[Research Note]

Simulated Process Evaluation of Synthetic Natural Gas Production Based on Biomass Gasification and Potential of CO₂ Capture Using Membrane Separation Technology

Ryo Nagumo*, Shuichi Iwata, and Hideki Mori

Dept. of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, JAPAN

Synthetic natural gas (SNG) production using biomass gasification has recently become important as SNG has been suggested as an alternative to fossil fuels. In the process, CH_4 synthesis (methanation) must be considered in addition to biomass gasification. By integrating exothermic methanation and endothermic gasification, the required heat energy can be lowered in an autothermal process. In this study, the performances of autothermal SNG production were estimated from process simulations. In this process, CO_2 separation after methanation is inevitably energy-intensive. Therefore, feasibility analysis was conducted on the autothermal SNG production process with CO_2/CH_4 membrane separation, which is expected to achieve drastically lower energy consumption. These assessments can determine whether membrane separation has the potential as an alternative to the conventional separation unit. Using a membrane process, CH_4 loss can become less than 2 %, if the separation factor of CO_2 over CH_4 exceeds 50. Therefore, we conclude that this value should be set as the minimal target value for the CO_2/CH_4 separation factor. Achievement of this goal will probably facilitate widespread use of SNG production by biomass gasification.

1. Introduction

Biomass is expected to provide a renewable energy source that can reduce the present dependency on fossil fuels such as oil, coal, and natural gas. Natural gas is the main energy source worldwide, so the production of synthetic natural gas (SNG) from biomass could be a promising approach to replacing non-renewable fuels, partly because SNG can be stored using the fully developed natural gas storage facilities, and because SNG can be supplied using the existing natural gas grid. Therefore, biomass-to-SNG conversion technology is an important area to study.

Production of SNG from biomass has generally been proposed using a two-step process, using the schematic flow diagram shown in **Fig. 1(a)**[1]. In the first step, fuel gas is produced by biomass gasification, based on endothermic pyrolysis reactions mainly producing CO, H_2, CO_2, CH_4, hydrocarbons, tars, etc. In the second step, after gasification and gas cleaning, the fuel gases are fed into a methanation reactor, in which methanation occurs together with water-gas shift reactions and steam reforming of hydrocarbons. Methanation is exothermic, as described by the following reaction.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (1)$$
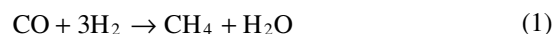
In the conventional process, no heat integration is conducted between the gasification and methanation steps, because the gasifier requires heat at a much higher temperature (600-1000 ℃) than the methanation reactor (200-500 ℃) can provide.

To use the heat released in exothermic methanation effectively, autothermal gasification of biomass has recently been studied[1],[2]. The block diagram of the process modeling is illustrated in **Fig. 1(b)**. Here the gasification unit utilizes a high-pressure steam gasifier, in which heat derived from methane formation can be supplied to the gasification process, possibly resulting in the omission of the air/oxygen supply to the gasifier. Elimination of air addition can avoid nitrogen dilution of the fuel gas, and elimination of oxygen addition will omit the requirement for a costly air separation unit. Therefore, the autothermal gasification of biomass to produce SNG would be an energy-saving option to supply a renewable energy source.

The biomass-to-SNG conversion technology, including autothermal biomass gasification and methanation,

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* To whom correspondence should be addressed.
* E-mail: manu6107@yahoo.co.jp

(a)

(b)
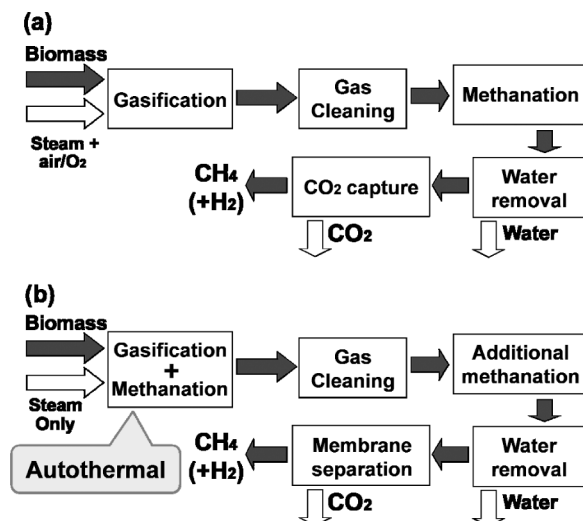
(a) Conventional process and (b) autothermal process.

Fig. 1 Block Diagram of a SNG Production Process by Integrating a Biomass Gasification and Methanation

Table 1 Proximate and Ultimate Analyses of the White Pine Pellets[5]

Proximate analysis (wt% on a dry basis)	
ash	3.13
volatile matter (VM)	80.75
fixed carbon (FC)	16.12
moisture (wt%, as received)	5.3
HHV (MJ/kg, dry)	20.6

Ultimate analysis (wt% on a dry basis)	
carbon	47.99
hydrogen	6.25
nitrogen	1.31
sulfur	0.58
oxygen	40.73
chlorine (10^{-6} g/g)	312
bromine (10^{-6} g/g)	203
fluorine (10^{-6} g/g)	<18

could also incorporate a CO_2 capture unit such as the absorption process to enhance the heating value of the flue gas for the final SNG product. However, the CO_2 absorption process is generally energy-intensive and a highly efficient technology is very desirable[2]. The membrane separation unit could be an alternative approach to achieving drastically lower energy consumption. Many studies on CO_2-permselective membranes have recently been reported[3],[4]. Nevertheless, the target values of membrane performances are uncertain for CO_2/CH_4 separation after biomass gasification and methanation. Definite goals for practical applications are now needed, to accelerate the research and development of CO_2-permselective membranes. Estimation of the target performances, based on systematic and quantitative assessment, is now essential.

The present study conducted process simulations to estimate the CO_2/CH_4 membrane performances necessary for use in the CO_2 capture unit for SNG production, using the Aspen Plus® V7.3 process simulator, released by Aspen Technology, Inc.

2. Simulation Modeling

2. 1. Gasification and Methanation

This study modeled an autothermal SNG production process for a biomass input of *ca.* 115 MW, using the block diagram in **Fig. 1(b)**. The model biomass was white pine pellet. The data on proximate and ultimate analyses are listed in **Table 1**[5]. The outlet gas compositions of the gasifier and the methanation reactor were calculated by minimization of the Gibbs free energy under the operating conditions, using the Peng-Robinson property method. Here we assumed that

only the five components (CH_4, CO, CO_2, H_2, and H_2O) were at chemical equilibrium, as in previous studies[1],[2]. Other components were not considered in further calculations, resulting in the omission of a gas cleaning process in our simulations. This is certainly reasonable because the aim of this study was to evaluate the target performances for CO_2/CH_4 membrane separation to allow the establishment of a highly-efficient CO_2 capture unit. Steam and biomass at 25 ℃ and 1 bar (1 bar= 10^5 Pa) was fed into the autothermal gasifier. The steam/carbon (S/C) molar ratio was set to *ca.* 2.11, at which thermodynamically solid carbon-free operation of the gasifier is ensured. In our simulation, the gasifier was operated at 60 bar and 600 ℃. These conditions are within those investigated in the previous study[1].

To increase the methane yield of the biomass-to-SNG process, an additional methanation reactor can also be introduced, as illustrated in **Fig. 1(b)**. The operation conditions in the reactor are highly sensitive to the composition of the outlet raw SNG gas. The reaction temperature of fluidized bed methanation is reported to vary between 200 ℃ and 500 ℃[6], to be 350-500 ℃ at a pressure of 35 bar[2], and to be 270 ℃ at 10 bar[7]. In the present study, to evaluate the performance of the additional methanation reactor, two criteria were introduced: unreacted hydrogen molar fraction in the outlet raw gases after water removal, and methane yield of the autothermal SNG production process shown in **Fig. 1(b)**. Methane yield is given by the ratio of the molar flow rate of methane in the outlet raw gases to the carbon flow rate in the biomass fed into the gasifier. We calculated these values using temperatures between 250 ℃ and 400 ℃ and pressure from 10 to 50 bar, to identify the optimal operation conditions of the methanation reactor. After the methanation reaction, the raw gas is cooled to 43 ℃ and water is removed, before the dried raw gas is cooled to 35 ℃ and sent to a CO_2 capture unit.
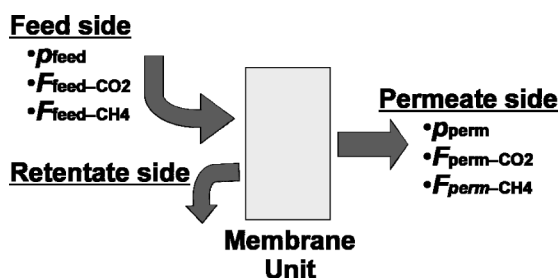
Total pressures and molar flow rates on the feed and permeate sides of the membrane are shown.

Fig. 2 Schematic Figure of a Single-stage Membrane Separation Unit

Fig. 3 Schematic Diagram of Single-stage Membrane Separation for CO_2 Removal, with Typical Temperatures and Pressures

2. 2. CO_2 Capture

The gas after water removal is fed into a CO_2 capture unit as shown in **Fig. 1(b)**. An energy-effective CO_2 capture system was modeled using a single-stage membrane separation process for the separation of components based on specified flows or split fractions. A schematic figure of the membrane unit is presented in **Fig. 2**, where p_{feed} is the feed total pressure, $F_{feed\text{-}CO_2}$ and $F_{feed\text{-}CH_4}$ are the feed-side molar flow rates of CO_2 and CH_4, respectively, p_{perm} is the permeate total pressure, and $F_{perm\text{-}CO_2}$ and $F_{perm\text{-}CH_4}$ are the permeate-side molar flow rates of CO_2 and CH_4, respectively. Using the membrane unit, the separation factor of CO_2 over CH_4, α_{CO_2/CH_4}, is determined by

$$\alpha_{CO_2/CH_4} = \frac{F_{perm\text{-}CO_2}\big/F_{perm\text{-}CH_4}}{F_{feed\text{-}CO_2}\big/F_{feed\text{-}CH_4}} = \frac{F_{perm\text{-}CO_2}\big/F_{feed\text{-}CO_2}}{F_{perm\text{-}CH_4}\big/F_{feed\text{-}CH_4}}$$

In this study, α_{CO_2/CH_4} was set to 10, 20, 30, 50, 100, and 300 to investigate the target values of membrane performances for practical use. In determining α_{CO_2/CH_4}, the ratio of $F_{perm\text{-}CO_2}$ to $F_{feed\text{-}CO_2}$ was set to 0.96 in all our simulations. This value ensured that the membrane separation in our models achieved CO_2 removal efficiencies of not less than 96 %. A typical flow diagram of membrane separation is presented in **Fig. 3**. The raw gas at 35 ℃ and 35 bar was fed into the feed side of the membrane. Permeate and retentate pressures were set to 1 bar and 33 bar, respectively, without involving any endothermic or exothermic processes. In our modeling, some of the CH_4-rich gas on the retentate side was recycled back to the feed side, which can lead to the enhancement of CH_4 purity on the retentate side. The recycling rates were set to 0, 10, 30, 50, and 70 %. Consequently, SNG at 35 ℃ and 33 bar can be obtained from the retentate side.

Quantitative evaluation used two criteria: CH_4 loss and CO_2 purity. CH_4 loss is given by the ratio of CH_4 molar flow rate in the permeate-side CO_2 rich gases to that in the feed-side raw gases, whereas CO_2 purity 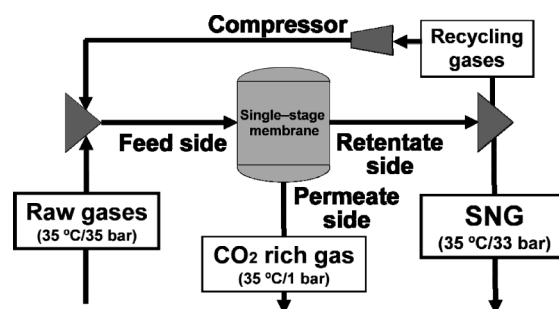is defined by the ratio of the CO_2 molar flow rate to the total molar flow rate in the permeate-side CO_2 rich gases. Using these models and criteria, we investigated the effects of recycling on the CH_4 loss and CO_2 purity, and evaluated the process performances of membrane separation for CO_2 removal in the biomass-to-SNG conversion technology.

3. Results and Discussion

3. 1. Methanation

The compositions of the outlet raw SNG gas are highly sensitive to operation conditions in the additional methanation reactor after the autothermal gasifier. The chemical equilibrium of methanation favors the generation of methane at lower temperature and the reaction kinetics at higher temperature. In this study, unreacted hydrogen molar fraction and methane yield were calculated to evaluate the performance of the reactor, with temperature between 250 and 400 ℃ and pressure from 10 to 50 bar. **Figure 4** shows the pressure and temperature dependence of these criteria. As we expected, the unreacted hydrogen molar fraction decreased with higher reaction pressures and lower reaction temperatures. On the other hand, methane yield became lower at 250 ℃ under reaction pressure of more than 30 bar because the methanation reaction was less dominant than unfavored reactions at lower temperature, resulting in the formation of solid carbon. **Figure 4(b)** certainly suggests that the lower limit of the reaction temperature is 300 ℃, which was set as the operating temperature of the additional methanation reactor in our simulations.

Table 2 shows the relationship between the reaction pressures in the additional methanation and molar fractions of the components in the outlet gases after water removal, with the reactor is operated at 300 ℃. The higher operating pressure definitely lead to higher methane yield and smaller amount of unreacted hydrogen, but could result in higher additional operational and facility costs. In this study, considering that hydrogen with smaller molecular size is highly likely to permeate through a membrane as an unfavored impure

(a)

(b)
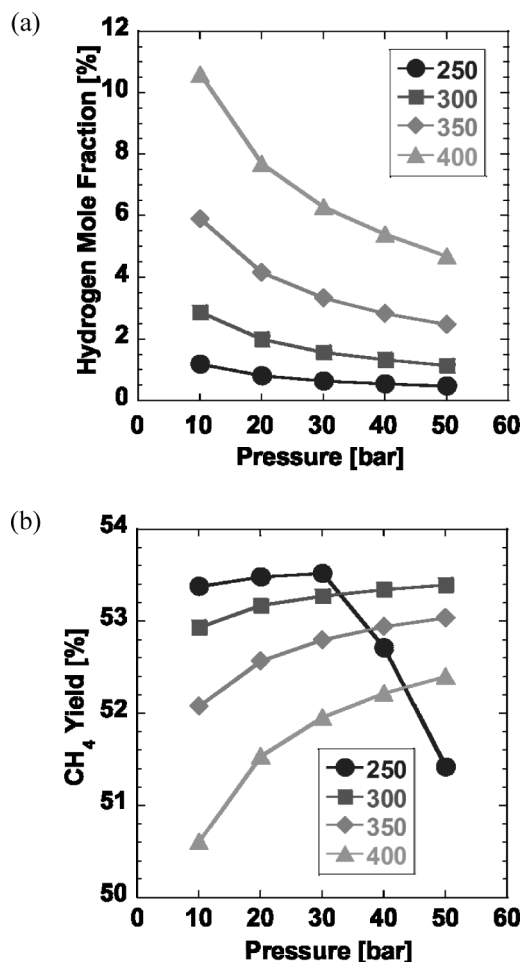
Operational temperature of the additional methanation reactor varies between 250 ℃ and 400 ℃.

Fig. 4 (a) Unreacted Hydrogen Molar Fraction of the Raw Gases after Water Removal and (b) Methane Yield of the Autothermal SNG Production Process

Table 2 Molar Fractions of the Components in the Raw Gases after Water Removal

	10 bar	20 bar	30 bar	40 bar	50 bar
CH_4	50.7	51.4	51.7	51.9	52.0
CO_2	45.0	45.2	45.3	45.3	45.4
H_2	2.89	2.00	1.58	1.33	1.15
N_2	1.12	1.13	1.14	1.14	1.14
H_2O	0.30	0.30	0.30	0.30	0.30
CO	0.018	0.013	0.011	0.009	0.008

Operational temperature of the additional methanation reactor is 300 ℃, and pressure between 10 bar and 50 bar. Values are %.

component of CO_2 rich gases, the operating pressure of the additional methanation reactor was set to 35 bar. The dried raw gases after the water removal process were cooled and sent to a membrane separation process at 35 ℃ and 35 bar.
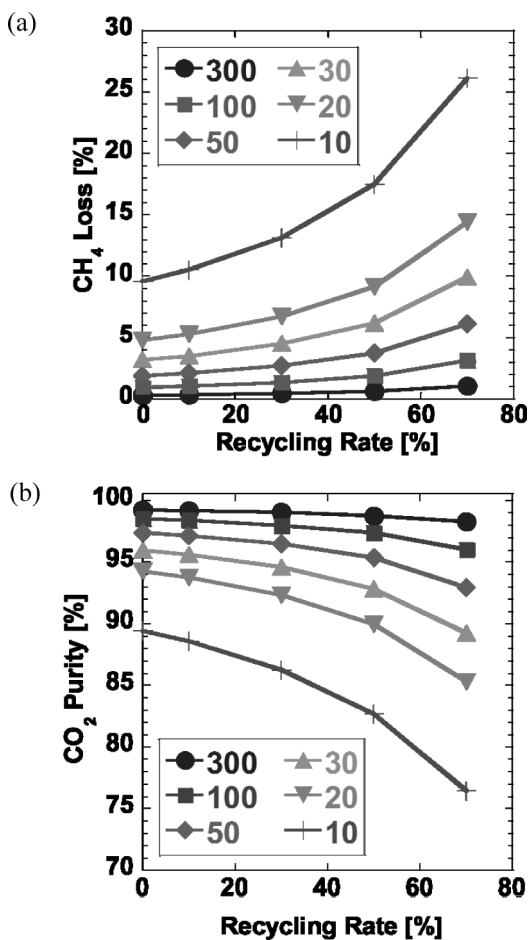
3. 2. CO_2 Capture

After the second methanation, raw gases were fed

into a single-stage membrane separation process for CO_2 capture. We investigated the CH_4 loss in the CO_2 capture unit and CO_2 purity in the permeate stream, as mentioned above. In our simulations for membrane separation, CH_4, CO_2, and H_2O were considered as components of the feed-side raw gases. H_2O was considered is to allow comparison of the performances of membrane separation with other types of CO_2 removal unit such as gas absorption in a future study, because the flow rate of water generally influences the performances in CO_2 absorption processes. It should be noted that our omission is not sensitive to the values of CH_4 loss by definition, whereas the compositions of the permeate-side and retentate-side gases can be changed by a few percent, as can be seen from **Table 2**. Although our main objective was to evaluate the potential of CO_2 capture using a membrane separation process, the appropriate compositions also need to be clarified, depending on the different ways of processing the permeate-side CO_2 rich gas and the retentate-side SNG, respectively. These compositions can also affect the heating value of SNG.

Figure 5 shows the dependence of CH_4 loss and CO_2 purity on recycling rates, where α_{CO_2/CH_4} is changed from 10 to 300. CH_4 loss increased and CO_2 purity decreased with reduced separation factor, because a decrease in α_{CO_2/CH_4} leads to an increase in the flow rate of CH_4 on the permeate side. Any increase in the recycling rate also resulted in increased CH_4 loss and decreased CO_2 purity, mainly because the flow rate of the permeate-side CO_2 rich gases increased. CH_4 purities in the retentate stream are more than 95 % in all our simulations. Therefore, recycling from the retentate to the feed side was not certainly the best policy in our simulations. It should be noted that all our simulations assure CO_2 removal efficiencies of not less than 96 %. If the efficiencies are somewhat lower, the recycling could be significant to improve the performance. Here we focus only on non-recycling processes to investigate the feasibility of CO_2/CH_4 membrane separation for the SNG production process.

3. 3. Potential

In a recent study[7], the setting value of CH_4 loss was 2 %. This value is certainly a prerequisite for considering that CO_2/CH_4 membrane separation is highly feasible in the biomass-to-SNG production system, although this value can vary depending on the various process conditions. To gain an insight into the target values of membrane performances, we investigated the relationship between CH_4 loss and CO_2 purity for the non-recycling single-stage membrane separation processes as shown in **Fig. 6**, where the added values from 10 to 300 are α_{CO_2/CH_4}. This figure shows that CH_4 loss and CO_2 purity had a linear relationship, naturally because the increase in flow rate of CH_4 as an impure component in the permeate stream directly leads to
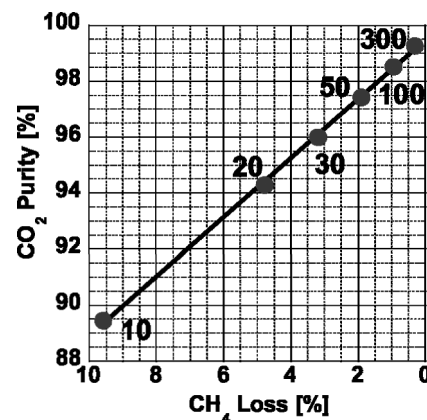
(a)

(b)

Separation factor of CO_2 over CH_4 varies between 10 and 300.

Fig. 5 (a) CH_4 Loss in CO_2 Capture Unit by Membrane Separation and (b) CO_2 Purity in the Permeate Stream

Separation factor of CO_2 over CH_4 varies between 10 and 300.

Fig. 6 Relationship between CH_4 Loss and CO_2 Purity in Non-recycling Membrane Separation Processes

reduced CO_2 purity. This figure also indicates that a target value of 50 for α_{CO_2/CH_4} is preferable to reach the 2 % CH_4 loss necessary for practical use of membrane separation. If α_{CO_2/CH_4} exceeds 50, CO_2 purity reaches 97 %, although the absolute values can vary by a few percent, as mentioned above. Higher CO_2 permeance is also essential for practical use, because lower permeance generally leads to a drastic increase in the cost of membrane materials and modules. To design and develop higher performance membrane materials, a molecular simulation approach may be useful for elucidating permeation mechanisms at the atomistic levels[8),9)]. In the future, detailed techno-economic evaluations should be conducted to assess energy efficiencies and costs for membrane separation, as well as other CO_2 capture processes such as chemical absorption.

4. Conclusions

In biomass-to-SNG conversion technology, the energy requirements for the CO_2 separation are inevitably intensive. In this study, process modeling was conducted on the autothermal SNG production process with CO_2/CH_4 membrane separation to determine whether membrane separation has the potential as an alternative to the conventional separation unit. The results showed that recycling from the retentate to the feed side cannot be the best policy in a membrane process, because of the considerable CH_4 loss. Specifically, our simulations showed that CH_4 loss can become lower than 2 % if the recycling is not used, and the separation factor of CO_2 over CH_4 exceeds 50. Therefore, this value should be set as the minimal target value of the CO_2/CH_4 separation factor. Achievement of this goal will probably promote widespread use of SNG production by biomass gasification.

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要　　旨

バイオマスのガス化による合成天然ガス製造プロセスの性能評価と膜分離技術による CO_2 回収の可能性

南雲　　亮，岩田　修一，森　　秀樹

名古屋工業大学大学院工学研究科物質工学専攻，466-8555 名古屋市昭和区御器所町

　近年，バイオマスのガス化によって CH_4 を主成分とする合成天然ガス（SNG）を製造し，化石資源の代替燃料に活用するアプローチの実用化が検討されている。バイオマスのガス化は吸熱反応であるため，メタネーションの発熱反応と統合することで，オートサーマル方式で SNG を製造できる可能性がある。そこで本報告は，オートサーマル型 SNG 製造のプロセス性能を，未反応の H_2 モル分率や CH_4 収率という重要な指標に基づいて評価した。特に，SNG 製造後の CO_2 分離には多大な熱エネルギーを要する点を踏まえ，省エネルギーな CO_2 回収を実現する有力候補としての膜分離法に着目した。その上で，オートサーマル型 SNG 製造システムに膜分離ユニットを導入することの可否を，プロセス計算によって評価した。その結果，膜分離のユニット性能を表す CO_2/CH_4 分離係数の値が50を上回ると，CH_4 損失率が2％未満に抑えられることが判明した。本報告で得られた結果は，CO_2 膜分離型 SNG 製造プロセスの実現可能性を検証するための基礎データとして位置づけられる。

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