Methanation Process for Methane Synthesis from Waste Gas: Process Simulation

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Waste gas from the fermentation of bioethanol production consists of high carbon dioxide concentration. The CO_2 emissions cause global climate change. The conversion of carbon dioxide to chemical products or fuels is an interesting solution for reducing the amount of carbon dioxide emissions. The methane synthesis via carbon dioxide methanation reaction has attracted much attention. The suitable operation of the methanation process for methane synthesis from waste gases should be studied. This work aims to investigate the methane production from the waste gas of the fermentation process. The composition of impurities in waste gases on the performance of the methanation process is investigated. The effects of hydrogen to carbon dioxide ratio and operating temperature on the carbon dioxide conversion and methane yield of the methanation are also studied. The simulation results from the thermodynamic analysis show that the methane yield of the methanation from waste gases is 3.11 - 4.61 % higher than that from pure carbon dioxide in the temperature range of 300 - 500 °C. The methane yield of the methanation process decreases with increasing temperature. The increase in the hydrogen to carbon dioxide ratio of 1 to 4 and the operating pressure of 1 to 8 bar have a significant effect on the enhancement of carbon dioxide conversion and methane yield.

1. Introduction

Due to the increasing requirement for global energy consumption, carbon dioxide emissions have been rising. Carbon dioxide is released into the atmosphere from various sources, i.e., human activity, fossil fuel combustion for transportation or electricity generation, and industrial processes. The ethanol production process is a source of carbon dioxide emissions due to carbon dioxide produced during the fermentation process. Waste gas from ethanol fermentation is a high carbon dioxide concentration. Carbon dioxide as a greenhouse gas is the main cause of global warming, climate change, and other environmental issues. To reduce carbon dioxide emissions, carbon dioxide utilization by conversion of carbon dioxide into fuels and chemicals has received attention.

Hydrogen is required in the process of the conversion of carbon dioxide into fuels. In general, hydrogen is produced from fossil fuels. However, the consumption of fossil fuels increases carbon dioxide emissions. Renewable energies that are low-carbon resources have been conducted to replace the use of fossil fuels. Hydrogen can be produced via electrolysis or photocatalytic processes from renewable energies (Saebea et al., 2017). Wind and solar energies are clean and readily available renewable energy. Although they are unlimited sources of energy, fluctuating and intermittent power generation due to weather conditions, they are trouble on the stable energy grid. The power-to-gas technology which converts excess electricity produced from renewable energy to chemical form has been considered an efficient alternative for storing renewable energy (Park et al., 2021).

To utilize the carbon dioxide emitted from the process and hydrogen generated from renewable energy, hydrogen and carbon dioxide are converted to high-added value fuels, i.e., methanol, dimethyl ether, methane.

etc. The conversion of hydrogen and carbon dioxide to methane form as the final product is interesting because it can be used in the existing infrastructure for storage and transportation. Methane is produced via the Sabatier reaction or called methanation reaction. There are two routes: biological methanation and thermochemical methanation (Götz et al., 2014). Biological methanation with an anaerobic digester is operated at a lower temperature compared with thermochemical methanation. Nevertheless, a long reaction time that results from the low hydrogen solubility in the liquid phase is a limitation of this process (Hervy et al., 2021). Another route is thermochemical methanation, which uses the catalyst to operate at a moderated temperature between 300 to 450 °C. A commercial catalyst of methanation is a Ni-based catalyst. Ahmad et al. (2022) indicated that CO_2 conversion and methane selectivity of CO_2 methanation over Ni-Ce/eg-C_3N_4 catalyst at 297 °C achieved 83 % and 99 %. CO_2 methanation with Fe-modified hydrotalcite-derived Ni-based catalysts (Ni_3-$Fe_{0.5}$-calc) was studied by Yin et al. (2022). The CO_2 methanation with Ni_3-$Fe_{0.5}$-calc achieved 78 % CO_2 conversion at 200 °C. The methane yield of the thermochemical methanation process depends on the operating condition, i.e., temperature, pressure, hydrogen to carbon dioxide, and feed components. The effect of impurities, i.e., N_2, steam, and O_2 in CO_2 methanation was investigated by Ren et al. (2022). Their results indicated that CO_2 methanation was increased by feed with trace O_2 because of generating more *OH groups which facilitate the conversion of intermediates to methane. According to the aforementioned, the waste gas from the fermentation process of ethanol production composed of high carbon dioxide is possible to be used directly for methane production. Besides carbon dioxide, the waste gas is composed of other components, i.e., ethanol, and methanol which have an effect on methane yield in the methanation process. To date, no studies have investigated the methane production from the waste gas of bioethanol fermentation process. This work aims to study the methane production from the waste gas of bioethanol fermentation process via thermochemical methanation by thermodynamic analysis. To study the effect of other components in the waste gas, the performances of methanation from waste gas are compared with that of pure carbon dioxide. Moreover, the effects of the operating condition in the methane production from waste gases on the methane yield are investigated.

2. Process simulation

In the methane production process, the hydrogen and waste gas are fed to the methanator. In this work, the waste gas of the ethanol fermentation was collected from the ethanol production plant of ESPOWER CORPORATION LIMITED by a gas sampling bag. The waste gas compositions were analyzed by a gas chromatograph Varian (Model CP-3800). The components of the waste gas of ethanol fermentation were concluded in Table 1. From Table 1, the waste gas has a high carbon dioxide concentration of 93.5 %. Moreover, some ethanol, nitrogen, and methanol are mixed in the waste gas of ethanol fermentation.

Table 1: *Components of the waste gas from the ethanol fermentation process*

Composition	Volume (%)
Carbon dioxide	93.50
Nitrogen	3.710
Ethanol	2.734
Methanol	0.045

To study the use of waste gas from ethanol fermentation for methane production, the product composition of the methanation process was analyzed from thermodynamic equilibrium. The Gibbs free energy minimization method that minimizes the change of total Gibbs free energy at specified temperature and pressure is used for computing the equilibrium composition as shown in the following equation.

$$(dG)_{T,P} = 0 \tag{1}$$

where G is total Gibbs free energy that is explained by Equation (2).

$$G = \sum_{i=1}^{n} n_i \Delta G_{f,i}^0 + \sum_{i=1}^{n} n_i RT \ln \frac{\hat{f}_i}{f_i^0} \tag{2}$$

where n_i are the moles of species i, $\Delta G_{f,i}^0$ is the Gibbs free energy of species i at standard state, R is gas constant, P is pressure, T is temperature, $\hat{f}_i$ and f_i^0 are the fugacities of species i at system condition and standard state.

The methanation process was simulated by using Aspen plus™ software. RGibbs model in Aspen plus™ software was implemented. RGibbs model is the reactor for the simulation of equilibrium reactions by calculation

based on the minimum` Gibbs free energy. The possible reactions in the methanation process of waste gas from ethanol fermentation are included in Table 2. The RKSMHV2 property method which is based on the Redlich - Kwong-Soave equation of state with modified HuroneVidal mixing rules was used to calculate thermodynamics property.

Table 2: *Components of the waste gas from the fermentation process*

Reaction	Equation	Reaction	Equation
R1	$4H_2 + CO_2 \leftrightarrow CH_4 + 2H_2O$	R14	$2CH_4 + O_2 \leftrightarrow C_2H_4 + 2H_2O$
R2	$H_2 + CO_2 \leftrightarrow CO + H_2O$	R15	$4CH_4 + O_2 \leftrightarrow 2C_2H_6 + 2H_2O$
R3	$3H_2 + CO \leftrightarrow CH_4 + H_2O$	R16	$2CH_4 + O_2 \leftrightarrow 2HCHO + 2H_2$
R4	$2H_2 + 2CO \leftrightarrow CH_4 + CO_2$	R17	$2CH_4 \leftrightarrow C_2H_6 + H_2$
R5	$C + H_2O \leftrightarrow CO + H_2$	R18	$2CH_4 + O_2 \leftrightarrow 2CH_3OH$
R6	$CO_2 + 2H_2 \leftrightarrow C + 2H_2O$	R19	$CH_4 + 0.5O_2 \leftrightarrow CO + 2H_2$
R7	$CO + H_2 \leftrightarrow C + H_2O$	R20	$CH_4 + H_2O \leftrightarrow CH_3OH + H_2$
R8	$2CO \leftrightarrow C + CO_2$	R21	$3H_2 + CO_2 \leftrightarrow CH_3OH + H_2O$
R9	$CH_4 \leftrightarrow 2H_2 + C$	R22	$2H_2 + CO \leftrightarrow CH_3OH$
R10	$2CH_4 + CO_2 \leftrightarrow C_2H_6 + CO + H_2O$	R23	$C_2H_4 + H_2O \leftrightarrow C_2H_5OH$
R11	$2CH_4 + 2CO_2 \leftrightarrow C_2H_4 + 2CO + 2H_2O$	R24	$2CO + 4H_2 \leftrightarrow C_2H_5OH + H_2O$
R12	$5H_2 + 2CO \leftrightarrow C_2H_6 + 2H_2O$	R25	$2CO + 6H_2 \leftrightarrow C_2H_5OH + 3H_2O$
R13	$4H_2 + 2CO \leftrightarrow C_2H_4 + 2H_2O$	R26	$CH_4 + CO + H_2 \leftrightarrow C_2H_5OH$

The performance of the methanation unit is evaluated from the methane yield, carbon monoxide and carbon dioxide conversion, hydrogen conversion, and methane selectivity, which were calculated according to the following formula:

$$CH_4 \text{ yield (\%)} = \frac{F_{CH_4}^{out}}{F_{CO}^{in} + F_{CO_2}^{out}} \times 100 \tag{3}$$

$$CO_2 \text{ conversion (\%)} = \frac{(F_{CO}^{in} - F_{CO}^{out}) + (F_{CO_2}^{in} - F_{CO_2}^{out})}{F_{CO}^{in} + F_{CO_2}^{in}} \times 100 \tag{4}$$

$$H_2 \text{ conversion (\%)} = \frac{(F_{H_2}^{in} - F_{H_2}^{out})}{F_{H_2}^{in}} \times 100 \tag{5}$$

where F_i^{in} and F_i^{out} is the molar flow rate of species i

3. Results and discussion

3.1 Comparison of using waste gas and pure carbon dioxide

Table 1 shows the composition of waste gas from the fermentation process of bioethanol production. The waste gas from the fermentation consists of high carbon dioxide concentration which is the reactant required for the methanation for the methane production. However, the waste gas is composed of other gases, i.e., ethanol and methanol. To study the methane synthesis from the waste gas of the fermentation process, the methane product from the methanation of waste gas is compared with that of pure carbon dioxide. Figure 1 shows the hydrogen conversion, carbon dioxide conversion, and methane yield of the methanation from using waste gas and pure carbon dioxide at the range of temperatures between 300 and 600 °C. The operating condition of the methanation unit was specified at the hydrogen to carbon dioxide ratio of 4 and atmospheric pressure. Figure 1 indicates that the high operating temperature has an adverse effect on the methanation performance. The hydrogen conversion, carbon dioxide conversion, and methane yield decrease with increasing temperature. This is because the methanation reaction is exothermic. The equilibrium will shift in the backward direction at high temperatures.

From Figure 1(b), hydrogen conversion in both cases are an insignificant difference. The carbon dioxide conversion of using waste gas is lower than that of using pure carbon dioxide, as shown in Figure 1(a). Figure 1(c) shows that the methane yield of using waste gas is 3.11 - 4.61 % higher than that of using pure carbon dioxide in the temperature range of 300 - 600 °C. It can be noted that the dehydration and reforming of ethanol and methanol in the waste gas as shown in Table2 (R20) - (R26) cause the enhancement of hydrogen, carbon monoxide, and carbon dioxide, resulting in the increment of methane production (Korneeva et al., 2017). Moreover, the increase of carbon monoxide in the methanation of waste gas leads to a decrease of carbon dioxide conversion, compared to the methanation of pure carbon dioxide, because the carbon monoxide can convert to methane in Table2 (R3). The occurrence of carbon monoxide methanation (R3) is easier than carbon dioxide methanation (R1). Thus, the carbon dioxide conversion in the methanation of waste gas is lower than that of pure carbon dioxide.
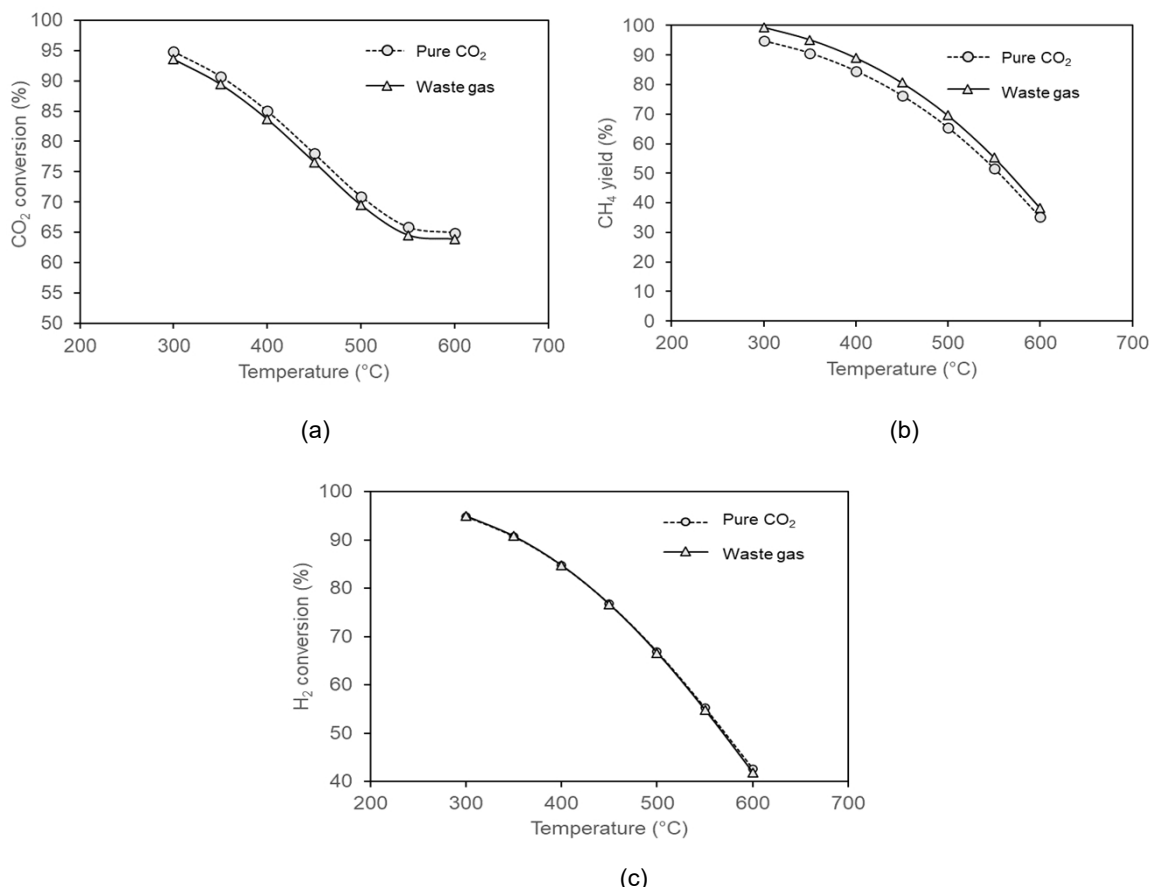

(a)

(b)

(c)

Figure 1: *Comparison of using waste gas and pure carbon dioxide for the methanation at various temperatures on (a) carbon dioxide conversion, (b) hydrogen conversion, and (c) methane yield*

3.2 Effect of hydrogen to carbon dioxide ratio

The effect of the hydrogen to carbon dioxide ratio in the range of 1 to 7 on the carbon dioxide conversion, hydrogen conversion, methane yield, and methane selectivity at various temperatures is shown in Figure 2. The operating pressure was fixed at 1 bar. In Figure 2(a), the carbon dioxide conversion considerably increases with excess hydrogen supply, particularly in the range of hydrogen to carbon dioxide ratio between 1 and 4 as shown in Figure 2(a). Figure 2(c) shows the effect of hydrogen to carbon dioxide on methane yield aligns in the same trend with the carbon dioxide conversion. The excess hydrogen drives forward the methanation and the reverse water-gas shift reactions, leading to the increase in methane production. At low temperatures between 200 - 300 °C, nearly 100 % carbon dioxide conversion and methane yield are obtained at the hydrogen to carbon dioxide ratio of 4. The excess hydrogen is required further to achieve a methane yield of 100 % at high temperatures in the range of 300 - 500 °C. However, the hydrogen conversion reduces at the hydrogen to carbon dioxide above 4 as shown in Figure 2(b). This indicates that the efficiency of hydrogen utilization reduces a high amount of excess hydrogen.
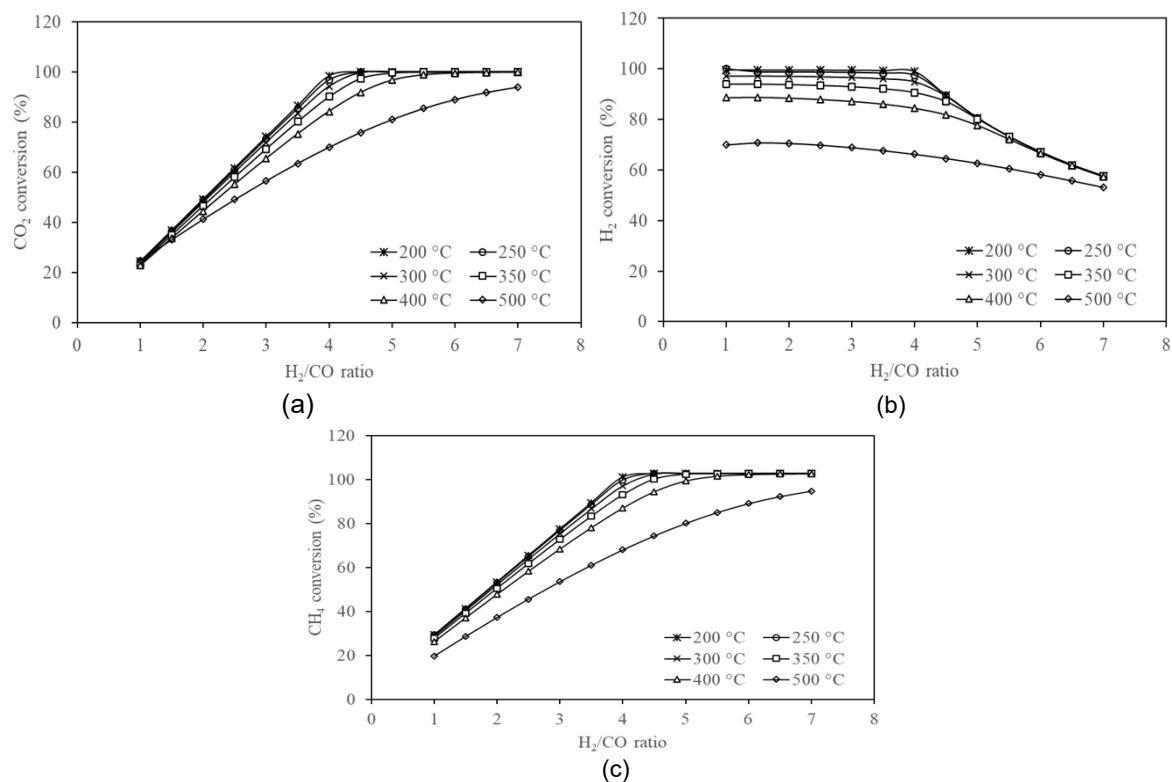
Figure 2: Effect of hydrogen to carbon dioxide ratio at various temperatures on (a) carbon dioxide conversion, (b) hydrogen conversion, and (c) methane yield of the methanation of waste gas
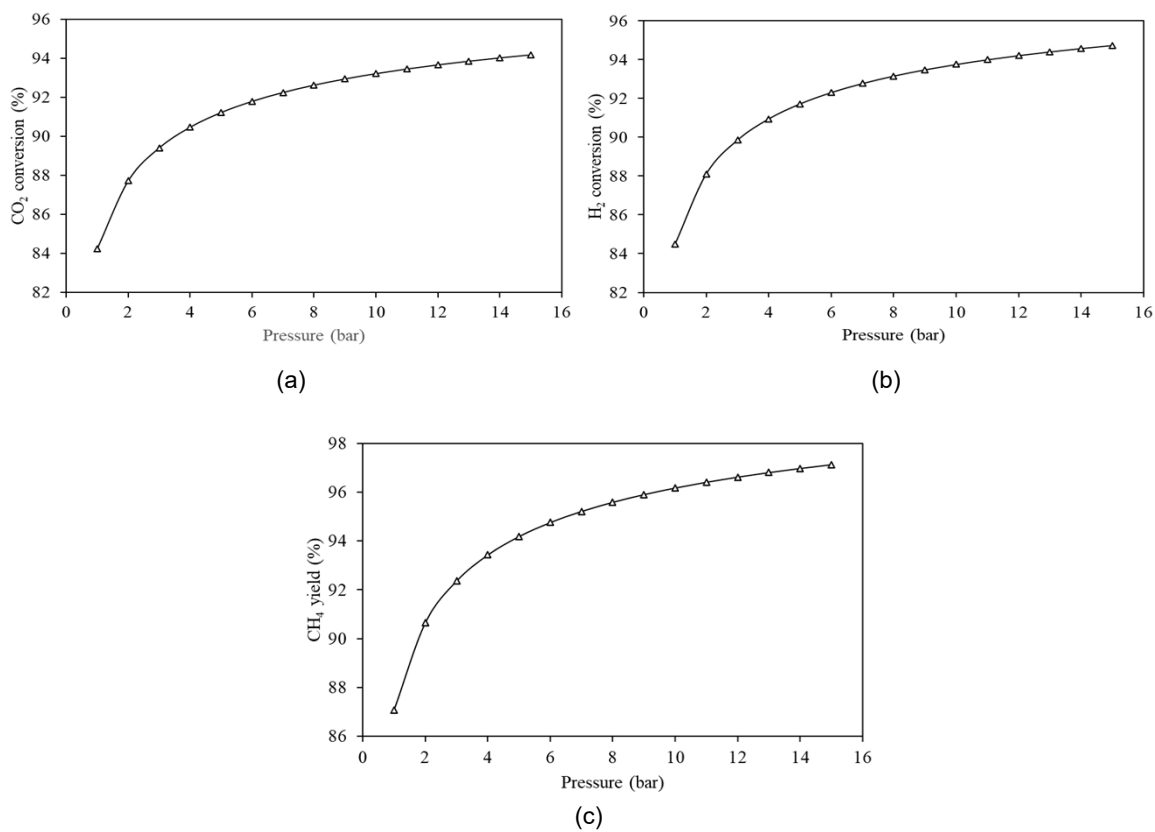
3.3 Effect of pressure

Figure 3: Effect of pressure on (a) carbon dioxide conversion, (b) hydrogen conversion, and (c) methane yield

The effect of operating pressure on hydrogen conversion, carbon dioxide conversion, and methane yield at a temperature of 400 °C and hydrogen to carbon dioxide ratio of 4 is shown in Figure 3. From 3(a) and 3(b), the increase of operating pressure between 1 and 8 has a significant effect on the increase of carbon dioxide conversion and hydrogen conversion about 8.39 % and 8.67 %. At a pressure above 8 bar, carbon dioxide conversion and hydrogen conversion slightly increase. It can be noted that increasing the pressure drives the forward reaction (R1-R4 in Table 2), resulting in carbon dioxide and hydrogen being used increasingly and converting to more methane product, as shown in Figure 3(c). The enhancement of pressure on the methane yield is in accord with carbon dioxide conversion.

4. Conclusions

To consider the possibility of methane production from waste gas, the methanation of the waste gas from ethanol fermentation was studied in this work. The composition of waste gas in the ethanol production plant was first analyzed. The waste gas is composed of high carbon dioxide concentration and some ethanol, nitrogen, and methanol. The methanation process from the waste gas was analyzed by thermodynamic analysis. To investigate the use of waste gas from the ethanol fermentation plant, the methane production from the waste gas was compared with that of pure carbon dioxide. Thermodynamic analysis results indicated that the methane yield of the methanation from waste gas is higher than that of pure carbon dioxide. When considering the effect of operating parameters, high carbon dioxide conversion and methane yield are obtained at low temperatures. The increase of the hydrogen to carbon dioxide ratio and the operating pressure greatly affects the enhancement of methane yield at high temperatures. However, the operation of the methanation process at high hydrogen to carbon dioxide ratio and pressure leads to an increase of process costing. Thus, the optimization between the suitable operating condition and process cost should be considered in the next work.

Acknowledgments

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