Dehydrogenation of ammonia for electricity production: Effect of recirculation fraction

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Abstract. Hydrogen (H2) has been widely studied as a promising energy carrier. However, H2 has a challenging technology in the storage and transportation. Since, it is a critical technology for H2 energy system implementation, the H2 storage and transportation is remain to be solved. This work proposes an integrated system of energy utilization of ammonia (NH3), which has been known as one of the promising methods of H2 storage. The system includes the decomposition of ammonia (NH3) through thermo-catalytic process and also power generation process using H2 as fuel. The heat generated from oxy-fuel combustion of H2 is utilized to supply the thermal energy required for the endothermic process of NH3 decomposition, and the remaining heat is converted to electricity by a combined cycle. A portion of exhaust gas is recirculated to the combustion chamber, and the heat circulation of the system is designed and optimized based on enhanced process integration (EPI), resulting in a highly efficient system. The result shows an optimum configuration of the integrated system with a recirculation fraction of 0.5-0.55, which is resulting in high system efficiency of 51.4%. The proposed work demonstrated an integrated system of H2-based energy utilization of NH3 with CO2-free while maintaining a highly efficient system.

1. Introduction
Recent technology development is putting a serious concern on the environmental aspect, including climate change. Carbon dioxide (CO2), which is considered as one of the greenhouses gases (GSGs), has shown an increasing atmospheric concentration up to 400 ppm [1], increasing interest in research and development of non-carbon-based fuels and their processes. For the same reason, the utilization of renewable energy (RE) sources has drawn research interest, including the energy storage/carrier that is one of the critical technologies for RE implementation.

Hydrogen (H2) has been studied as one of the most promising secondary fuel (or energy carrier) due to its remarkably high gravimetric chemical energy density of 142 MJ kg\(^{-1}\), which nearly three times of gasoline [2]. However, the storage and transportation of H2 are challenging technology, due to its gas phase at standard pressure and temperature. There has been a number of studies on H2 storage and transportation, such as compressed H2, liquid H2, and metal and liquid hydrides [3]. The compression of H2 has to consider the safety risk, while the liquefaction requires cryogenics technology with a super-insulated storage method and consumes a large amount of energy, leaving chemical storage as a promising method for H2 storage.
Many studies have been reported on chemical storage of H₂, including liquid organic H₂ carrier and ammonia (NH₃), with the technical and economic comparison is reported by Wijayanta et al. [4]. The comparison result showed a promising H₂ storage performance of NH₃, represented by high gravimetric H₂ density (17.8 wt%), volumetric H₂ density (120.3 kg-H₂/m³), total energy efficiency (~46% through NH₃-direct fuel cell), and low total cost (approximately 21 JPY/Nm³) [4]. NH₃ is the second most-produced chemical substance in the world with well-established infrastructure and process technology. Despite its relatively high toxicity level and pungent odor, NH₃ is colorless, alkaline, and, most importantly, easy to be stored and transported under a mild condition of pressure and temperature. NH₃ can be stored in a liquid phase at atmospheric pressure and temperature of -33 °C, or at ambient temperature and equilibrium pressure, allowing relatively easy storage with a common vessel for LPG [5]. Moreover, due to its strong odor, NH₃ can be easily detected that can be used for leakage detection to prevent the further effect of toxicity and corrosion. In addition, compared to liquid H₂, NH₃ shows higher round-trip conversion efficiency [6].

As one of the most utilized chemicals, NH₃ is currently produced over 150 Mt/y [7] through various methods, such as the Haber-Bosch process, electrochemical synthesis [8], and catalytic N₂ reduction [9]. Haber-Bosch process dominates the NH₃ production for more than 90% of total NH₃ produced [10]. However, Haber-Bosch, which is an exothermic reaction under temperature and pressure of 300–600 °C and 15–30 MPa, respectively, has a relatively NH₃ low conversion of 15% and energy demand to maintain the reaction. Many studies proposed to improve the NH₃ production through the Haber-Bosch process, such as an innovative integrated system [11], catalysis development [12], and reactor development [13], and also alternative process, such as the thermochemical cycle of NH₃ production [14].

Besides its current primary utilization in agriculture as a nitrogen source for fertilizer, NH₃ has other potential utilization as fuel for power generation. There are two options of NH₃ utilization: direct utilization and indirect utilization through decomposition to H₂. Direct utilization can be performed by combustion and fuel cell conversion. In terms of combustion performance, the flammability of NH₃ (15.5 vol% in air) is much lower than H₂ (27 vol%), which makes H₂ is preferable for the combustion process. In addition, the dominant NOx emission from NH₃ combustion gives another challenge for the direct utilization of NH₃. Therefore, the indirect utilization of NH₃ by decomposition to H₂ is the potential method for NH₃-based power generation. However, the NH₃ decomposition is commonly a catalytic reaction that requires a relatively high temperature above 800 °C, consuming a large amount of energy, which is resulting in a low energy efficiency process. In this work, an integrated system of NH₃ decomposition by a membrane reactor is coupled with a power generation system, with improved heat circulation and minimum exergy loss, resulting in a highly efficient NH₃ utilization system.

2. Methodology
An integrated system of NH₃ utilization is designed based on energy balance and heat circulation in each module, which is enhanced by process integration to optimize the exergy recovery between modules[15]. The heat recovery in each process is evaluated and improved. The stream coupling is also applied in order to improve the heat recovery between processes, which leads to less wasted energy and finally enhance the overall energy efficiency of the system. This method has been applied in many process simulations, including drying [15] and the production and storage of H₂ [14,16].

2.1. Conceptual design
The proposed system consists of three major modules: NH₃ decomposition, combustion, and power generation, as shown in Figure 1. The NH₃ decomposition is carried out in a Packed Bed Membrane Reactor (PBMR), and the required heat energy is supplied from the combustion module. The product of decomposition is H₂ gas, which is supplied to combustion to be reacted with O₂ in the air. The high-temperature fuel gas is fed to the power generation module that consists of a combined cycle system, converting heat to electricity.
2.2. Detailed system design

Detail schematic of the process flow diagram is shown in Figure 2. The system is modeled and evaluated using Aspen Plus (Aspen Technology, Inc.). Several assumptions are used for simulation, such as NH₃ is under the pressurized condition at 30°C, counter flow heat exchangers with minimum pinch temperature of 10°C, ambient pressure is 101.33 kPa and temperature is 25°C, and the changes of kinetic energy, potential energy, and heat losses are neglected due to steady state and ideal condition.

The NH₃ is initially pressurized at the liquid phase; therefore, the pressure is released and preheated by exhaust gas and hydrogen produced by decomposition reaction at HE1 and HE2, respectively. The thermo-catalytic decomposition reaction of NH₃ has been observed under different reactions and types of catalysts and analyzed for several critical parameters of the reaction, such as reaction temperature, conversion rate, etc. [17]. Among potential catalysts, Ruthenium (Ru) has been considered as the most active single-metal catalyst, under different conditions of conversion rate and reaction temperature [17]. With the reaction temperature of 600°C, the Ru-based reaction produces a high conversion rate of 97%. The endothermic reaction of NH₃ decomposition is carried out in PBMR, with heat energy supplied from the combustion reaction of H₂ and O₂ in the air.

After the H₂ gas is reacted with O₂, the high-temperature fuel gas is utilized in PBMR for the NH₃ decomposition reaction. The remaining thermal energy is converted to electricity by a combined cycle module. The combined cycle consists of a gas turbine (GT), steam turbine (ST), and heat recovery steam...
generator (HRSG) with the specification shown in Table 1. Heat circulation optimization is applied by EPI on the steam cycle by utilizing the heat on N2 gas for feedwater preheating. Also, a portion of the exhaust gas is recirculated to the combustion chamber. The waste heat of exhaust gas, which is mostly H2O, is utilized to improve the energy efficiency of the combustion, resulting in higher energy efficiency. In addition, the ratio of recirculation and the flow rate of air is utilized to manage the combustion temperature, which is strongly influencing the GT inlet temperature. Moreover, this air-fuel combustion of H2 and recirculation of exhaust gas also provides a better performance than the Graz cycle which is employing oxy-fuel combustion [16].

| Parameter                      | Value         | Stream (Figure 2) |
|--------------------------------|---------------|-------------------|
| **Gas turbine (GT) [15], [18]**|               |                   |
| Isentropic efficiency (%)      | 90            | -                 |
| Turbine inlet temperature (ºC)| 1500          | F10               |
| Turbine Inlet pressure (MPa)   | 3.0           | F10               |
| **Steam turbine (ST) [15], [18]**|             |                   |
| Isentropic efficiency (%)      | 90            | -                 |
| Turbine inlet pressure (MPa)   | 20            | F20               |
| Turbine inlet temperature (ºC)| 550           | F20               |
| Minimum vapor quality          | 0.88          | -                 |

3. Results and discussion

In this work, the recirculation fraction of exhaust gas is varied and evaluated for its effect on the system performance. The recirculation fraction is defined as the ratio of the recirculated flow rate to the overall flow rate of exhaust gas. The system efficiency is used to evaluate the system performance, and calculated as the ratio of net power generated (\(W_{\text{net}}\)) to the calorific value of the NH3, as shown in equation (1). \(W_{\text{net}}\) is calculated based on total electricity which is generated by both gas (\(W_{\text{GT}}\)) and steam (\(W_{\text{ST}}\)) turbines, considering the power consumption auxiliaries (\(W_{\text{Aux}}\)), such as pumps and compressors, as shown in equation (2). Another performance parameter is power generation efficiency (\(\eta_{\text{power}}\)), which is the ratio of net generated power (\(W_{\text{net}}\)) to the heating value of H2, which is the fuel for power generation. By calculating both of system and power generation efficiency, both of overall system performance and each module performance are evaluated.

\[
\eta_{\text{system}} = \frac{W_{\text{net}}}{\dot{m}_{\text{NH3}} \times LHV_{\text{NH3}}} \quad (1)
\]

\[
W_{\text{net}} = W_{\text{GT}} + W_{\text{ST}} - W_{\text{Aux}} \quad (2)
\]

\[
\eta_{\text{power}} = \frac{W_{\text{net}}}{\dot{m}_{\text{H2}} \times LHV_{\text{H2}}} \quad (3)
\]

Figure 3 shows the effect of recirculation fraction on both of the system efficiency and power efficiency. At a relatively low fraction of recirculation flow, the system efficiency shows an increasing trend as the recirculation fraction increases. Since the recirculation stream has a higher temperature from the remaining heat, there is less energy required to increase the temperature of fuel gas in order to maintain the GT inlet temperature at 1500°C. Therefore, there is more thermal energy converted to electricity, which is resulting in a higher power generation efficiency. The increasing trend of power generation efficiency can be observed for recirculation fraction up to 0.4 and then relatively insignificant change, although the recirculation fraction is increased to 0.5. The GT inlet temperature is majorly determined by combustion energy and the mass flow rate of fuel gas, which is the mixture of air and recirculation stream. Therefore, in order to maintain the combustion temperature, the flow rate of air shall be reduced as the recirculation stream flow rate is increased. On the other hand, the increase of recirculation fraction
will increase the compressor inlet temperature. An increase of compressor inlet temperature will increase the power consumption of compressor, which is the primary power consumption of auxiliary equipment. Therefore, the trade-off relationship between the recirculation fraction and auxiliary power consumption creates a balanced exchange at recirculation fraction between 0.4 – 0.55, with a peak of power generation efficiency of 46.3% at recirculation fraction of 0.5.

![Figure 3. The effect of recirculation fraction on the system and power generation efficiency.](image)

However, a further increase in the recirculation fraction at 0.6 significantly reduce the power generation efficiency to 45.6%. This is caused by a further decrease in airflow rate, which is caused by the increase of recirculation flow rate, is limited by the minimum required amount of \( \text{O}_2 \) for combustion. At recirculation fraction of 0.6, the flow rate of the air stream is too low that has effect of incomplete combustion of \( \text{H}_2 \) in the combustion module due to lack of \( \text{O}_2 \) flow rate.

A similar trend is also observed from the system efficiency as the effect of the recirculation fraction. As shown in equation (1), the system efficiency is determined by net power generation and ammonia decomposition performance. Since the same catalyst is employed at the same reactor temperature, which is resulting in the same theoretical conversion rate of \( \text{NH}_3 \), leaving the net power generation as the only parameter that determines the system efficiency. Therefore, the system efficiency shows a similar trend of the effect of the recirculation fraction with the power generation efficiency.

In summary, the recirculated flue gas to the combustion module can increase the overall system performance, because it also recirculates the waste heat of flue gas to reduce the thermal energy required to increase the feed stream temperature. However, the higher temperature of the feed stream to the compressor may increase the power consumption, resulting in the optimum recirculation fraction at 0.5. In addition, a further increase of the recirculation fraction may reduce the airflow rate, resulting in the lack of \( \text{O}_2 \) required for the combustion reaction.

4. Conclusion

In this work, an integrated system of \( \text{NH}_3 \) decomposition by membrane reactor, is coupled with power generation system, with improved heat circulation and minimum exergy loss, resulting in a highly efficient \( \text{NH}_3 \) utilization system. A portion of flue gas, which is nominated by \( \text{H}_2 \), is recirculated back to the combustion module and the flow rate is varied and evaluated for its effect on the system performance. The results reveal that the recirculated flue gas to the combustion module can increase the overall system performance, because the waste heat of flue gas is utilized. However, a higher temperature of feed stream to the compressor may increase the auxiliary power consumption, resulting the optimum recirculation fraction at 0.5. In addition, further increase of the recirculation fraction may reduce the airflow rate, resulting in the lack of \( \text{O}_2 \) required for combustion reaction.
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