CH₄ Production from Hydrothermal Gasification of Ethanol Using Carbon-supported Ni Catalysts

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Carbon-supported Ni catalysts were prepared and used to convert an ethanol/water mixture to CH₄. When using 5 wt% ethanol, successful conversion to CH₄ and CO₂ was achieved at a temperature as low as 250°C. Marginal amounts of undesired by-products such as acetaldehyde were produced even at a low conversion of ethanol. The composition of the product gas was similar to that in the equilibrium state. The rate of ethanol conversion was independent of ethanol concentration, and the activation energy was assumed to be 105 kJ/mol. Our carbon-supported Ni catalysts were found to show high activity for ethanol conversion from the comparison with literature data. The energy balance shows that this process needs little thermal energy to convert the ethanol/water mixture when heat of the outlet stream of the reactor is recovered by heat exchange with the inlet stream since the reaction is a slightly exothermic reaction. CH₄ produced in the reactor can be purified by physical absorption of CO₂ in water; however, CH₄ can be also absorbed in the water at high operating pressure. CH₄ can be recovered at 94% when the operating pressure of the absorber is 3 MPa from equilibrium consideration.

Introduction

Biomass has been expected to be an alternative feedstock for fossil resources since the oil crises of the 1970s. Increasing attention has been drawn to biomass as a renewable energy resource to prevent global warming. Therefore, the conversion of biomass to fuel has been actively investigated (McKendry, 2002a, 2002b, 2002c). Bio-ethanol production was 98.3 billion liters in 2015, which was more than three times larger than bio-diesel production (Renewable Energy Policy Network for the 21st Century, 2016). Bio-ethanol is the most widely used biofuel for transportation worldwide. The net energy balance (NEB), which is the ratio of energy output to energy input, is one of the most important indices for biofuel production because it requires energy to grow resource crops such as corn and convert to biofuels. Hill *et al.* (2006) have reported that the NEB ratio is 1.25 for corn grain ethanol based on LCA analysis, including farming energy. Half of the energy in ethanol is consumed for the conversion process in their analysis.

Bio-ethanol is typically produced through saccharification, fermentation, distillation, and dehydration in the case of corn grain. Dehydration is necessary for concentrating up to 99.5 mol% because the ethanol/water mixture has azeotropic properties. These concentration processes are known to be energy intensive. Luyben (2012) optimized these processes, and 25% of the energy in ethanol was consumed when 5 mol% ethanol was concentrated up to 99.5 mol%

using a conventional distillation column, an azeotropic column, and a recovery column with benzene as an entrainer. Energy consumption seems to be inevitable as long as distillation is used for concentration processes. Development of processes to convert high-water-content ethanol to another form of energy medium that can be used easily is necessary. Conversion of high-water-content ethanol to H₂, CH₄, CO, CO₂, which is so called reforming, has been investigated for this purpose.

Many studies have reported the reforming of ethanol, which can be categorized as gas phase or aqueous phase reforming according to the reaction phases. Gas phase reforming is so-called steam reforming (SR). Various catalysts have been developed for this purpose, and many reviews have been published (Ni *et al.*, 2007; Contreras *et al.*, 2014; Hou *et al.*, 2015; Zanchet *et al.*, 2015; Sohn and Ozkan, 2016). Steam reforming can produce hydrogen in high yield from ethanol; however, much energy is required for the evaporation of water and the reforming, which is a very endothermic reaction. Side reactions to produce aldehydes, which are unfavorable products, possibly occur in SR. Aqueous phase reforming (APR), which is operated under hydrothermal conditions, is a promising process for the utilization of ethanol because evaporation energy is not required (Davda *et al.*, 2005). The Dumesic group reported APR of ethylene glycol, glycerol and sorbitol, which are biomass-derived carbohydrates, to produce hydrogen and alkanes below 300°C (Davda *et al.*, 2003; Shabaker *et al.*, 2004a). As for ethanol, conversion above 90% could be achieved using Pt catalysts (Tang *et al.*, 2009; Tokarev *et al.*, 2010). It has also been reported that a significant deactivation is observed for a commercial Al₂O₃ support catalyst within 72 h of APR (Roy *et al.*, 2012). From the viewpoint of stability under

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hydrothermal conditions, carbon is promising as a support material. We have previously developed carbon-supported catalysts with highly dispersed Ni nanoparticles and utilized them to gasify organic water pollutants in aqueous phase (Nakagawa *et al.*, 2004, 2007; Sharma *et al.*, 2006). This process produces fuel gas containing CH₄, and hence, it is an energy production process as well as a wastewater treatment process. In this study, we utilized our carbon-supported Ni catalysts to convert ethanol to CH₄ in the aqueous phase and gasification behavior of ethanol was examined. CH₄ is actually less valuable than H₂; however, it is easily transported compared with H₂. Municipal pipeline can be possibly used. Therefore, this process can be an optional process for utilizing low concentration ethanol if ethanol can be converted at low temperature efficiently. The reaction rate was analyzed and compared to that in previous studies. To present the advantage of this process, heat balance was also considered, and a purification process utilizing physical absorption was discussed for CO₂ removal.

1. Experimental

1.1 Catalyst preparation

A metacrylic acid type ion exchange resin (WK-11, Mitsubishi Chemical Corp.) was used as a source material for the catalysts. This resin had carboxylic acid groups as ion exchange groups, and its capacity was 10 mol/kg on a dry resin basis. Ten grams of wet resin as-received was treated in a flask with 150 mL of aqueous solution of Ni(NO₃)₂·6H₂O using a rotary shaker at room temperature for 24 h. H⁺ is released from the resin with the ion exchange to lower the pH of the solution. Ion exchange cannot proceed under acidic conditions; therefore, NH₃ aq. (approx. 28%) was added to enhance the degree of ion exchange. Various ion-exchanged-resins were prepared by varying the amounts of the Ni(NO₃)₂·6H₂O and NH₃ aq. added. The resin was then washed with deionized water, followed by air-drying at room temperature for 12 h. The air-dried resin was carbonized in a nitrogen atmosphere to 500°C at the rate of 10°C/min to prepare the carbon-supported Ni catalyst. Catalysts were abbreviated by the Ni, followed by the amount of loaded (wt%), such as Ni38. All catalysts were reduced by 40 vol% H₂ at 350°C for 1 h before use.

It is likely that tar formed during carbonization deposits as carbon on the surface of catalyst particles, deactivating the catalyst activity. The conventional air-combustion

method cannot be applied since the carbon support is also combusted. The loss of support carbon must be minimized when removing the carbon covering the surface of the catalyst. To address this situation, subcritical water treatment of as-carbonized catalysts was conducted at 350°C and 20 MPa for 2 h, at which carbon support was stable in a flow of water. To examine the effect of the subcritical water treatment, non-treated sample, Ni38*, was also served to the hydrothermal experiments. **Table 1** shows the properties of catalysts prepared. The BET surface area of Ni36 is 160 m²/g, which is lower than that of others. Hydrogen treatment must have a marginal effect on BET surface area since no gasification of carbon occurs at low temperature such as 350°C. The BET surface area of Ni38* was 197 m²/g. Subcritical water treatment also has an insignificant effect. Therefore, a variation in BET surface area may be due to the variation in carbonization behavior of the resin resulting in the different carbon structures.

1.2 Hydrothermal gasification experiment

Figure 1 shows a schematic of the experimental setup. A fixed bed reactor, which was assembled using Swagelok fittings, was used for gasification experiments. The bed volume of the catalyst was 0.63 cm³ (Diameter: 4.6 mm; Height: 38 mm). An ethanol solution (3, 5, 10 wt%) was continuously supplied to the reactor using a high-pressure LC pump at the rate of 0.05 to 1.05 mL/min, which corresponded to 5–100 h^{−1} of liquid-hourly-space-velocity (LHSV). The pressure inside the reactor was controlled by a backpressure regulator equipped on the downstream of the reactor. After passing through the backpressure regulator and reaction media, the mixture of gas and liquid was introduced to a gas–liquid separator, where the product gas was swept by a nitrogen flow. The reactor was heated by an electric heater to gasification temperature, *T*, which was in the range 225–275°C. After reaching steady-state, product gas and liquid were collected in a gas bag and a glass bottle.

Table 1 Preparation condition and BET surface area of catalysts

	[Ni ²⁺] [M]	[NH ₃]/[Ni ²⁺] [—]	η _M [%]	Y _C [—]	S _{BET} [m ² /g]
Ni36	1	1	32	0.52	160
Ni38	0.4	5	36	0.56	213
Ni53	1	2.5	66	0.73	196

[Ni²⁺], [NH₃]: Concentration of Ni²⁺ and NH₃. η_M: Degree of carboxylic group exchanged to Ni²⁺. Y_C: Solid yield on carbonization; S_{BET}: BET surface area

Fig. 1 Experimental setup of the hydrothermal gasification experiment

1.3 Analysis and catalyst characterization

Product gas was analyzed by a micro-GC apparatus (CP-4900, Varian Inc.) equipped with two channel TCD detectors. The column temperatures for PoraPLOT Q and Molsieve 5A were 80 and 100°C, respectively. The liquid product was analyzed by a total organic carbon analyzer (TOC-V_{CSH}, Shimadzu Corp.) to measure the TOC concentrations from which the carbon conversion of ethanol was estimated. Acetaldehyde, acetic acid, and unreacted ethanol in the liquid were also analyzed by gas chromatography (GC-14A, Shimadzu Corp.) with SBS-200 column. The column oven was initially kept at 50°C for 7 min, and then heated to 200°C at 15°C/min.

Ni content of the catalyst or the resin sample was estimated from the ash contents of the sample combusted at 800°C using a thermogravimetric analyzer (TGA-50, Shimadzu Corp.). Ash was assumed to be NiO for calculation. N₂ adsorption isotherm of the catalyst was measured at -196°C using a Belsorp-mini II (Microtrack-bell) to calculate the BET surface area. The X-ray diffraction pattern of the powdered catalyst sample was measured using an X-ray diffractometer with Cu K α radiation (Ultima IV, Rigaku Corp.). The active surface area of the catalyst samples was evaluated by the amount of CO chemisorbed on the pulse experiment using BELCAT (Microtrack-bell).

2. Results and Discussion

2.1 Hydrothermal gasification behavior of ethanol

The effect of subcritical treatment of catalysts on the activity was examined here. Evolution of CO₂ was observed in an exit flow during subcritical water treatment, indicating that some carbon was gasified to produce CO₂. Migration of Ni nanoparticles was another concern in this treatment. X-ray diffraction patterns were measured to evaluate Ni dispersion. **Figure 2** shows X-ray diffraction patterns of catalysts before and after treatment. Very broad peaks at $2\theta = 44.5^\circ$ and 51.9° associated with Ni are observed before treatment (Ni38*), indicating that Ni particles are highly dispersed. The Ni particle size is estimated to be 1.9 nm from Scherrer's equation. Little change was observed in this broad peak of after treatment, although slight sharp peaks appeared for Ni and only a small portion of Ni was oxidized to NiO. This result indicated that the migration of Ni particles could be suppressed. Active surface area, which was determined by CO pulse experiments, was significantly improved to 50 m²/g for Ni38, whereas that of Ni38* was 37 m²/g.

The effect of subcritical water treatment on the carbon conversion was examined at 250°C in **Figure 3**. Carbon conversion, X_C , is used to evaluate the activity of the catalyst here. X_C is defined as the ratio of the amount of the gasified carbon to the amount of carbon in ethanol, and is estimated from the concentration of TOC, which is the organic carbon remaining in the water. X_C of Ni38*, which is not treated in the subcritical water, was 0.67, whereas that of Ni38 was 0.96 when the gasification was conducted at LHSV = 20 h⁻¹.

Fig. 2 X-ray diffraction patterns of the catalyst before and after treatment

Fig. 3 Comparison of the carbon conversion before and after treatment of the catalyst

The activity of the catalyst was significantly improved by the subcritical water treatment. The improvement was also observed at LHSV = 50 h⁻¹. It was found that subcritical water treatment was effective for enhancing the catalytic activity. All the catalysts were treated in subcritical water except for Ni38*.

Various reactions possibly occur, yielding various products, in our experiments so the carbon balance should be considered. We collected gas and liquid products at ambient temperature and pressure. The amount of organic carbon remaining in treated water can be directly quantified by TOC concentration. Inorganic carbon, which was dissolved as CO₂ in water, was negligible in all experiments. As for gas fraction, CH₄, CO, CO₂, and C₂H₆ were quantified as the carbon-containing gas. The yields of TOC and quantified gas components are summarized in **Figure 4(a)**, which shows the carbon balance. The amount of inlet carbon was estimated using the flow rate of an ethanol/water mixture and ethanol concentration precisely determined by TOC concentration. Figure 4(a) shows that the carbon balance is almost unity, indicating that most of the carbon released as gaseous products could be successfully quantified. As for the analysis of the treated water, ethanol, acetaldehyde and acetic acid were quantified; however, acetaldehyde and acetic acid were not detected in our experiments. The yield of "others" in the figure was the difference between TOC and the ethanol yield. Unreacted ethanol nearly accounted for TOC fraction while CH₄ and CO₂ were the dominant carbon-containing gas for Ni catalysts. The yields of CO and C₂H₆ were both marginal compared to those of CH₄

Fig. 4 Carbon balance and hydrogen content in the product gas

and CO₂. The yield of other intermediate products such as acetaldehyde, which is often obtained in gas phase reforming was marginal even when ethanol conversion was as low as 0.2, as was the case for Ni36. Therefore, ethanol was immediately converted to CH₄ and CO₂ when reacted on our Ni catalysts. Hydrogen content in the product gas on the dry gas base is shown in Figure 4(b). Hydrogen content was 12% at most, indicating that our Ni catalysts are not suitable for hydrogen production.

2.2 Effect of reaction temperature and pressure

Figure 5 plots the carbon conversion against LHSV value at various temperatures for Ni38. Reaction pressure was elevated to maintain liquid phase in the reactor. The higher temperature gave higher carbon conversion. Ethanol was completely converted at 250°C and LHSV = 10 h⁻¹. When the temperature was raised to 275°C, more than 90% of ethanol was converted even at LHSV = 50 h⁻¹. Rapid conversion was achieved below 300°C by using Ni38 as a catalyst.

We assumed that the following reactions mainly occur in ethanol conversion with Ni catalysts from the experimental results.

Reaction (1) is the reforming reaction of ethanol to produce CO and H₂, and is assumed to proceed irreversibly in this temperature region since ethanol was completely converted as shown in Figure 5. Reactions (2) and (3) were the water-gas shift reaction and methanation reaction, respectively. Both reactions are known to be reversible so the product gas composition under an equilibrium state can be estimated from equilibrium constants. Equilibrium gas composition is compared with experimental results conducted at various temperatures and LHSV = 10 h⁻¹ using Ni38 in Figure 6. Gas composition was represented on the dry gas

$P = 4 \text{ MPa } (T = 225^\circ\text{C}), 5 \text{ MPa } (T = 250^\circ\text{C}), 8 \text{ MPa } (T = 275^\circ\text{C})$

Fig. 5 Effect of reaction temperature on the carbon conversion

$P = 4 \text{ MPa } (T = 225^\circ\text{C}), 5 \text{ MPa } (T = 250^\circ\text{C}), 8 \text{ MPa } (T = 275^\circ\text{C}), \text{LHSV} = 10 \text{ h}^{-1}$

Fig. 6 Comparison of product gas composition between equilibrium state and experimental results

Fig. 7 Effect of pressure on the carbon balance and hydrogen content in the product gas

base. Equilibrium gas composition was almost independent of reaction temperature in this temperature region, and CO content was low enough to be neglected. H₂ content was also very low compared to CH₄ and CO₂. The experimental results showed that H₂ content was as low as 5% and CO cannot be detected. The ratio of CH₄ to CO₂ was roughly consistent with equilibrium calculation, indicating that product gas nearly reached an equilibrium state. Our catalysts show very high activity for the methanation reaction, reaction (3); therefore, hydrogen cannot be obtained in high yield. If the activity for methanation reaction can be suppressed by the modification of the catalyst such as the addition of another component, this process can be a hydrogen production process at low temperature from ethanol. This is reserved for a

future work.

Effect of pressure on the carbon balance and hydrogen content in the product gas is shown in **Figure 7** when Ni38 was used as a catalyst at 250°C. H₂O was wholly vaporized only in the case of 0.1 MPa where other experiments were under hydrothermal conditions. Gas composition was significantly dependent upon reaction pressure. H₂ content was rather high at 0.1 MPa, whereas that was very low above 5 MPa under hydrothermal conditions. This result was reasonable considering the molar fraction of H₂O in the gas phase of the reactor. H₂O partial pressure was the saturation pressure in the gas phase when water existed as a liquid. For example, the H₂O molar fraction in the gas phase of the reactor, $y_{\text{H}_2\text{O}}$, was 0.8 at 250°C and 5 MPa since the saturation pressure of H₂O is 3.98 MPa at 250°C. On the other hand, $y_{\text{H}_2\text{O}}$ was 0.98 at 250°C and 0.1 MPa since water was completely vaporized, which is so-called gas phase reforming. It was likely for reaction (2) to proceed compared to liquid phase reforming. When the reaction pressure was above 5 MPa, the H₂ content decreased with the increase in pressure. The equilibrium H₂ content was extremely low at $P=5$ MPa as shown in Figure 6. A higher pressure gives a lower $y_{\text{H}_2\text{O}}$ because the saturation pressure is independent of pressure. Therefore, it was assumed that the reaction rate for reaction (3) is enhanced at higher pressure, giving a lower H₂ yield.

2.3 Kinetic analysis of ethanol conversion

Ethanol conversion, X_{EtOH} , was plotted against $W_{\text{Ni}}/F_{\text{A0}}$ for Ni38 with various initial concentrations of ethanol at 250°C in **Figure 8(a)**, where W_{Ni} and F_{A0} are the weight of Ni in a reactor and the molar flow rate of ethanol. A linear relationship was obtained irrespective of ethanol concentration. This result means that the same conversion was given at the same F_{A0} even when the initial concentration of ethanol was different. The amount of ethanol converted, $F_{\text{A0}}X_{\text{EtOH}}$, is irre-

Fig. 8 Relationship between $W_{\text{Ni}}/F_{\text{A0}}$ and X_{EtOH}

spective of the initial ethanol concentration, indicating that the reaction rate was independent of ethanol concentration. Zero-order reaction kinetics concerning ethanol can be assumed. **Figure 8(b)** shows X_{EtOH} vs $W_{\text{Ni}}/F_{\text{A0}}$ plot for Ni36, Ni38 and Ni53 when the initial ethanol concentration was 5 wt%. A linear relationship between X_{EtOH} and $W_{\text{Ni}}/F_{\text{A0}}$ was also obtained for all catalysts although the slope is dependent upon the catalyst.

Therefore, the reaction rate of ethanol for our system is assumed as follows.

$$r_{\text{m-Ni}} = k_{\text{m-Ni}} \quad (4)$$

Here, $r_{\text{m-Ni}}$ is reaction rate on the Ni weight basis [$\text{mol kg-Ni}^{-1} \text{s}^{-1}$] and $k_{\text{m-Ni}}$ is zero-order rate constant on the Ni weight basis [$\text{mol kg-Ni}^{-1} \text{s}^{-1}$].

The slope of the line in Figure 8 gives $k_{\text{m-Ni}}$ value. **Table 2** lists the values of $k_{\text{m-Ni}}$ and Ni diameter, d_{Ni} , which was determined by X-ray diffraction pattern. The $k_{\text{m-Ni}}$ value was dependent on catalysts, whereas Ni diameter was almost the same. $k_{\text{m-Ni}}$ value for Ni38 was 2.5 times higher than that for

Table 2 Rate constant, Ni diameter, and active surface area of the catalysts

	$k_{\text{m-Ni}}$ [$\text{mol kg-Ni}^{-1} \text{s}^{-1}$]	d_{Ni} [nm]	S_{A} [$\text{m}^2 \text{g-Ni}^{-1}$]
Ni36	6.7×10^{-3}	2.0	17
Ni38	1.8×10^{-2}	1.9	57
Ni38*	1.1×10^{-3}	1.9	37
Ni53	1.2×10^{-2}	2.4	50

Fig. 9 Relationship between S_{A} and $k_{\text{m-Ni}}$

Fig. 10 Arrhenius plot of $k_{\text{m-Ni}}$

Table 3 Comparison of the activity of catalysts with literature

Catalyst	T [°C]	C_{EtOH} [wt%]	WHSV [h^{-1}]	X_{EtOH} (—)	P_R [—]	Ref.
Raney-Ni/Sn	225	0.7	32	0.154	8.9	Shabaker and Dumesic (2004b)
3%Pt/ Al_2O_3	225	0.7	60	0.089	8.2	Shabaker and Dumesic (2004b)
0.5%Pt/NaY	225	1	0.8	0.898	43	Tang <i>et al.</i> (2009)
PdZn/CNT	250	10	0.9	0.295	39	Xiong <i>et al.</i> (2015)

Ni36. This result indicated that the effective surface area of the Ni particle was different among catalysts. Therefore, we introduced the active surface area, S_A , of the catalyst determined from CO pulse experiments. S_A is also listed in Table 2 and plotted against the $k_{\text{m-Ni}}$ value in Figure 9. A linear relationship was roughly established between them. We also conducted the experiments at 225 and 275°C to obtain $k_{\text{m-Ni}}$ values. Figure 10 shows the Arrhenius plot of $k_{\text{m-Ni}}$ values, and the activation energy of $104.5 \text{ kJ mol}^{-1}$ was obtained. Thus, we could formulate the reaction rate constant for Ni38 as follows.

$$k_{\text{m-Ni}} = 4.45 \times 10^8 \exp\left(-\frac{104.5 \times 10^3}{RT}\right) \quad (5)$$

Here, we compare the activity of Ni38 with the data of the literature. Table 3 lists the data of the literature, T , C_{EtOH} , weight hourly space velocity, WHSV value, and X_{EtOH} . X_{EtOH} cannot be compared directly because the experimental conditions were different among the literature. Since we formulate the reaction rate as Eq. (5) including temperature dependency, we calculated the WHSV value (WHSV*) to give the same X_{EtOH} under the same conditions as the literature using following equation.

$$\text{WHSV}^* = \frac{3600 \times M_{\text{EtOH}} k_{\text{m-Ni}} w_{\text{Ni}}}{X_{\text{EtOH}} C_{\text{EtOH}} / 100} \quad (6)$$

Herein, M_{EtOH} is molar mass of ethanol [kg mol^{-1}] and w_{Ni} is Ni content of the catalyst [$\text{kg-Ni kg-catalyst}^{-1}$].

Performance ratio, P_R , was introduced to compare the activity of the catalyst. It is defined as $\text{WHSV}^*/\text{WHSV}$, which corresponded to the ratio of the treatment rate capacity of ethanol/water mixture under the same conditions as those of the literature. P_R ranged from 8.2–43, indicating that the activity of our catalyst was very high.

2.4 Energy balance and the purification process

CH_4 production from an ethanol/water mixture is an optional process for utilizing bio-ethanol when much energy has to be input for purifying low concentration ethanol. The hydrothermal gasification proposed in this study is a process to heat up ethanol/water mixture to 200–300°C. This process also requires much energy for heating; however, the heat of the outlet stream can be recovered by heat exchange with the inlet stream. Therefore, heat balance including heat exchange has to be considered. Data of the standard heat of formation, heat capacity for each component at atmospheric pressure are obtained from the literature (Smith *et al.*, 2001). The steam table is also obtained from the same literature,

Fig. 11 Mass and energy balance of the proposed process

and the enthalpy of hot compressed water at saturated pressure is used for calculation, although the operating pressure is above saturated pressure.

To simplify the reactions in the reactor, the following overall reaction was assumed from the equilibrium state. The ratio of CH_4/CO_2 under equilibrium state at 250°C is 2.95 when complete conversion of 5 wt% ethanol is assumed.

This reaction is an exothermic reaction ($\Delta H_R^\circ = -30.8 \text{ kJ/mol}$). The heat balance in the case of $C_{\text{EtOH}} = 5 \text{ wt\%}$ is presented in Figure 11. The ethanol/water mixture enters the reactor at 250°C, and the temperature is raised by 7.6°C at the exit of the reactor. The outlet stream is then cooled to 30.5°C by heat exchange with the inlet stream. The minimum temperature difference of the heat exchanger is 5.5°C. Therefore, it was found that little thermal energy is required for this conversion process.

The purification process after reaction is examined utilizing physical absorption. The scheme of the process is also shown in Figure 11. After cooling the outlet stream of the reactor, a part of CO_2 and CH_4 is dissolved in the water in the gas-liquid separator. Most of the CH_4 is contained in the gas phase since the solubility of CH_4 is much less than CO_2 . The water phase is separated from gas phase in the gas-liquid separator, and CO_2 in the water can be recovered by depressurization. The gas phase from the separator is then introduced to the absorber, in which water is used as absorbent for CO_2 . Water absorbing CO_2 from the absorber is depressurized for the recovery of CO_2 , and circulated as the absorbent. A high operating pressure is favorable for

Fig. 12 Plots of P_g vs W_{H_2O} and R_{CH_4}

CO_2 absorption; however, much CH_4 can be absorbed. The absorption of CH_4 must be considered since the absorbed CH_4 is loss of the process. The operating pressure, P_g , can be controlled by depressurization at the entrance of the gas-liquid separator. Therefore, the effect of P_g on the amount of circulation water, W_{H_2O} , and recovery ratio of CH_4 , R_{CH_4} , is considered below 10 MPa. It was confirmed that CO_2 solubilization obeys Henry's law under the pressure range examined here (Hou *et al.*, 2013). Henry's constants used for CO_2 and CH_4 were 167 MPa and 4185 MPa, respectively (Smith *et al.*, 2001). W_{H_2O} and R_{CH_4} were estimated under the assumption of equilibrium state in the separator and the absorber.

Figure 12 shows W_{H_2O} and R_{CH_4} vs P_g . W_{H_2O} is expressed as the ratio to the amount of water in the ethanol/water mixture supplied to the reactor. W_{H_2O} value is high at low P_g , and the dependency is not significant above 3 MPa. On the other hand, R_{CH_4} is linearly decreased with the increase of P_g . It is less than 0.9 when P_g is 10 MPa. The data at $P_g = 3$ MPa is shown in Figure 11. In the separator, 33% of CO_2 produced in the reactor is dissolved in the water. About 94% of CH_4 can be recovered from the absorber. W_{H_2O} is 2.1, and is corresponding to the minimum liquid-gas ratio. Considering that the liquid-gas ratio is generally 2–3 times higher than the minimum ratio, 94% of CH_4 can be recovered through the purification process by the circulation of an amount of water 4–6 times as much as the amount of ethanol/water mixture. Under this condition, the reactor is operated at above 3.98 MPa to keep hydrothermal condition, and then the pressure is reduced to 3 MPa at the entrance of the gas-liquid separator.

Conclusion

We conducted hydrothermal gasification of ethanol using carbon-supported Ni catalysts. The main products were CH_4 and CO_2 , and reaction intermediates such as acetaldehyde were not produced. The composition of the product gas was roughly the same as that in the equilibrium state. The rate of ethanol conversion was expressed by zero-order reaction kinetics concerning the ethanol concentration, and the activation energy was assumed to be 104.5 kJ/mol. We compared the treatment rate of ethanol/water mixture with the

literature using the rate equation determined in this study. Our carbon-supported Ni catalysts showed high activity for ethanol conversion. The energy balance showed that little thermal energy was required for the reactor by heat exchange of the inlet stream with the outlet stream of the reactor. Physical absorption of CO_2 was considered for the purification process of CH_4 . CH_4 can be recovered at 94% with the operating pressure of 3 MPa.

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