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Production of methane from hydrogen and captured CO$_2$

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ABSTRACT

This study was conducted to develop an efficient method for methane production from hydrogen and captured CO_2. Such a method can be used for constructing a new energy system that can use the produced methane as a feedstock for natural gas supply networks.

Reaction simulation was conducted to identify an efficient and simple method for methanation production from hydrogen and captured CO_2. There were two pathways for this reaction, a direct path and an indirect path that produces CO as an intermediate product.

The optimum temperature, pressure, and H_2/CO_2 molar ratio for the direct reaction were 300°C, 2.0–3.0 MPa, and 4.1–4.2, respectively. When the temperature is 300°C, the pressure is 2.0 MPa and the H_2/CO_2 molar ratio is 4.13, the components of the gas produced by the direct reaction will be as follows: CH_4 87.5%; H_2 11.5%, N_2 0.9%, CO_2 670 ppm, and CO 1.2 ppm after drying without additional gas purification. When the amount of CO_2 included is less than 1,000 ppm, it will not have a great effect on combustion. CO poisoning will not be caused by the produced gas when the amount of CO is less than 1 ppm. Accordingly, the produced gas can be use as a feedstock for natural gas supply networks without gas purification if the concentration of H_2 is acceptable. Even when the concentration of H_2 is not acceptable, the capacity of the hydrogen separation unit can be minimized by controlling the feeding rate of H_2/CO_2 at 4.1-4.2.

The indirect reaction includes a reverse shift reaction as the first reaction and a methanation reaction of CO and CO_2 as the second reaction. A parameter based on the gas components after the second reaction, $Pcr = 1/\{(3CO + 4CO_2)/H_2\}$, was developed to identify the best conditions for this reaction. The optimal conditions for the indirect reaction were found to be 500°C for the first reaction, 250–300°C for the second reaction, 2.0–3.0 MPa for the first and second reactions, and a Pcr of 1.0–1.1. When the temperature is 500°C for the first reaction and 282°C for the second reaction, the pressure is 3.0 MPa for the first and second reactions, and the Pcr is 1.01, the gas components of gas produced by the indirect reaction will be as follows: CH_4, 93.7%; H_2, 5.3% N_2, 0.9%; CO_2, 952 ppm; and CO, 0.8 ppm after drying without CO_2 and H_2 recycling.

CONTENTS

PAPER

1. Introduction

Natural gas supply networks have already been constructed in many countries. The feedstocks of these networks are primarily composed of methane. This means that many countries are currently using methane as an energy source. Since among hydrocarbons, methane has the maximum proportion of hydrogen, natural gas emits a lesser amount of CO_2 than other fossil fuels when it is burned. Accordingly, switching from coal and oil to natural gas is an immediate solution for reducing CO_2 emissions. Figure 1 shows the key technologies that can help reduce CO_2 emissions under the IEA's BLUE Map scenario, which aims to halve global energy-related CO_2 emissions by 2050 relative to the 2005 level [1]. By 2050, in addition to energy saving, increased efficiency, and use of alternative fuels, CO_2 capture and storage (CCS) will be required to reduce CO_2 emissions significantly.
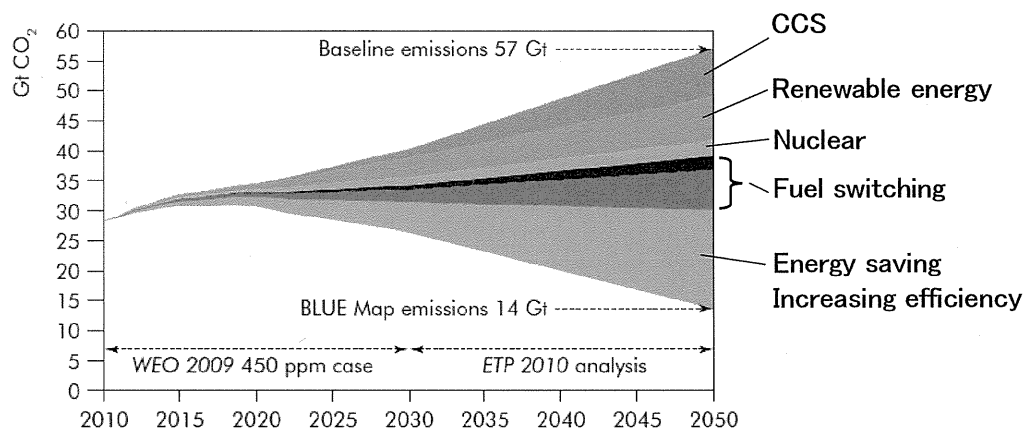

Figure 1. Key technologies for reducing CO_2 emissions under the IEA's BLUE Map scenario [1]

Figure 2 shows an energy system that supplies CO_2-free hydrogen to FCVs via an on-site natural gas reforming hydrogen station with CO_2 capture. The captured CO_2 reacts with CO_2-free hydrogen, which results in its conversion into methane at a methane production plant. The produced methane is then supplied to the hydrogen station through a natural gas pipeline, where it is converted into hydrogen via a steam reforming reaction. The produced CO_2 is then captured and transported to the methane production plant. Picture and system flow chart in figure 2 show the demonstration site of hydrogen station with CO_2 capture which was started by Tokyo Gas in December, 2010.
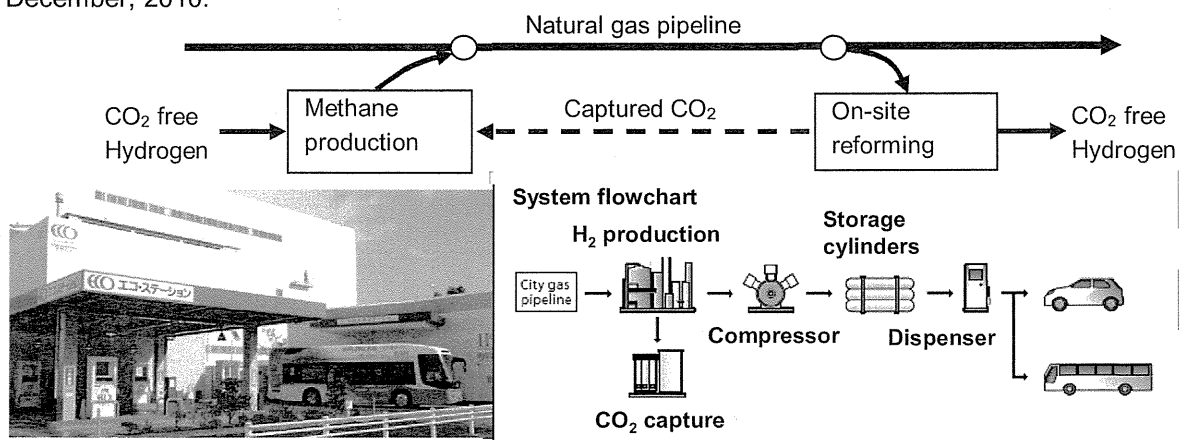

Figure 2. CO_2-free hydrogen supply system supported by a natural gas pipeline

Figure 3 shows an energy system that supplies CO_2-free heat and power from a combined heat and power (CHP) with a CO_2 capture system. CO_2 captured at the CHP reacts with CO_2-free hydrogen and is converted into methane at a methane production plant. The produced methane is then supplied to the CHP through a natural gas pipeline, where it is converted into heat and power. The produced CO_2 is captured and transported to the methane production plant. The system flow chart and spec sheet in figure 3 show a PAFC with CO_2 capture, developed by Tokyo Gas and Fuji Electric.

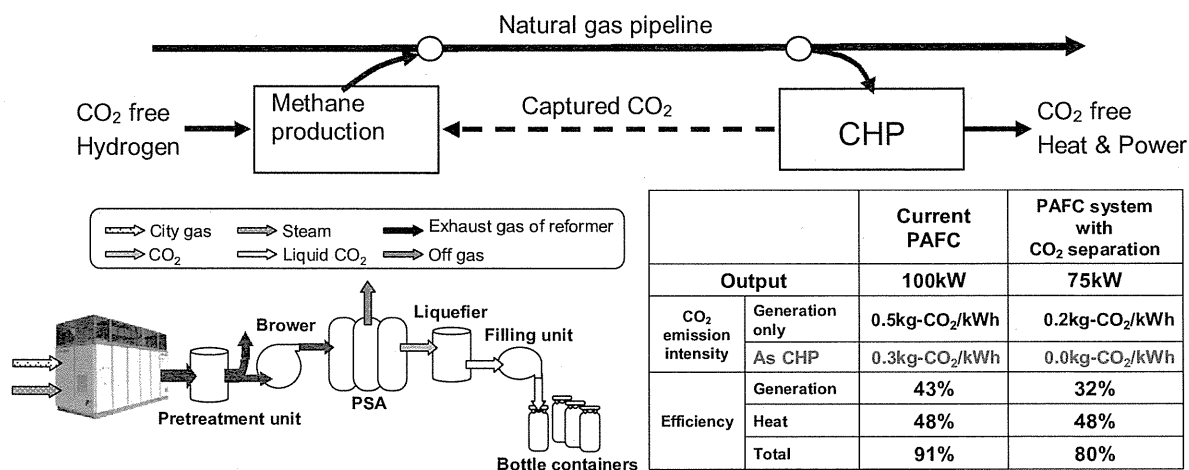|		Current PAFC	PAFC system with CO_2 separation
Output		100kW	75kW
CO_2 emission intensity	Generation only	0.5kg-CO_2/kWh	0.2kg-CO_2/kWh
	As CHP	0.3kg-CO_2/kWh	0.0kg-CO_2/kWh
Efficiency	Generation	43%	32%
	Heat	48%	48%
	Total	91%	80%

Figure 3. CO_2-free heat and power supply system supported by a natural gas pipeline

There are vast quantities of renewable energy that are not currently being utilized, such as solar energy in the Sahara Desert and wind energy in Patagonia. Together with promotion of fuel switching, gas industries can and should try to use the large and unused CO_2-free energy using current natural gas supply networks. Such actions will not only reduce CO_2 emissions by natural gas consumers, but also lead to indirect utilization of remotely situated renewable energy sources.

2. Outline of this study

The development of technology for efficient methane production from hydrogen and captured CO_2 is important for the realization of the new energy systems shown in figures 2 and 3. Many studies have previously been conducted to evaluate the use of methanation reactions in several processes such as the production of synthetic natural gas (SNG). Most of these studies have focused on the reactivity of catalysts in the methanation reactions in the process of SNG production [2][3][4]. In the SNG process, feed hydrogen and CO_2 are usually produced by coal gasification, and the generated gas includes CO, O_2, N_2, H_2O, and heavy metals containing hydrogen and CO_2. In the process of methane production from hydrogen and captured CO_2, the purities of feed CO_2 and feed hydrogen are greater than 99%. The high values are a consequence of the CO_2 capture plant producing highly concentrated CO_2 and performing water electrolysis using renewable power to produce highly concentrated hydrogen. When feed hydrogen is produced by steam reforming of coal or natural gas, the produced hydrogen is not highly concentrated at first. However, the hydrogen transportation process, which uses a hydrogen carrier such as liquefied hydrogen or organic chemical hydrate, will purify the generated hydrogen.

Methane can be synthesized by the following methanation reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
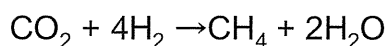
It is expected that methanation starting from highly purified CO_2 and hydrogen will be very simple. In this study, process simulation studies of methanation reactions conducted using highly purified CO_2 and hydrogen as raw materials are reported. There are two reaction pathways for methanation. One reaction path is a direct reaction and the other is an indirect one. Optimal reaction conditions such as pressure, temperature and H_2/CO_2 ratio of the two paths are identified by process simulation studies using Aspen. Table 1 shows the reactions of the two pathways. The direct reaction is simple because it involves only one reactor. However, two different reactions occur at the same time in the same reactor, which makes it difficult to select the best reaction conditions for this path. The indirect reaction uses two reactors and therefore requires more effort than the direct reaction requires, to make the system simple. However, the best reaction conditions for the two reactions can be determined.

Table 1. Reaction paths for methanation

	Reaction	$\triangle H$, kcal/kmol
Direct	(1) $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-39.4
Indirect	(2) $CO_2 + H_2 \rightarrow CO + H_2O$ (3) $CO + 3H_2 \rightarrow CH_4 + H_2O$	+9.8 -49.3

Detailed simulations of the two reaction paths shown in table 1 were conducted in this study to make the production of methane from hydrogen and captured CO_2 as efficient and simple as possible. The simulation software used for this study was Aspen Plus. Pure chemical materials considered in this study were H_2, N_2, CH_4, CO, CO_2, and H_2O. The Predictive Soave-Redlich-Kwong (PSRK) equation-of-state model was selected as the thermochemical model because it is the most reliable model in the pressure range targeted in this study.

3. Direct methane production from hydrogen and captured CO_2

Figure 4 shows a block flow diagram of the direct methanation process. In this process, the purity of the feed H_2 is 100%, while that of the feed CO_2 is 99%. Additionally, 1% N_2 is included. It is assumed that the feed CO_2 will include 1% N_2 during the CO_2 capture process. The recommend catalyst for this reaction is a transition metal, such as Ni, or a noble metal such as Rh, Ru, Pd, or Pt. The catalyst will be supported by an appropriate carrier.
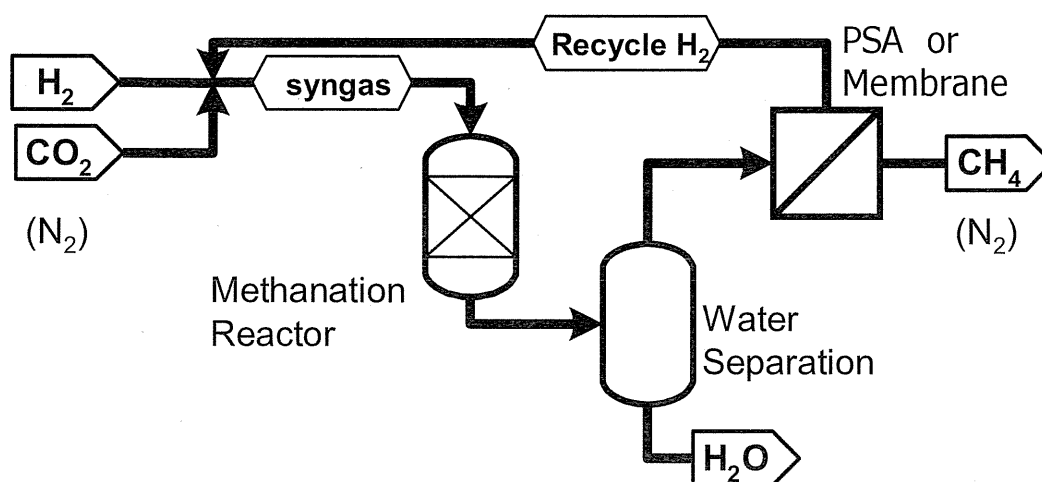

Figure 4. Block flow diagram of the direct methanation process

Reaction (1) shown in table 1 is a strong exothermal reaction that decreases the mole number after the reaction. High pressure and low temperature will accelerate the reaction at the point of equilibrium behavior. However, if the reaction temperature becomes too low, the reaction speed becomes too slow. The reaction temperature of the CO methanation reaction, which has a good track record in the chemical industry, is normally 300-500°C. The same reaction temperature range is considered to be desirable for reaction (1) in table 1, even though the reaction heat and temperature dependency of the equilibrium are slightly smaller than those of the CO methanation reaction. Figure 5 shows the simulation results of temperature dependency against the equilibrium reaction rate of methane production obtained by direct reaction. The equilibrium reaction rate reaches around 100% when the reaction temperature becomes greater than 350°C at each reaction pressure. Effective increasing of the equilibrium reaction rate stops when the reaction pressure becomes more than 5.0 MPa. When the reaction pressure becomes greater than 7.0 MPa, methanol will be produced as a by-product. Considering these conditions, 2.0-5.0 MPa is considered to be a desirable pressure for the reaction (1) listed in table 1.
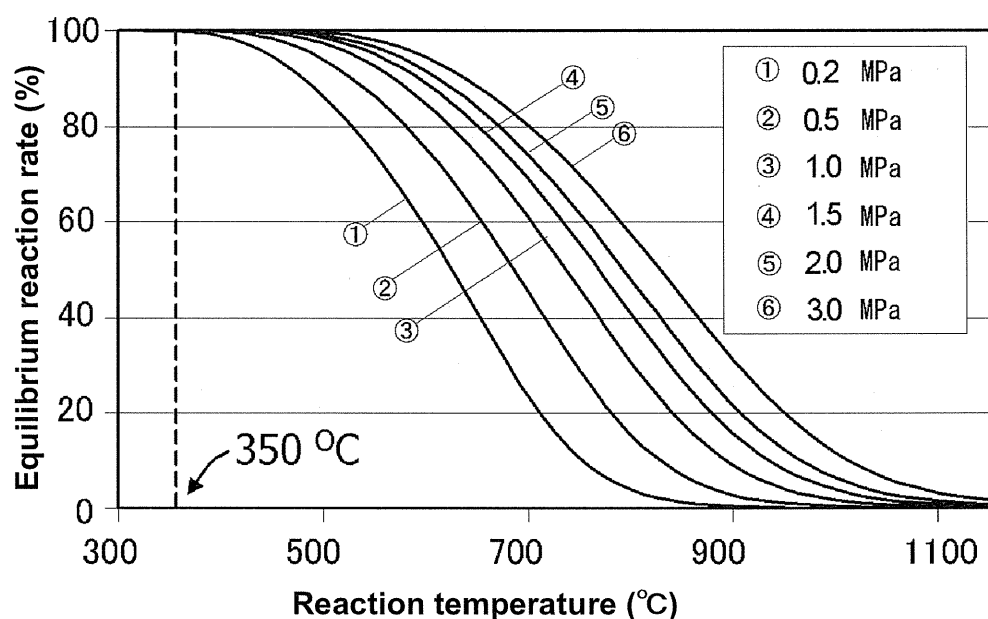

Figure 5   Temperature dependency against the equilibrium reaction rate of
methane production by direct reaction

To simulate the direct path in this study, the inlet and outlet temperature of the reactor was set to 300°C, while the maximum temperature inside the reactor was set to 450°C. The reaction pressure was set to 2.0 MPa.

Simulation of the reaction (1) listed in table 1 was conducted under the reaction conditions described above while changing the feeding rate of H_2/CO_2. Figure 6 shows the influence of the feeding rate of H_2/CO_2 against the concentration of CO_2 and H_2 in the gas generated after the methanation reaction. Figure 7 shows this influence against CO and H_2. The results revealed that there is an inflection feeding rate of H_2/CO_2 in this reaction.
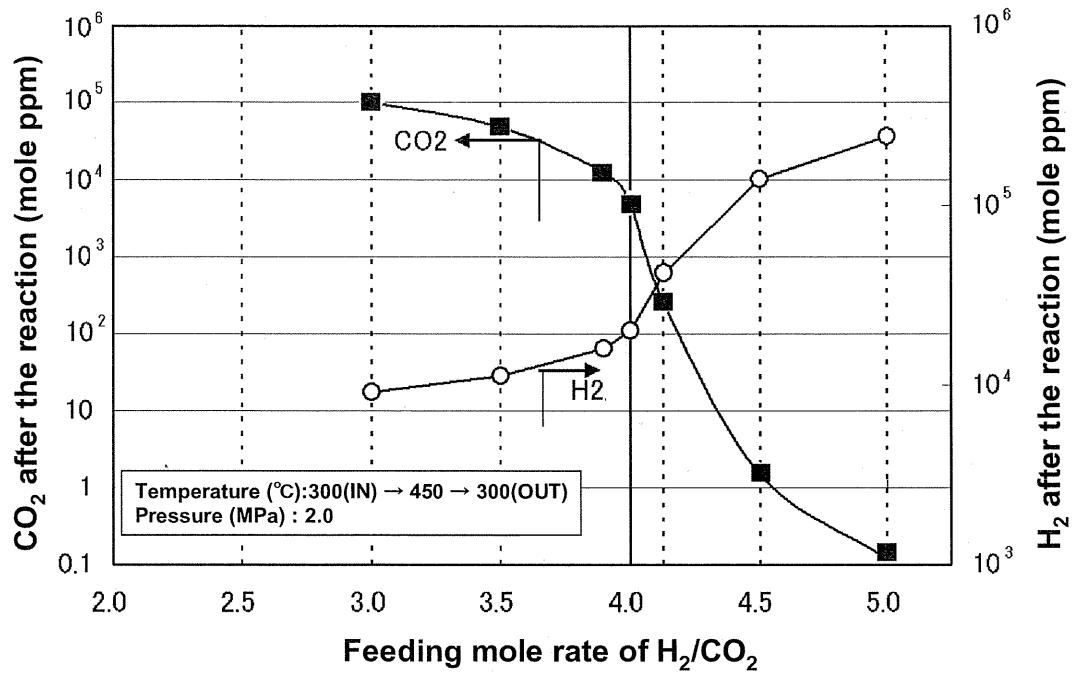
Figure 6   Influence of the feeding rate of H_2/CO_2 against the concentration of CO_2 and H_2 in the gas produced after the methanation reaction
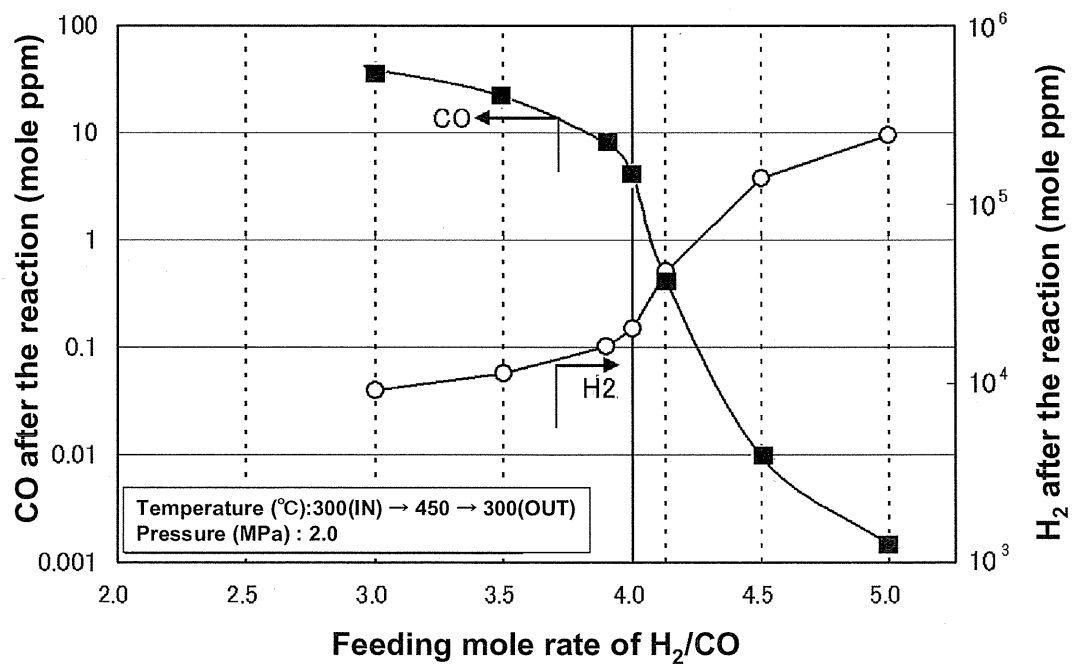

Figure 7   Influence of the feeding rate of H_2/CO_2 against the concentration of CO and H_2 in the gas produced after the methanation reaction

The inflection feeding rate of H_2/CO_2 was found to be around 4.13. When the rate was smaller than this, concentrations of CO_2 and CO in the produced gas were not reduced enough. To ensure that the concentrations of CO_2 and CO are low enough, the feeding rate of H_2/CO_2 should be over 4.13, and a larger rate will lead to better results. However, the concentration of excess H_2 in the produced gas becomes excessively large when the feeding rate of H_2/CO_2 is greater than 4.13. The concentration of excess hydrogen in the produced gas will be over 10% when the rate reaches

4.5. These findings indicate that the concentrations of CO_2, CO and H_2 in the gas produced in this reaction will be minimized when the feeding rate of H_2/CO_2 is controlled at 4.1-4.2.

Table 2 shows the simulation results of gas components obtained before and after the direct methanation reaction. For this simulation, the feeding rate of H_2/CO_2 was set to 4.13. Under an ideal catalyst, the gas components after direct methanation with drying are as follows: CH_4, 87.5%; H_2, 11.5%; N_2, 0.9%, and these include 670 ppm of CO_2 and 1.2 ppm of CO. When the amount of CO_2 included is less than 1,000 ppm, it will not have a great effect on combustion. CO poisoning will not be caused by the produced gas when the amount of CO is less than 1 ppm. Accordingly, the produced gas can be use as a feedstock for natural gas supply networks without gas purification if the concentration of H_2 is acceptable. Even when the concentration of H_2 is not acceptable, the capacity of the hydrogen separation unit can be minimized by controlling the feeding rate of H_2/CO_2 at 4.1-4.2.

Table 2   Gas components before and after the direct methanation

		Before methanation	After methanation ( ) with the drying process
Temperature (°C)		300 (IN) 450(MAX) 300 (OUT)	
Pressure (MPa)		2.0 MPa	
Concentration (mole fraction)	CH_4	0.3%	32.1% (87.5%)
	N_2	0.2%	0.3% (0.9%)
	H_2	80.1%	4.2% (11.5%)
	CO_2	19.4%	250 ppm (670 ppm)
	CO	-	0.4 ppm (1.2 ppm)

4. Indirect methane production from hydrogen and captured CO_2

Figure 8 shows a block flow diagram of the indirect methanation process. In this process, the purity of the feed H_2 is 100%, while that of the feed CO_2 is 99%; the remaining 1% in CO_2 is N_2.
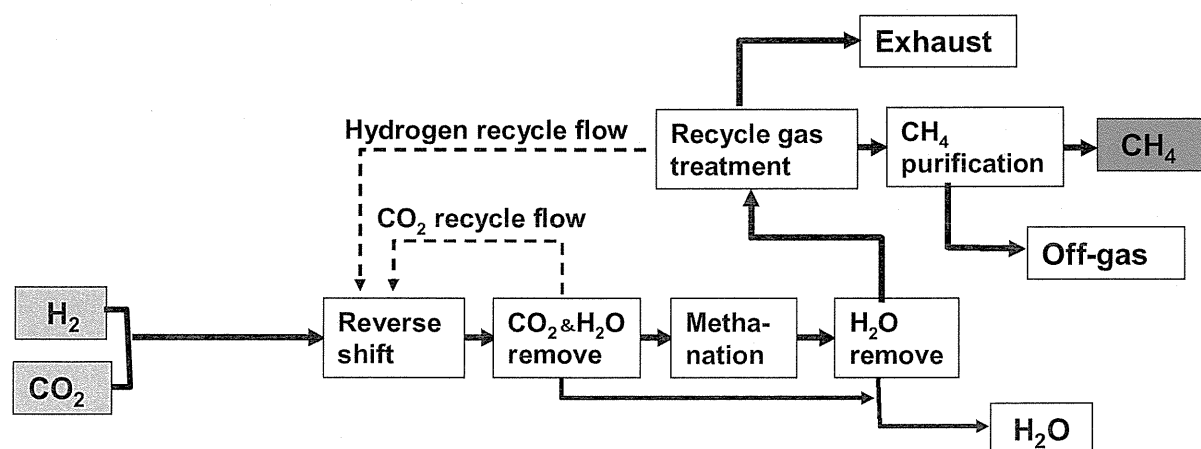

Figure 8   Block flow diagram of the indirect methanation process

The reaction (2) listed in table 1, which is the first reaction in the indirect methanation process, is a reverse shift reaction. The recommended catalyst for this reaction is a metal oxide, such as ZnO, Cr_2O_3, FeO or CuO, supported by an Al_2O_3 carrier. This reaction is a mild endothermic reaction that does not lead to a change in the mole number. There is no pressure dependency on the equilibrium reaction rate for this reaction. Therefore, the pressure of the first reaction should be the same as that of the second reaction, which is reaction (3) listed in table1, to make the entire process simple. Higher temperatures are desirable for the first reaction at the point of temperature dependency. However, when the temperature becomes too high, catalyst poisoning by CO will start and the lifetime of the catalyst becomes short. Therefore, 460-550°C is desirable for the first reaction. Figure 9 shows the simulation results of temperature dependency against the equilibrium reaction rate of the reverse shift reaction. The feeding rate of H_2/CO_2 was set to 1.0. The equilibrium reaction rate of the reverse shift reaction could not reach 100%; therefore, the unreacted CO_2 must be included in the gas fed to the second reactor.
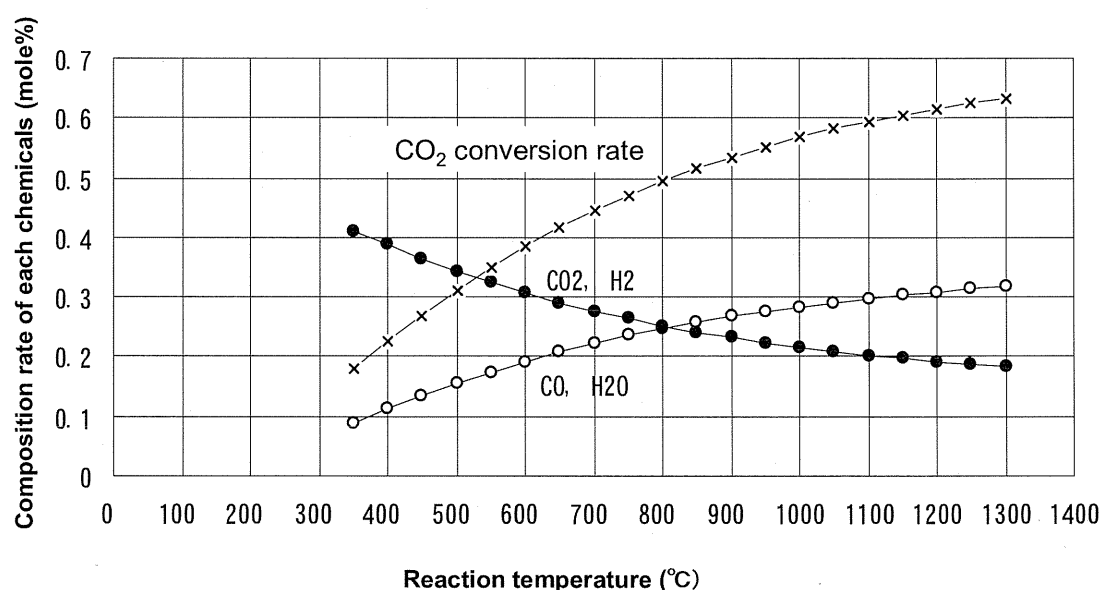

Figure 9　Temperature dependency against the equilibrium reaction rate of the reverse shift reaction

The reaction (3) listed in table 1, which is the second reaction in the indirect methanation process, is the methanation reaction of CO. The catalyst recommended for this reaction is a Ni based catalyst, although Ru or Pb-Rh can also be used. This reaction is a strong exothermic reaction that decreases the mole number after the reaction. High pressure and low temperature will accelerate the reaction at the point of equilibrium behavior. Figure 10 shows the simulated results of temperature dependency against the equilibrium reaction rate of methane production obtained by the indirect reaction. The results revealed that even when the reactant is diluted 50% by methane, the equilibrium reaction rate will reach 100% when the reaction temperature is over 700 K (427°C). The reaction speed becomes too slow when the reaction temperature is less than 200°C. Therefore, 250–450°C is desirable for the reaction temperature of the second reaction. For the same reason, for the direct reaction, 2.0–5.0 MPa is desirable.
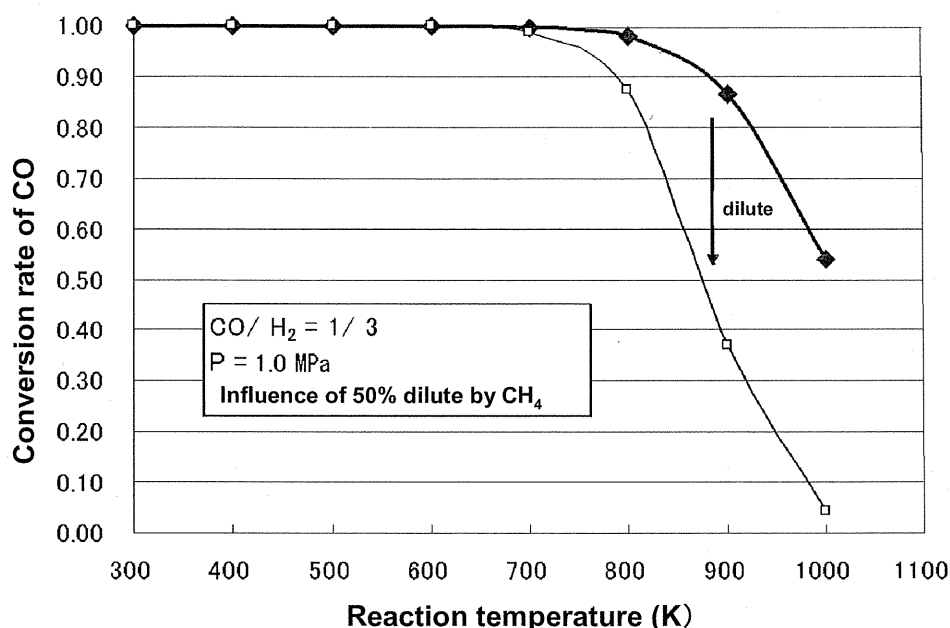
Figure 10   Temperature dependency against the equilibrium reaction rate
of the methanation reaction of CO

To simulate the indirect path in this study, the inlet temperature of the first reactor was set to 500°C, while the inside temperature of the reactor was controlled at 460-550°C. The inlet temperature of the second reactor was set to 300°C, while the inside temperature was controlled in the range of 250-450°C. The reaction pressure of the first and the second reaction was set to 3.0 MPa.

Simulation of the indirect methanation reaction was more complicated than that of the direct methanation reaction. This is because the reaction conditions of the first and second reactor will change at the same time. Simulation of the first and second reaction was conducted by changing the rate of feeding H_2/CO_2 and the CO_2 recycling rate after the first reaction and the H_2 recycle rate after the second reaction. Simulations were conducted for 37 cases. In each case, the reaction pressures of the first and second reactor were assumed to be 3.0 MPa. The reaction temperature of the first reactor was assumed to 500°C. The reaction temperature of the second reactor was assumed to be 300°C, except for one case. To find better conditions of no CO_2 and H_2 recycling, the reaction temperature of the second reaction was assumed to be 282°C in one case.

For the indirect methanation reaction, controlling of a second reaction is important. This is because the second reaction produces methane, which is the desired product of the methanation reaction. As shown in figure 9, the gas fed to the second reaction should include CO_2 added to the CO because the conversion of the first reaction cannot reach 100%. To optimize the reaction of the second reactor, CO and CO_2 must be considered from the beginning to the end of the reaction. Therefore, we attempted to understand this reaction by using the parameter $Pcr = 1/\{(3CO + 4CO_2)/H_2\}$. Figure 11 shows the influence of the feeding rate of Pcr against the concentration of CO_2 and H_2 in the gas produced after the second reaction, and Figure 12 shows it against CO and H_2.

The results revealed that there is an inflection point in the second reaction when Pcr is 1.01. When Pcr is smaller than 1.01, the concentrations of CO_2 and CO in the produced gas didn't become low. Therefore, Pcr should be greater than 1.01, and larger numbers produced better results.

However, the concentration of excess H_2 in the produced gas became excessively large when Pcr is greater than 1.01. The concentration of excess hydrogen in the produced gas was greater than 15% when the rate reaches 1.5. Overall, the concentrations of CO_2, CO and H_2 in the gas produced by this reaction were minimized when CO, CO_2 and H_2 in the gas fed to the second reaction wass controlled so that Pcr = $1/\{(3CO + 4CO_2)/H_2\}$ was between 1.0-1.1.
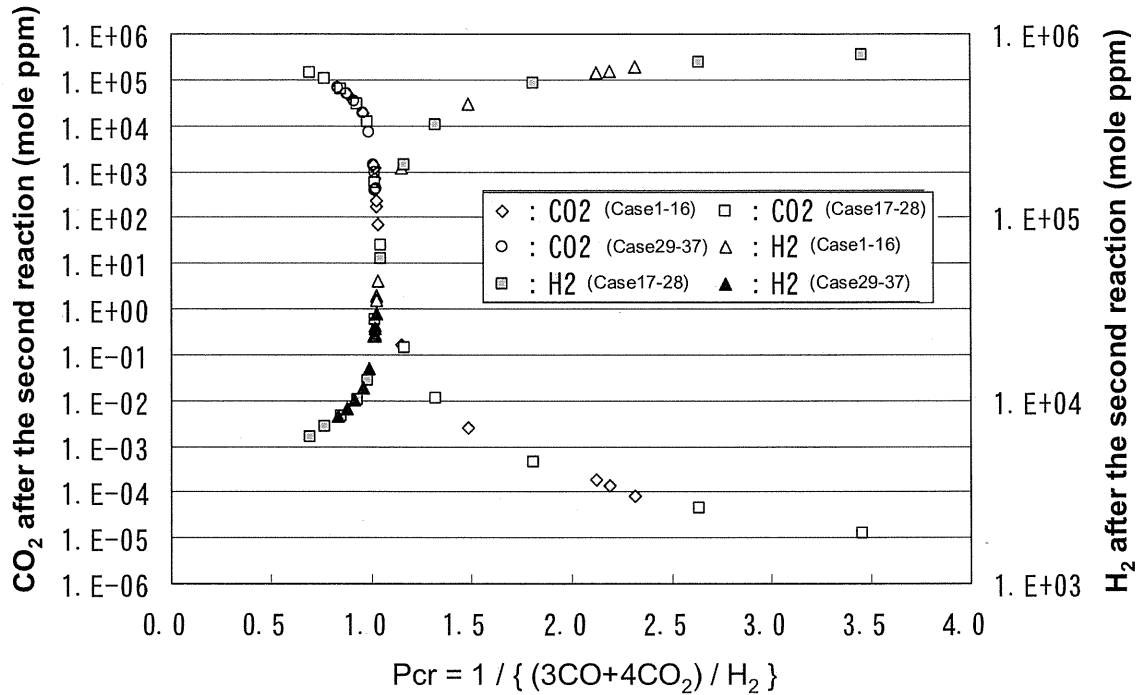

Figure 11   Influence of Pcr against the concentration of CO_2 and H_2 in the gas produced after the second reaction (methanation)
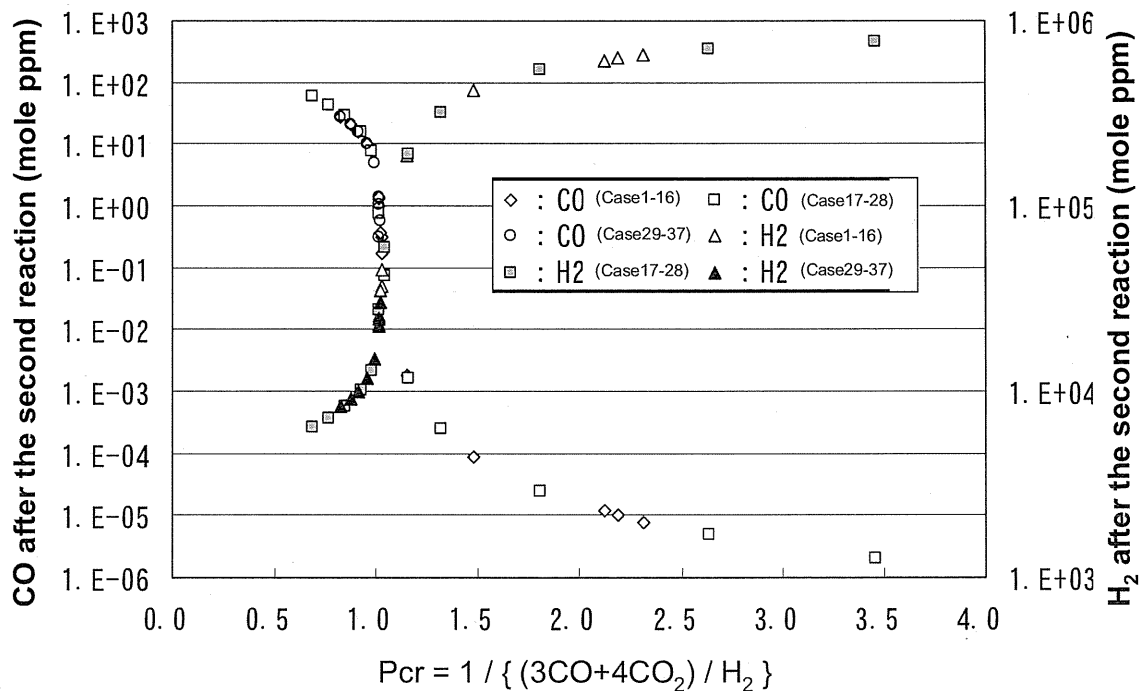
Figure 12   Influence of Pcr against the concentration of CO and H_2 in the gas produced after the second reaction (methanation)

Figure 13 shows the influence of the feeding rate of H_2/CO_2 against the concentration of CO_2 and H_2 in the gas produced after the first reaction. The inflection feeding rate of H_2/CO_2 for the indirect methanation reaction was around 4.0, that is equal to equilibrium ratio, while that of the direct methanation reaction was 4.13 as shown in figure 6. This result is considered to show the effect of optimization of the methanatio reaction via the indirect reaction path.
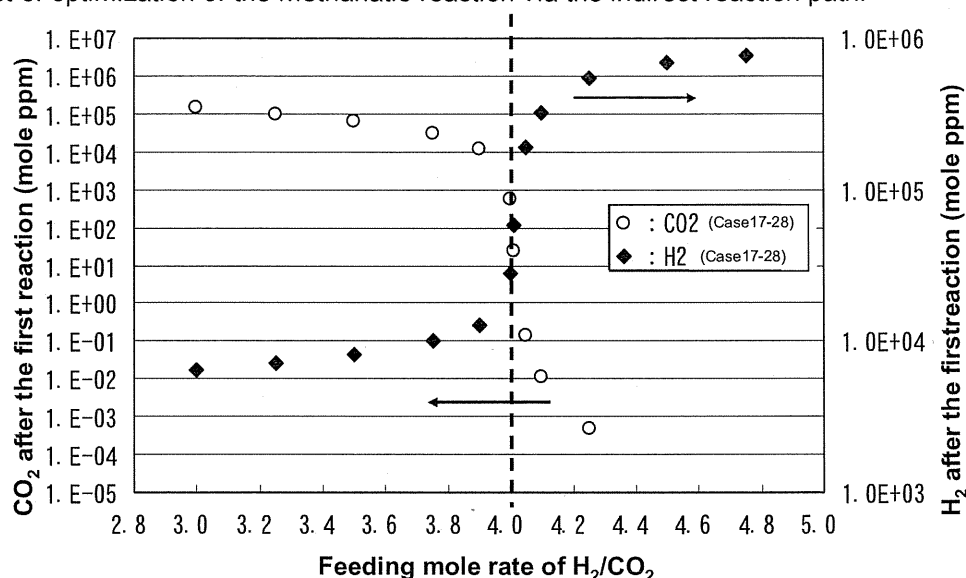

Figure 13   Influence of the feeding rate of H_2/CO_2 against the concentration of CO_2 and H_2 in the gas produced after the first reaction (reverse shift)

Table 3 shows the simulated results of the gas components after the indirect methanation reaction. In one case, 90% of the CO_2 and H_2 was recycled after the first and second reaction, while neither were recycled in the other case. When an ideal catalyst was used, the gas components after indirect methanation reaction with 90% recycling and a drying process were as follows: CH_4, 98.3%; H_2, 1.0%; N_2, 0.6%, and 1,187 ppm CO_2 and 1.7 ppm CO were included. These concentrations of H_2, CO_2, and CO were considered to be acceptable as a feedstock for a natural gas supply network. The indirect methanation reaction with a drying process in which CO_2 and H_2 were not recycled resulted in the production of 93.7% CH_4, 5.3% H_2 and 0.9% N_2, and 952 ppm CO_2 and 0.8 ppm CO. If a natural gas supplying network can accept this level of H_2, the produced gas can be used as a feedstock for the network without additional gas purification.

Table 3   Gas components after the indirect methanation reaction

		90% recycled after drying	No recycling after drying
Temperature (°C)		First reaction: 500 Second reaction: 300	First reaction: 500 Second reaction: 282
Pressure (MPa)		3.0 MPa	
Concentration (mole fraction)	CH_4	98.3%	93.7%
	N_2	1.0%	0.9%
	H_2	0.6%	5.3%
	CO_2	1,187 ppm	952 ppm
	CO	1.7 ppm	0.8 ppm

5. Conclusion

Reaction simulation was conducted to identify an efficient and simple method for methanation production from hydrogen and captured CO_2. There were two pathways for this reaction, a direct path and an indirect path that produces CO as an intermediate product.

The optimum temperature, pressure, and H_2/CO_2 molar ratio for the direct reaction were 300°C, 2.0–3.0 MPa, and 4.1–4.2, respectively. When the temperature is 300°C, the pressure is 2.0 MPa and the H_2/CO_2 molar ratio is 4.13, the components of the gas produced by the direct reaction be as follows: CH_4 87.5%; H_2 11.5%, N_2 0.9%, CO_2 670 ppm, and CO 1.2 ppm after drying without additional gas purification. When the amount of CO_2 included is less than 1,000 ppm, it will not have a great effect on combustion. CO poisoning will not be caused by the produced gas when the amount of CO is less than 1 ppm. Accordingly, the produced gas can be use as a feedstock for natural gas supply networks without gas purification if the concentration of H_2 is acceptable. Even when the concentration of H_2 is not acceptable, the capacity of the hydrogen separation unit can be minimized by controlling the feeding rate of H_2/CO_2 at 4.1-4.2.

The indirect reaction includes a reverse shift reaction as the first reaction and a methanation reaction of CO and CO_2 as the second reaction. A parameter based on the gas components after the second reaction, $Pcr = 1/\{(3CO + 4CO_2)/H_2\}$, was developed to identify the best conditions for this reaction. The optimal conditions for the indirect reaction were found to be 500°C for the first reaction, 250–300°C for the second reaction, 2.0–3.0 MPa for the first and second reactions, and a Pcr of 1.0–1.1. When the temperature is 500°C for the first reaction and 282°C for the second reaction, the pressure is 3.0 MPa for the first and second reactions, and the Pcr is 1.01, the gas components of gas produced by the indirect reaction will be as follows:CH_4, 93.7%; H_2, 5.3% N_2, 0.9%; CO_2, 952 ppm; and CO, 0.8 ppm after drying without CO_2 and H_2 recycling.

In future studies, an adequate catalyst should be selected and evaluated. Because the methanation reaction is strongly exothermic, adequate design for removing the heat from the reaction is also necessary.

6. Acknowledgements

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