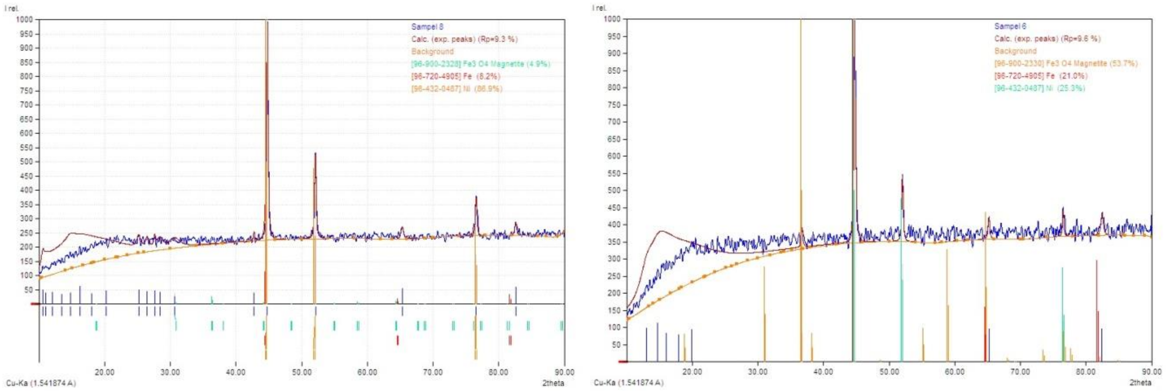
Table 1. Gas Analysis Results, Observations, and CO_2 Conversion Calculations

No	Sample Treatment (gr)			Analysis Results			Observation result	The calculation results
	Ni	Al	Fe	CO_2 (%)	CH_4 (%)	H_2 (ppm)	End Reaction Temperature(℃)	CO_2 conversion (%)
1	1	1	1	0.91	4.32	7.9412	97.8	-
2	1	2	1	0.81	7.22	10.765	99.0	-
3	1	3	1	0.78	7.31	11.765	99.3	-
4	1	1	2	0.72	7.65	8.176	99.8	-
5	1	2	2	0.68	7.77	8.765	100.3	-
6	1	3	2	0.65	7.86	8.888	100.8	-

7	2	1	1	0.63	8.12	11.000	101.2	0.36
8	2	1	2	0.61	8.34	12.471	102.5	0.11
9	3	1	1	0.54	9.52	8.706	102.9	0.19
10	3	1	2	0.40	10.07	8.471	103.4	2.70



(a) sample 7 (b) sample 8



(c) sample 9 (d) sample 10

Figure 2. XRD results graph (a), (b), (c), and (d).

3.1 Effect of Catalyst Mass Variations on the Gas Produced

Based on Figure 3 plotted from Table 1, it turns out that the more Ni catalyst used, the more methane gas produced and the less CO_2 gas remaining because a lot of CO_2 gas reacts. The unreacted H_2 gas fluctuates due to the conditions and variations in the mass of Al and Fe. The more Al, the more H_2 is produced. However, the H2 recorded in Table 1. is unreacted H_2 caused by the influence of variations in the mass of the Ni catalyst and the Fe promoter.

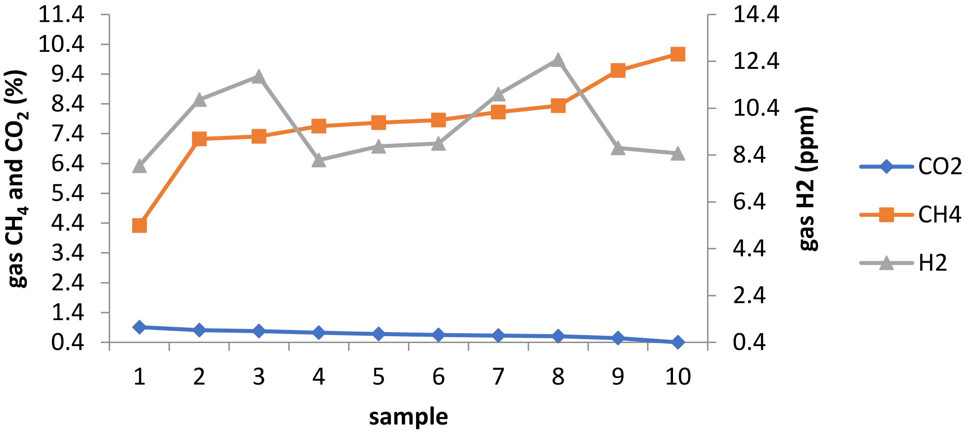


Figure 3. Graph of the effect of catalyst variation samples on gas production

3.2 Effect of Adding Al Mass on Gas

Based on Figure 4 plotted from Table 1, it turns out that the relationship between the addition of Al mass with the mass of Ni and Fe remains the same with the CH_4 gas produced experiencing an increase. The unreacted CO_2 gas decreased, while the unreacted H_2 gas increased. The variation of the addition of Al mass to the gas examined showed that the more Al mass was added, the more CH_4 was produced, and more CO_2 gas reacted with H_2.

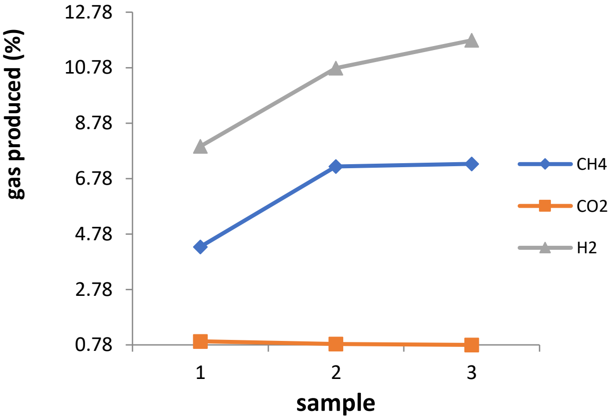


Figure 4. Graph of the effect of addition mass of Al against gas

The more Al mass is added, the more H_2 gas is produced. This is based on the reaction between Al and NaOH produces H_2 gas by research conducted by (Casanova et al. 2021), which uses reaction (1). However, unreacted H_2 gas increased. Based on research conducted by (Zhong et al. 2019), this is due to the lack of adsorption of H_2 gas by Ni nanoparticles which increases unreacted H_2 gas.

$$2Al + 2NaOH + 6H_2O \rightarrow 2NaAl(OH)_4 + 3H_2 \quad ..(1)$$

3.3 Effect of Mass Addition of Al and Fe on Gas

Based on Figure 5 plotted from Table 1, it turns out that the relationship between the addition of Al and Fe masses with a fixed Ni mass to the CH_4 gas produced has increased. Unreacted CO_2 gas has decreased, while unreacted H_2 gas has increased. The more Al mass added, the more H_2 gas produced. The addition of Fe in Figure 4 has an effect on H_2 that reacts with CO_2 based on the research of Zhong et al. (2019) that Ni nanoparticles catalyze the reduction of CO_2 gas with Fe as a reductant and have an effect on increasing methane yield. The addition of Fe to the Ni/Al_2O_3 sample also increases H_2 adsorption (Valinejad Moghaddam et al. 2018).

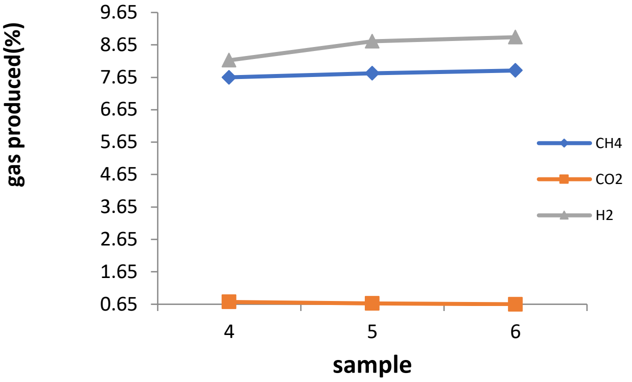


Figure 5. Graph of the effect of addition mass of Al and Fe against gas

3.4 Effect of Adding Ni Mass on Gas

Based on Figure 6 plotted from Table 1 it turns out that the relationship between the addition of Ni mass with the mass of Al and Fe remains the same with the CH_4 gas produced, increasing. Unreacted CO_2 and H_2 gases fluctuate. The variation in the addition of Ni mass to the gas examined shows that the more Ni mass is added, the more CH_4 is produced and the more CO_2 gas reacts with H_2 compared to the previous sample. This is because Ni has an effect on CO_2 adsorption and in producing H_2 (Zhong et al. 2019). The increase and decrease in H_2 is caused by the lack of Fe as a reductant, which is proven in Figure 2 shows the XRD results of samples 7 and 9 that Fe that changes to Fe_3O_4 is only 13.2% in sample 7 and only 4.9% in sample 9. In a study conducted by Zhong et al. (2019), it was shown that the total yield of HCOOH, CH_3COOH, and CH_4 obtained with Fe was still much lower than that obtained with Zn. In addition, the standard redox potential of Fe^{3+}/Fe (-0.037V) is more positive than Zn^{2+}/Zn (-0.7618V) meaning that Fe has less reduction capacity than Zn.

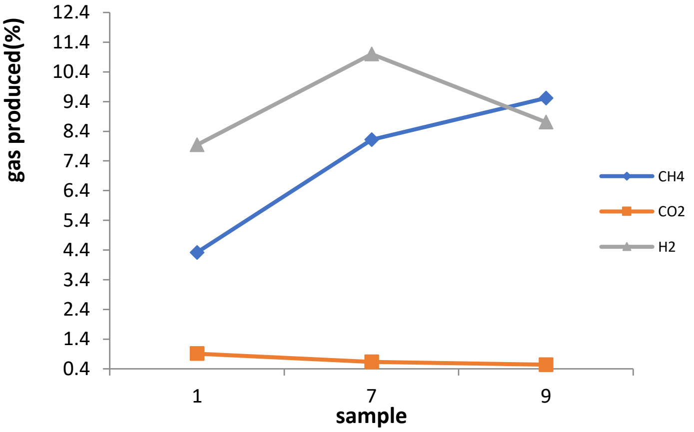


Figure 6. Addition effect graph mass of Ni to gas

3.5 Effect of Mass Addition of Ni and Fe on Gas

Based on Figure 7. plotted from Table 1, it turns out that the relationship between the addition of Ni and Fe mass with a fixed Al mass to the CH_4 gas produced is directly proportional to the increase. Unreacted H_2 gas experiences an increase and unreacted CO_2 gas experiences a decrease. The variation in the addition of Ni and Fe mass to the gas examined shows that the more Ni and Fe mass added, the more CH_4 is produced and the more CO_2 gas reacts with H_2. The increase and decrease of H_2 are caused by the lack of Fe activity as a reductant, which is proven in Figure 2 shows the XRD results of samples 8 and 10 that Fe that changes into Fe_3O_4 is only 2.7 % in samples 8 and only 53.7 % in sample 10.

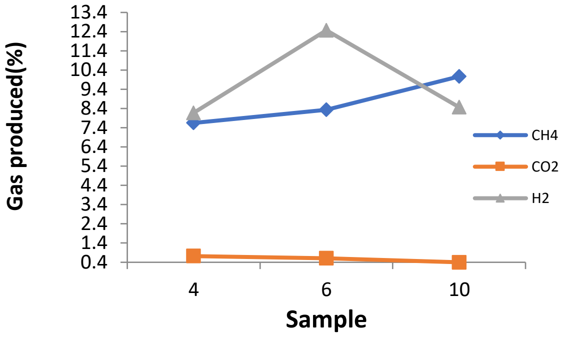


Figure 7. Graph of the effect of additions mass of Ni and Fe relative to gas

3.6 Effect of Catalyst Mass on CO2 Gas Conversion

Based on Figure 8 plotted from Table 1, it turns out that the relationship between the addition of catalyst mass variations and CO_2 conversion fluctuates. The increase and decrease in CO_2 conversion is caused by the lack of Fe as a reductant. The more nickel used, the more CO_2 is converted into CH_4 gas. This is because Ni has an effect on CO_2 adsorption and in producing H_2 and Fe functions as a reductant (Zhong et al. 2019). In the study of Valinejad Moghaddam et al. (2018), the 30Ni-5Fe/Al_2O_3 catalyst became the catalyst with the best performance, namely having a CO_2 conversion of 70.63 % and a CH_4 selectivity of 98.87 % at 35 ^{o}C among other catalysts at low temperatures.

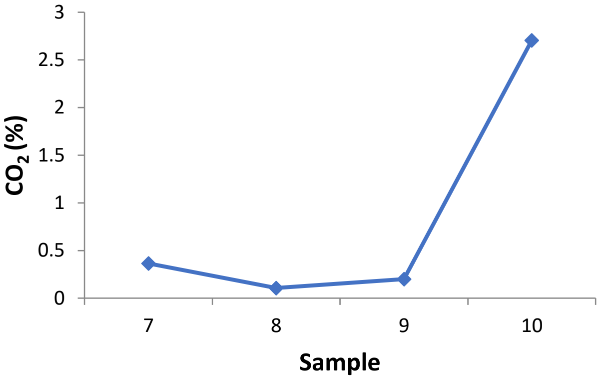


Figure 8. Graph of the effect of catalyst mass on CO_2 gas conversion

3.7 Effect of Time on Temperature

Based on Figure 9 plotted from Table 1, it turns out that the relationship between temperature and reaction time is seen the longer the reaction takes place, the higher the reaction temperature. In a study conducted by Zhong et al. (2019), when commercial Ni was used, almost no methane was formed in the first 3 hours and only 43 % of the methane yield was obtained after 4 hours. Interestingly, when Ni_R0 was used, a significant increase in methane yield was observed in just 1 hour. The methane yield increased with reaction time and reached 98 % after 4 hours. This is because Zn is oxidized to ZnO by Ni_R0 which acts as a precursor.

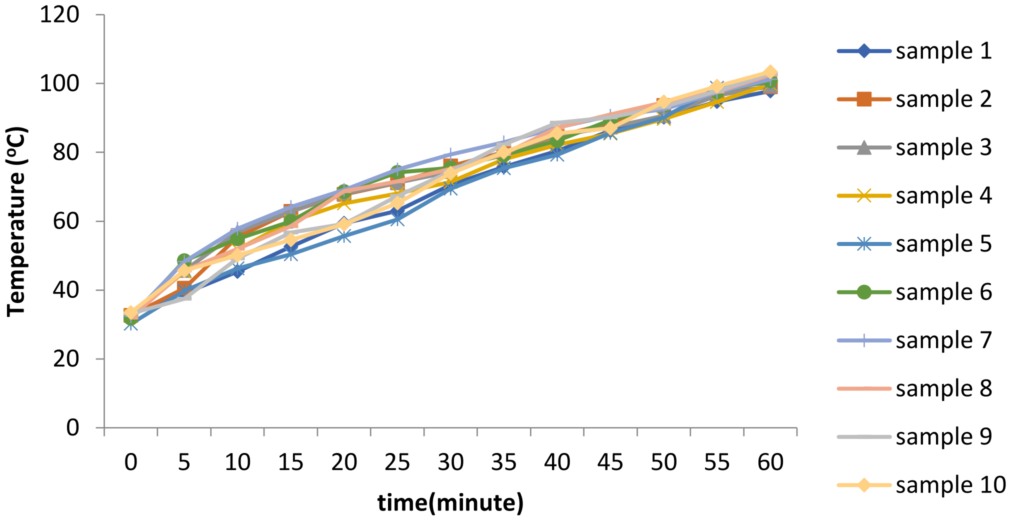


Figure 9. Graph of the effect of time on sample temperature

3.8 Effect of Final Reaction Temperature on Methane Gas

Based on Figure 10 plotted from Table 1, it turns out that the relationship between the final reaction temperature of samples 1 to 10 in sequence with the methane gas yield is seen to be directly proportional. In a study conducted by Zhong et al. (2019), it was written that the methane yield increased with increasing reaction temperature when the temperature was below 300 °C. However, a further increase in temperature can cause a decrease in methane yield. If the temperature is too high, it can cause sintering or coking of the catalyst, which causes decreased activity and stability. On the other hand, if the temperature is too low, the heat generated is not enough to drive the methanation reaction, which causes low catalyst activity (Fan and Tahir 2021).

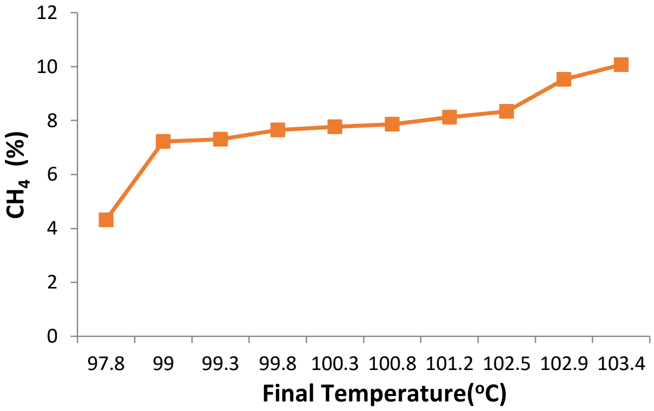


Figure 10. Graph of the effect of final reaction temperature against methane gas

4. CONCLUSION

Based on the results of the research that has been done, the following conclusions are obtained: The highest percentage of methane gas produced in situ was obtained in sample 10 with a mass of Ni, Al, and Fe of 3 gr, 1 gr, and 2 gr, which is 10.07 %; the highest percentage of CO_2 conversion was obtained in sample 10 with a mass of Ni, Al, and Fe of 3 gr, 1 gr, and 2 gr, which is 2.70 %; and the more Ni and Fe catalyst masses used, the higher the temperature and the more CH_4 produced.

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