Study of Carbon Dioxide Methanation Performance using Nickel-Based Catalyst and New Synthesised Catalyst

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Greenhouse gaseous emissions have increased significantly, leading to implement carbon capture, utilisation and storage technology. Among potential carbon utilisation strategies, carbon dioxide (CO2) methanation received much attention due to the advantage of producing non-fossil fuel energy sources using CO2 captured from flue gas. However, CO2 methanation is a highly kinetic limited reaction, so a catalyst needs to be applied to achieve targeted reaction performance. In recent years, nickel-based catalysts have been widely used in catalysing the CO2 methanation process due to high activity and availability but utilising nickel-based catalysts will lead to a high activation energy of 92 kJ/mol for the reaction to occur so NEMR5-8, an in-house synthesised catalyst, was developed to lower the activation energy. This study developed a simulation model to investigate the improvement in CO2 conversion with respect to temperature, pressure, catalyst-to-feed ratio and net energy produced. Based on the simulation result, the NEMR5-8 catalyst required methanation to be operated at a low temperature of 100 °C to achieve 100 % conversion, which led to a 10 % energy intensity saving compared to the nickel-based catalyst. NEMR5-8 was also capable of withstanding change in pressure and maintained 100 % CO2 conversion at pressures of 1 to 5 bar and could enhance CO2 conversion for the methanation process at a low catalyst-to-feed ratio, 0.25 (1 kg catalyst).

1. Introduction

Greenhouse gaseous (GHG) emissions increase with the development of economic and population growth throughout the years. The rise in growth has led to an increase in the CO_2 level in atmosphere. In order to deal with this situation, carbon capture utilisation and storage (CCUS) seems to be a promising approach in cutting down the emission of CO_2. Among all the carbon utilisation strategies available, methanation is promising in producing non-fossil fuel for future energy. From the perspective of an integrated power plant with methanation, the process is appropriate and relatively simpler due to the availability of hydrogen as its main constituent.

In Malaysia, the electricity production sector generates the largest share of CO_2 emissions so projects have been established to capture CO_2 from coal-fired and gas-fired power plants and convert them into valuable outputs. A mobile pilot facility for CO_2 methanation using renewable hydrogen has been developed under the Development of Sustainable CO_2 Utilisation System using Renewable Energy Technology (CURE) project. The facility comprises an electrolyser unit run with solar energy and a methanation reactor equipped with methane compression and storage to convert CO_2 captured from flue gas to methane.

In recent years, nickel-based catalysts have received much attention due to affordability and accessibility. Like other non-noble catalysts, the Ni catalyst is easily deactivated due to thermal sintering if worked at high temperatures (Stangeland et al., 2017). Methanation process, also known as the Sabatier reaction Eq(1), is a thermochemical conversion of carbon dioxide and hydrogen to methane (Saebea et al., 2022). The reaction has a high kinetic limitation, so a catalyst is needed to achieve desired process performance.

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O; \qquad \Delta H°_{298} = -165 \frac{kJ}{mol} \tag{1}$$
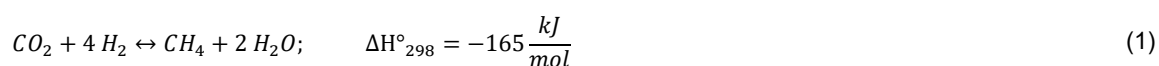
In this study, the simulation model of CO_2 methanation using Aspen was carried out to determine the optimal conditions, such as pressure, temperature, and the catalyst-to-feed ratio, to achieve maximum methanation yield using the in-house synthesised catalyst. The result obtained was compared with experimental data to check the robustness of the Aspen model. Afterwards, the model was used to study the net energy of the CO_2 methanation process using simulation data. This study is envisioned to improve resilience to climate change and reduce GHG emissions.

2. Literature Review

Nickel has been widely investigated for methanation due to its high activity and low price. It is also the most used active compound in commercial applications. The most common catalyst used is Ni/Al_2O_3 but utilising a nickel-based catalyst will lead to a high activation energy of 92 kJ/mol for the reaction. Numerous study higlighted that Group 8 metals such as Fe, Co, Ru, Rh, and Pd have been proven to become an active centres for the catalyst as shown in Table 1. Ru, Rh and Pd are precious metals with higher methane selectivity and lower temperature catalytic activities but are not appropriate for widespread application due to their expensive and scarce resources (Panagiotopoulou, 2017).

Traditional nickel-based catalyst preparation techniques are very mature technologies, hence novel techniques such as plasma and microwave-assisted methods has been explored (Xu et al., 2020) to enhance catalyst performance. Besides, incorporating catalytic dopants is one of the effective strategies to improve lower-temperature catalytic activities and thermal sintering issues due to advantage in regulating the dispersion of active component and surface properties (Xu et al., 2020). The additives dopant can be categorised into four groups: transition metals, rare earth metals, precious metals and alkaline earth metals.

Table 1: Catalyst development for CO_2 methanation

Catalyst	Reaction condition	CO_2 conversion	CH_4 selectivity	Remarks	Reference
Ni/Al_2O_3	300 °C, 1 bar	50 %	100 %	Small Ni metal particles in the catalyst are very selective to methane without CO formation.	Garbarino et al., 2014
Ni/CeO_2	350 °C, 1 bar	93 %	100 %	Large CO_2 adsorption is achieved with oxygen vacancy, which leads to high CO_2 conversion at low temperatures.	Tada et al., 2012
Ru/CeO_2	350 °C, 1 bar	>75 %	99 %	Ru, as an active metal site, promotes oxygen vacancy and reducibility of CO_2 to CH_4	Sakpal and Lefferts, 2018
Ru/Mn/Cu – Al_2O_3	220 °C	98.5 %	90 %	The optimum condition was found at 10.9 wt% Ru loading and 5 wt.g. catalyst loading.	Zamani et al., 2015
Ni/ZrO_2	350 °C, 1 bar	79.1 %	76.5 %	The plasma decomposition contributes to significantly improved catalytic activities.	Jia et al., 2019
Ru/ TiO_2	325 °C, 1 bar	>80 %	100 %	The catalyst provides surface oxygen vacancies and excellent durability.	Chai et al., 2019
NEMR5-8	100°C, 1 bar	100 %	-	Catalyst promotes CO_2 conversion of methanation process better at GHSV of $1200h^{-1}$.	This study

In this study, a new in-house NEMR5-8, has been synthesised with the combination with other metals and simulation study conducted to determine the effectiveness of this new catalyst to reduce the activation energy which will lead to the lower temperatures and energy required for CO_2 methanation process. The optimum operating condition is also investigated to improve CO_2 methanation conversion yield as opposed to Ni-based catalyst.

3. Methodology

3.1 Data Collection from Experimental Results and Literature

Kinetics data of CO_2 methanation, including rate law and rate constant, is one of the important data required for the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model as shown in Eq(2) when setting up a reactive mode in simulation. The kinetics data for the methanation process can be obtained from experimental results and literature.

$$r = \frac{kinetic\ factor \cdot driving\ force}{(adsorption\ expression)^n} \tag{2}$$

First, coefficients obtained from rate law were interpreted according to the Eq(3) to suit the driving force and adsorption expression section of the kinetics model.

$$Constant\ i = e^A e^{(\frac{B}{T})} T^C e^{DT} \tag{3}$$

Based on the article's rate constant or Arrhenius plots, activation energy (E_a) and pre-exponential factor (k) required for the kinetic factor data were identified according to the Eq(4).

$$Rate\ constant = k e^{(\frac{E}{RT})} \tag{4}$$

3.1.1 Case Study 1: Commercial Nickel-based Catalyst

For the commercial nickel-based catalyst, E_a and k were interpreted from the kinetic model for the methanation process (Lim et al., 2016) under the assumptions that (1) dissociation of CO was the rate-limiting step and (2) the most abundant species on the surface of the catalyst were adsorbed H, CO and H_2O. The Arrhenius equation for the rate constant defined in the previous research, Eq(5) is shown below.

$$K = 49.4 \times 10^6 e^{(\frac{-92000}{RT})} \tag{5}$$

3.1.2 Case Study 2: NEMR5-8 (In-house TNBR-synthesized Catalyst)

For the NEMR5-8 catalyst, E_a and k were determined through experimental research on the kinetic modelling of the CO_2 methanation process, which was operated with a gas hourly space velocity (GHSV) of 1,200 $g^{-1}mlh^{-1}$ and operating temperatures from 150 °C to 250 °C and 300 °C. The graph of ln(K) against 1/T was then plotted, and the Arrhenius equation was derived into a linear equation, Eq(6). In this case, the activation energy (E) was defined from the slope, while the pre-exponential factor (k) was defined from the y-intercept of the Arrhenius plots.

$$\ln(k) = -\frac{E}{R}\left(\frac{1}{T}\right) + \ln(A) \tag{6}$$

3.2 Development of Methanation Model using Aspen Plus v12.1

A simulation model for the CO_2 methanation process was set up as shown in Figure 1 (PFD of methanation plant) in Aspen Plus v12.1 to investigate the effect of operating parameters, i.e. temperature, pressure and catalyst-to-feed ratio towards CO_2 methanation yield. The default value was assigned for each operating parameter based on data provided by TNB Research Sdn Bhd. as shown in the Table 2.

Table 2: Default operating parameters used in the simulation

Operating Parameters	Reactor 1	Reactor 2
Temperature (°C)	100	100
Pressure (bar)	1	1
Catalyst-to-feed ratio (5 kg catalyst)	1.27	1.27
Catalyst	Nickel-based catalyst & NEMR5-8 catalyst	

3.3 Determination of Optimum Operating Condition for CO_2 Methanation

During the simulation, the temperature of reactors was varied within the range of 50 °C to 250 °C with an interval of 50 °C while other operating parameters remained as default values. Then, the overall conversion of CO_2 methanation was observed. Next, the simulation was repeated by manipulating the pressure of the reactors from 1 bar to 5 bar with an increment of 1 bar and catalyst-to-feed ratio by increasing the mass of the catalyst from 1 kg to 10 kg with an interval of 1 kg.

3.4 Comparison of CO_2 Methanation Performance Using Nickel-based and NEMR5-8 Catalyst

After the study was repeated by replacing the nickel-based catalyst with NEMR5-8, a comparison was made between the simulation results of the nickel-based catalyst and the NEMR5-8, including the CO_2 conversion and operating conditions to achieve optimum performance so that the advantages of replacing the nickel-based catalyst with NEMR5-8 could be determined.

3.5 Perform Net Energy Analysis for the CO_2 Methanation Process

Simulation data were used to study the net energy for the CO_2 methanation process, and the total energy required for the CO_2 methanation process comprised the energy consumed in the reactor, heater and cooler. The value was converted into energy intensity and translated into kJ energy required /kg of methane generated.

4. Results and findings

4.1 Development of Methanation Model Using Aspen plus v12.1

The CURE pilot plant simulation model used to test the impact of temperature, pressure and catalyst-to-feed ratio change on CO_2 conversion is illustrated through the process flow diagram (PFD) shown in Figure 1. the PFD comprises three main sections: (1) H_2 production using an electrolyser, (2) a reaction unit represented by methanation reactors and (3) a separation unit to separate water and methane. In this simulation, the kinetic model for Ni/Al_2O_3 from the literature was used to model the methanation reaction for Case 1. The kinetic for the NEMR5-8 catalyst obtained from our experiment was used to model the methanation reaction for Case 2.
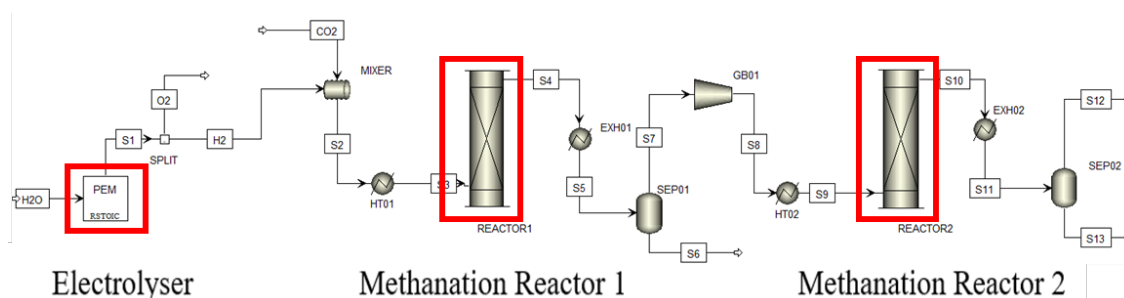

Figure 1: PFD of the methanation plant using Aspen Plus

4.2 Simulation Results and Analysis

4.2.1 Effect of Temperature on CO_2 Conversion

In this simulation, the temperature was varied from 50 °C to 250 °C with increments of 50 °C . The pressure and amount of catalyst used were maintained at 1 bar and 5 kg, respectively. The effect of temperature change on CO_2 conversion for the nickel-based catalyst and the NEMR5-8 is illustrated in Figures 2a and 2b.
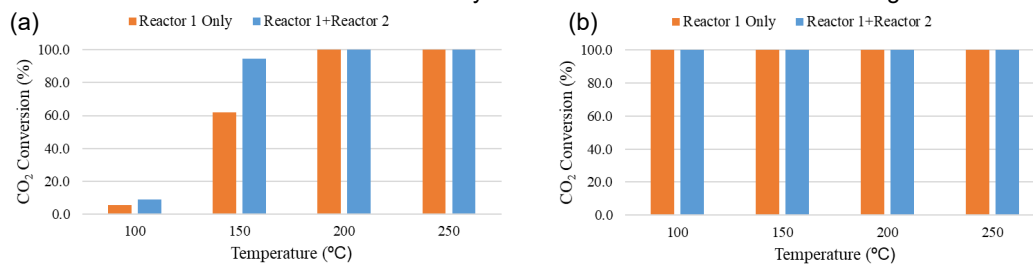

Figure 2: Effect of temperature change from 50 °C to 250 °C using (a) nickel-based catalyst, and (b) NEMR5-8

Generally, the overall CO_2 conversion increased with temperature. As shown in Figure 2a, when the temperature of the methanation reactor increased from 100 °C to 200 °C, the overall CO_2 conversion increased from 5 % at 100 °C to almost 100 % at 150 °C with the utilisation of two reactors. At a temperature higher than 200 °C, only one reactor was required to achieve 100 % conversion for the methanation process using the nickel-based catalyst; no methanation occurred in the first reactor if the methanation reactor operated below 100 °C.

NEMR5-8 was a very active catalyst that enhanced CO_2 conversion at lower temperatures than the Ni/Al_2O_3 catalyst. As shown in Figure 2b, 100 % CO_2 conversion was achieved at a temperature as low as 100 °C, and using the second reactor was not required for this process for all studied temperatures. The high conversion was due to the very low activation energy (E_a) of the NEMR5-8, which was around 15 kJ/mol to convert CO_2 to methane (from our experimental analysis) compared to the 92 kJ/mol required by the nickel-based catalys

4.2.2 Effect of pressure on CO_2 conversion

In this simulation, the pressure was varied from 1 bar to 5 bar with increments of 1 bar while the temperature and amount of catalyst used were maintained at 100 ºC and 5 kg, respectively. The effect of pressure on the overall CO_2 conversion using the nickel-based catalyst and NEMR5-8 is illustrated in Figures 3a and 3b.

As shown in Figure 3a, raising the pressure from 1 bar to 5 bar in both methanation reactors provided an inverse effect on CO_2 conversion as the CO_2 conversion dropped from 9 % to 2 % so the presence of the second reactor became significant. Next, the reduction of CO_2 conversion for the change of pressure from 4 bar to 5 bar was not as significant as when the pressure was changed from 1 bar to 2 bar and higher pressure might cause adverse effects in the form of catalyst sintering, leading to its faster deactivation.

Figure 3b illustrates that the optimal pressure that led to 100 % conversion using NEMR5-8 was 1 bar. A much higher pressure did not affect the CO_2 conversion, so the conversion remained at 100 % which proved the NEMR5-8 catalyst was more pressure-resistant than the nickel-based catalyst.
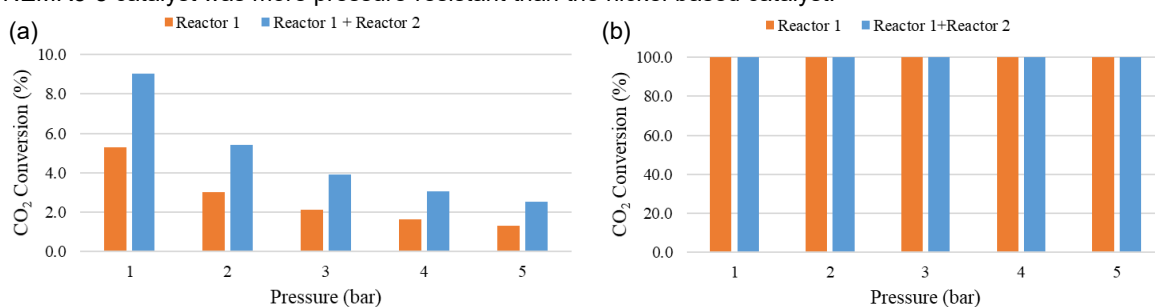

Figure 3: Effect of pressure variation from 1 bar to 5 bar using (a) nickel-based catalyst, and (b) NEMR5-8

4.2.3 Effect of catalyst-to-feed ratio on CO_2 conversion

The amount of catalyst used was varied from 1 kg to 10 kg with increments of 1 kg while the H_2 and CO_2 fed into the process were maintained at around 10 L/min. If translated into catalyst-to-feed ratio, the range was between 0.25 to 2.54. The temperature and pressure of reactors were kept constant at 100 ºC and 1 bar, respectively. The results of the catalyst-to-feed ratio effect on CO_2 conversion are shown in Figure 4a and 4b.
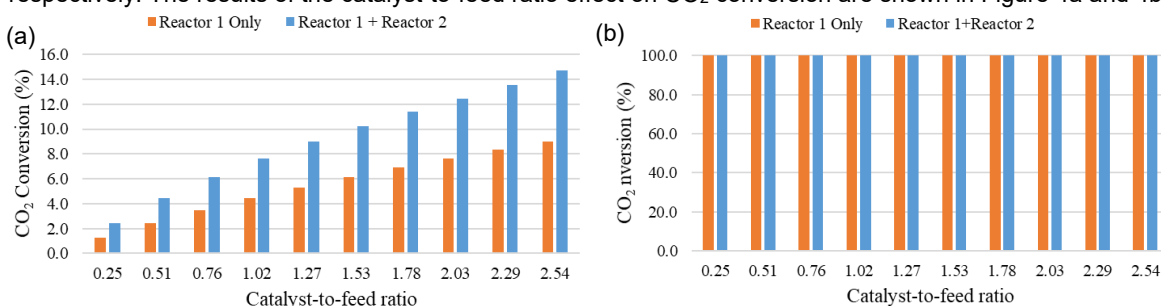

Figure 4: Effect of catalyst-to-feed ratio on CO_2 conversion using (a) nickel-based catalyst, and (b) NEMR5-8

Figure 4a shows that the overall CO_2 conversion using the nickel-based catalyst increased significantly with the catalyst-to-feed ratio. The catalyst-to-feed ratio 2.54 was considered the best within the range since the CO_2 conversion reached 15 %. The finding shows that the second methanation reactor was highly required if the catalyst-to-feed ratio increased to 2.54 to achieve higher conversion. Further raising the catalyst-to-feed ratio could lead to 100 % CO_2 conversion but with increased operational costs.

Another option to increase the CO_2 conversion without adding more catalyst weight was using the more active catalyst, NEMR5-8. Figure 4b shows that 100 % conversion was achieved at a lower catalyst-to-feed ratio, 0.25. This result indicates that much less NEMR5-8 was required to achieve 100 % CO_2 conversion.

4.3 Net energy analysis

In this study, total energy required for the CO_2 methanation process, which consisted of the energy consumed in the reactor, heater and cooler was taken from the Aspen Plus simulation as per shown in Figure 5.

As shown in Figure 5, it was found that NEMR5-8 was best operated at lower temperatures, as it required minimum energy intensity, 17,130 kJ/kg methane at a low temperature of 100 ºC while the nickel-based catalyst

was best operated at 200 ºC, which required minimum energy intensity, 19,133 kJ/kg methane. The analysis indicates that NEMR5-8 was an active catalyst that resulted in up to 10 % energy intensity savings due to the lower operating temperature.
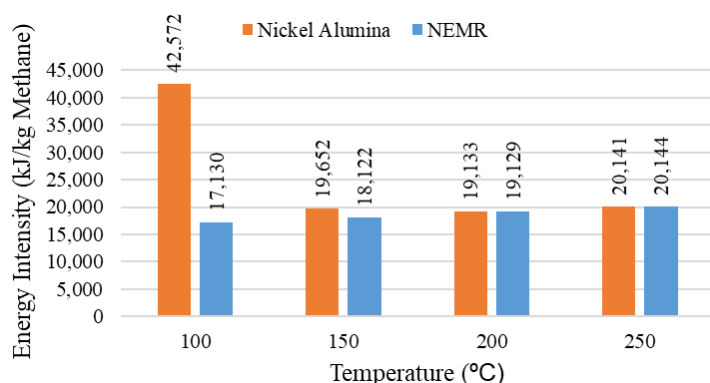

Figure 5: Energy intensity for CO₂ methanation process using nickel-based catalyst vs NEMR5-8

5. Conclusion

This study successfully developed a simulation model using Aspen Plus for CO_2 methanation to investigate CO_2 conversion performance for a new catalyst, NEMR5-8, against the commercial nickel-based catalyst. It was found that the temperature and catalyst to feed ration were highly sensitive parameters that effect the CO_2 methanation yield using Ni-based catalyst while for NEMR5-8 only temperature provide significant changes to CO_2 methanation yield. For future work, it is recommended to validate the operating conditions which better match between simulation results and experimental data.

Acknowledgments

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