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Combined nitrogen production, ammonia synthesis, and power generation for efficient hydrogen storage

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Abstract

An energy-efficient combined system consisting of nitrogen separation, ammonia synthesis and power generation is proposed and evaluated in this work. The integration of combined processes is carried out using the principles of enhanced process integration (EPI) technology. EPI unites two core technologies: exergy recovery and process integration. The former circulates the energy/heat and intensifies its heat exchange in any single process. In addition, the latter facilitates heat integration and utilization among involved processes. Therefore, the exergy loss throughout the combined processes can be reduced significantly, leading to high total energy efficiency. The proposed combined-processes convert the produced hydrogen, especially from coal and other renewable energy, to ammonia. Therefore, the hydrogen can be stored and transported more efficiently and stable. Haber-Bosch process in adopted as ammonia synthesis. In addition, power generation module is also included to recover the heat produced during ammonia synthesis, as well as supply the electricity consumed for nitrogen production. From process modeling and evaluation, the proposed combined-processes show very high energy efficiency, which is about 66.92%, including NH_3 conversion efficiency (66.69%) and power generation efficiency (0.23%).

Keywords: hydrogen; ammonia; nitrogen production; energy efficiency, enhaced process integration

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1. Introduction

The role of H_2 in future is believed to increase following a higher complexity of energy systems due to the increase of renewable energy share, more liberal energy market, and smarter energy management. H_2 is very potential and appropriate to be used as both energy carrier and storage. It is able store the energy effectively, can be produced and utilized with several established technologies, and has very low environmental impacts during its utilization [1].

However, H_2 faces the problem in its storage due to very low volumetric energy density, which is only about 3 Wh/L [2]. Hence, compact and economic H_2 storage becomes very challenging issue in the utilization of H_2. To store H_2 effectively, several methods and materials have been developed and evaluated. Among them, ammonia (NH_3) is considered potential in terms of efficient storage, technological applicability, and economic performance [3].

NH_3 is alkaline and has penetrating odor. NH_3 is the second largest produced chemical in the world. It has lower density than air, therefore, it dissipates quickly once any leak occurs. It is able to store H_2 as much as 17.8 wt%, which is the highest amongst available liquid organic H_2 carriers, such as methyl cyclohexane, methanol, and ethanol [2]. In addition, NH_3 can be stored in liquid conditions under relatively low pressure, 0.87 MPa under 20 °C of ambient temperature. Hence, it can be stored with inexpensive pressure vessel, as those been usually used for LPG [4]. NH_3 is widely used as both intermediate and end products including fertilizer (about 60%), energy carrier and fuel, pharmaceutics and explosive compounds [5].

In energy sector, NH_3 has been used in many applications including as a liquid fuel for the vehicle employing internal combustion engine, combustion fuel for space heating, direct combustion for power generation, and H_2 carrier for fuel cell. As a H_2 carrier, NH_3 is believed to have a significant role in the future H_2 economy. NH_3 also exhibits all excellent characteristics of H_2 [6]. In addition, compared to H_2, it has narrower flammability limit by volume in air (15.5% compared to 27%) and lower burning velocity [6]. As another option, at the demand side, H_2 can be released from NH_3 through several methods including thermal decomposition and electrochemical process [3].

Currently, NH_3 synthesis is performed mainly through Haber-Bosch, electrochemical process, and membrane reactor [5]. Unfortunately, both electrochemical process and membrane reactor are still immature for application although they have potential to reduce the required energy during synthesis. Haber-Bosch process demands high temperature (400-600 °C) and pressure (up to 30 MPa), due to high dissociation energy of triply bonded nitrogen molecule, in addition of metal catalysts. Although the research to reduce these conditions has been carried out [7], its application is still far. Furthermore, Haber-Bosch process requires N_2 and H_2 as the materials to be converted to NH_3. N_2 is produced through air separation, while H_2 can be derived from various materials including natural gas reforming, oil, coal gasification, and water electrolysis using electricity.

High pressure and temperature conditions leads to high demand of energy input during NH_3 synthesis. In addition, production of N_2 is also very energy intensive which finally reduce the overall energy efficiency during conversion of H_2 into NH_3 [8]. Therefore, some research related to the efforts to intensify the process and improve the energy efficiency have been conducted. A combined system consisting mainly of Haber-Bosch, solid oxide electrolyser and pressure swing adsorption for N_2 production has been proposed and evaluated in [9] using electricity generated from renewable energy. In addition, Frattini et al. [10] also evaluated the combined steam methane reforming and Haber-Bosch process. Unfortunately, those processes only coupled several processes without extensive process intensification, leading to low total energy efficiency.

Smith and Klosek [11] reviewed the integration of air separation with various energy conversion processes, including power generation and gas-to-liquid processes. However, those reviewed processes only integrated the available technologies without giving intensive attention to energy-efficient process integration.

To the best authors' knowledge, there is almost no study focusing on the effort to effectively integrate N_2 production and NH_3 synthesis processes, especially in terms of energy efficiency. Therefore, this study focuses on the effort to effectively integrate the system and circulate the energy/heat involved throughout the system to achieve high energy efficiency.

2. Proposed combined system

The combination of involved processes and heat circulation throughout the combined system is carried out with regard to the foundation of exergy recovery and process integration. The former focuses on the intensification of each process in which the energy/heat involved in any specific process is circulated intensively at first. This principles of this concept has been sufficiently described in [12] and applied in several processes including drying [13] and magnetocaloric effect utilization [14]. In addition, the latter relates to the utilization of unrecoverable heat in any specific process into another process, as well as minimizing the total exergy loss throughout the combined system. The combination of exergy recovery and process integration has been employed in several combined systems including woody biomass gasification [15], and power generation from algae [16], agricultural wastes [17] and pulping industry [18].

Fig. 1 shows process flow diagram of the combined system for NH_3 production. Three processes are involved: N_2 production, NH_3 synthesis (Haber-Bosch process), and power generation. In N_2 production, a cryogenic separation process is adopted. As the products of separation, high purity of N_2 is further reacted with H_2 in NH_3 synthesis. The following reaction occurs during this process.

$$N_2 + 3\,H_2 \rightarrow NH_3 \tag{1}$$

The produced NH_3 is ready for storage and transportation. On the other hand, O_2-rich gas, as the by-product from N_2 production, is used as the reactant for combustion of the purged gas, containing NH_3, H_2 and Ar, from the NH_3 synthesis. The produced heat from combustion of purged gas is used for power generation through combined cycle system. In addition, the generated electricity is partly consumed internally for the system, while another surplus electricity can be sold to the electrical grid as additional revenue.

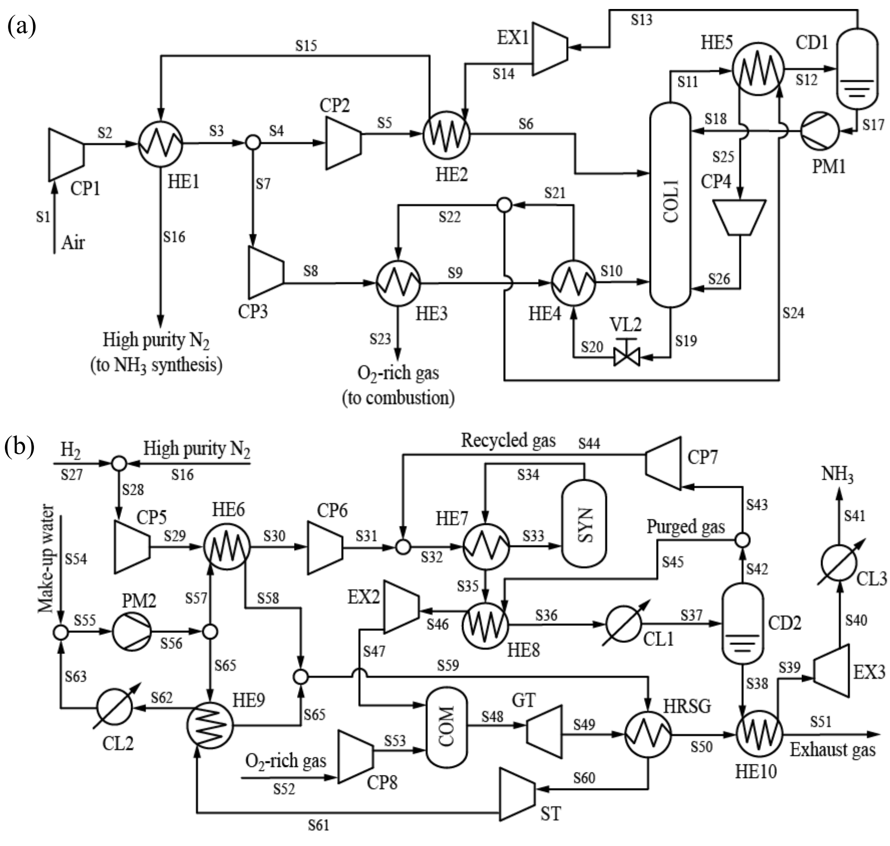

Fig. 1. Process flow diagram of combined NH_3 production system.

3. System analysis

In NH_3 synthesis, because a complete conversion per pass cannot be achieved, the synthesis process operates in a loop mode, in which the produced NH_3 is condensed out of the loop, while fresh input gases are added. To prevent a build-up of impurities, such as Ar, throughout the process, it is important to purge out the stream to the atmosphere. The purged gas also includes H_2 and small amount of gaseous NH_3. Among the available catalysts, wustite-based catalyst, $Fe_{1-x}O$, demonstrated a better performance than magnetite- but still significantly cheaper than Ru-based catalyst [19]. This kind of catalyst has advantages of easy reduction, low synthesis temperature, high activity, and high heat- and poisoning-resistant. In addition, inclusion of promoters including Al_2O_3, CaO, and K_2O can further increase the performance of catalyst.

In conventional system, NH_3 included in the purged gas is generally absorbed using the water at a pressure of about 7.6 MPa, although complete removal is very difficult to achieve. Unfortunately, water scrubbing means wasting NH_3 and a part of H_2 which is product/fuel. Therefore, utilization of purged gas for power generation to cover the energy required for N_2 production and NH_3 synthesis is considered as the best option to improve the total energy efficiency. Table 1 shows the assumed conditions used during process calculation.

The modeling and calculation of the developed combined-system is conducted using a steady state process simulator SimSci Pro/II (Schneider Electric Software, LLC). Additionally, several conditions are also assumed: (a) minimum temperature approach in all heat exchangers is 10 °C, (b) heat exchangers are in counter-current mode, (c) the ambient pressure and temperature are 101.33 kPa and 20 °C, respectively, and (d) air consists of 78.11% N_2, 20.96% O_2, and 0.93% Ar.

Table 1. Assumed calculation condition for the calculation of the combined system.s

Process	Properties	Value
N_2 separation	Column number of stages	48
	Top tray pressure (kPa)	540
NH3 synthesis	Operating temperature (°C)	450
	Operating pressure (MPa)	15
	Catalyst (-)	Iron-oxide base with K_2O and Al_2O_3
Power generation	Gas turbine max. inlet temperature (°C)	1,300
	Steam turbine max. inlet temperature (°C)	600
	Min. vapour quality at steam turbine outlet (-)	0.9
Others	Min. temperature approach in heat exchanger (°C)	10
	Adiabatic efficiency of compressor and pump (%)	87
	Polytrophic efficiency of turbine (%)	90

4. Results and discussion

4.1. N_2 production module

Fig. 2(a) shows the correlation of refed stream ratio to the total required duty to produce 1 tmol-N_2 h^{-1}. In general, lower bottom feed ratio shows lower total duty. In addition, the effect of refed stream ratio to the total duty seems to be relatively influenced by the bottom feed ratio. In addition, Fig. 2(b) shows the purity of produced N_2 in correlation with refed stream and bottom feed ratios. Higher refed stream ratio is demanded to achieve high purity of produced N_2 (higher than 99.0%). In addition, higher bottom feed ratio leads to higher purity at the same refed stream ratios. All the evaluated bottom feed ratios can produce N_2 with purity of higher than 99.0% in case that the refed stream ratio is set to 0.7. The total duties consumed in bottom feed ratios of 0.7, 0.8, and 0.9 to achieve purity higher than 99.0% are 3.16, 3.20, and 3.27 MW tmol-N_2 with N_2 purities of 99.20, 99.68, and 99.94%, respectively. The largest work in N_2 production module is one consumed for compression, especially air compressor.

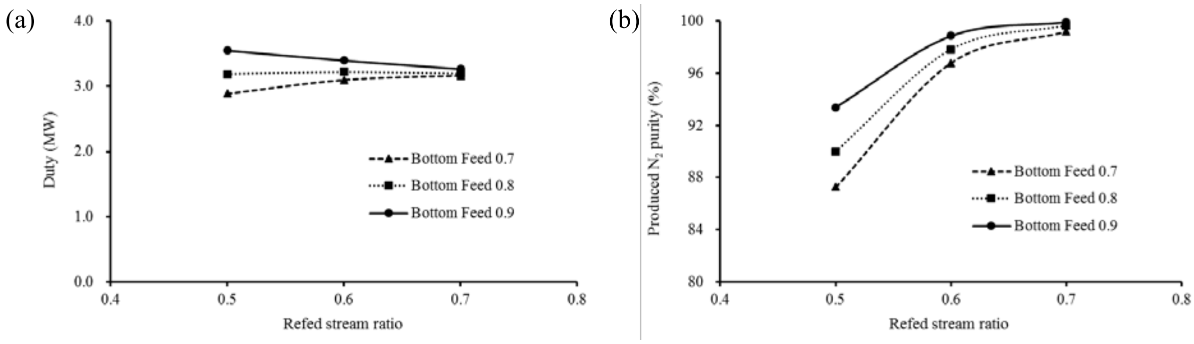

Fig. 2. Performance of the proposed N_2 production module under different refed stream and bottom feed ratios for production of 1 tmol-N_2 h^{-1}: (a) total required duty, (b) purity of produced N_2.

Compared to the recent study on N_2 production [20], the proposed system successfully reduce the energy by about 43% (3.27 compared to 5.76 MWh tmol-N_2^{-1}) with higher produced N_2 purity (99.9% compared to 98.0%).

4.2. NH_3 synthesis and power generation

To perform the evaluation of NH_3 synthesis module, the calculation results of N_2 production with the bottom feed and refed stream ratios of 0.9 and 0.7, respectively, is employed. Fig. 3 shows the performance of the integrated NH_3 synthesis and power generation module under different conversion rates per pass and purged stream ratios. In general, higher purged stream ratio leads to larger net generated power due to higher amount of purged stream used as fuel for combustion in power generation module. However, higher purged stream ratio results in lower total energy efficiency, mainly due to lower NH_3 production efficiency. It seems that conversion rate per pass during synthesis has no significant influence to the both produced work and consumed duty, except the compression work performed by compressor to recirculate the recycled stream. As the flowrate of recycled stream increases in lower conversion rate per pass, the compression duty consumed by the compressor of recycle stream increases accordingly, therefore the net generated power decreases in lower conversion rate per pass.

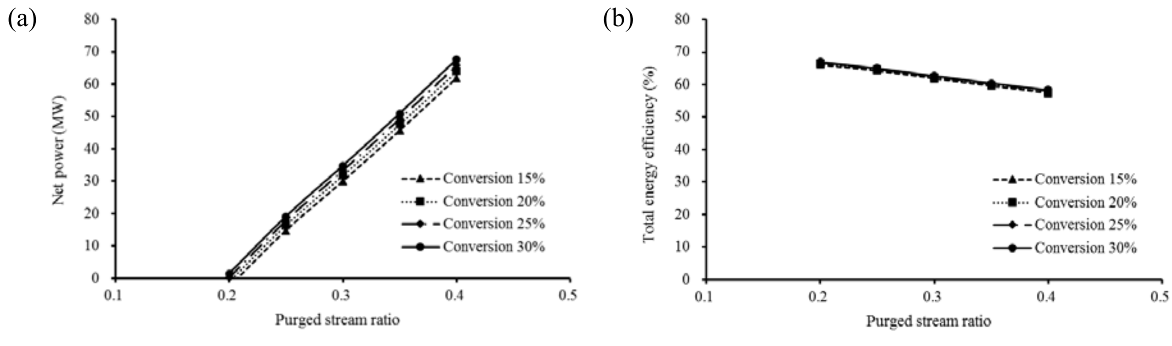

Fig. 3. Performance of the developed NH3 synthesis and power generation module under different conversion rates per pass and purged stream ratios: (a) the achievable net generated power, and (b) total energy efficiency including NH_3 production and power generation.

In case of purged stream ratio of 0.2 and conversions rate per pass of 15 and 20%, the total net generated power is negative (-2.71 and -1.04 MW, respectively) which means that the system requires additional power supply from outside. The highest total energy efficiency achieved by the integrated system is 66.92%, including NH_3 production and power generation efficiencies of 66.69% and 0.23%, respectively, which can be realized under the conditions of conversion rate per pass and purged stream ratio of 30% and 0.2, respectively. The developed system can cover its consumed electricity, therefore, no electricity supply from outside of the system is required.

5. Conclusion

A combined system to store and convert H_2 to NH_3 is proposed. The proposed combined-system consists of N_2 separation, NH_3 synthesis, and power generation. The purged gas containing of a part of H_2 and NH_3 is used as the fuel for combustion, utilizing the O_2-rich gas exhausted from N_2 separation process. The proposed system shows relatively high total energy conversion efficiency, which is about 67% in total including produced NH_3 and generated power.

Acknowledgements

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