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Integrated Nitrogen Production and Conversion of Hydrogen to Ammonia

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A novel integration of N_2 production, NH_3 synthesis, and power generation is performed to realize an effective H_2 conversion system to NH_3. The system employs the principles of exergy recovery and process integration to achieve high-energy efficiency. The produced high purity N_2 from N_2 production module is reacted with H_2 in NH_3 synthesis module to be converted to NH_3. In addition, the produced O_2-rich gas is utilized as the effective oxidant in power generation module. A single column is adopted in N_2 production module, and the feed is divided into two streams which are fed to the middle and bottom of the column. In N_2 production module, two operating parameters of bottom feed and refed stream ratios are evaluated in terms of the consumed energy, N_2 purity and O_2 molar fraction in O_2-rich gas. Compared to previous studies on an N_2 production system, the proposed N_2 production module can reduce the energy consumption of about 43 % (3.27 MW compared to 5.76 MW to produce 1 tmol-N_2 h^{-1}).

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 (Aziz et al., 2016). In addition, massive deployment of renewable energy, which is unpredictable and intermittent, demands energy storage to balance both demand and supply, as well as store the surplus harvested energy.

H_2 is very prospective and appropriate to be used as a secondary energy source (Murmura et al., 2017). It is able to store the energy effectively, can be produced and utilized through several established technologies, and has very low environmental impacts in its utilization (Aziz, 2015). However, H_2 faces problems in its storage due to very low volumetric energy density, which is only about 3 Wh/L (Aziz et al., 2017). Hence, compact and economical 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 storage efficiency, technological application, and economic performance (Goshome et al., 2016).

NH_3 is alkaline, odorless, and has a penetrating odor. NH_3 is the second largest produced chemical in the world. NH_3 has a lower density than air. Therefore, it dissipates quickly once any leak occurs (Angeles et al., 2017). It is able to store H_2 as much as 17.8 wt%, which is the highest amongst the available liquid organic H_2 carriers, such as methyl cyclohexane, methanol, and ethanol (Goshome et al., 2016). In addition, NH_3 can be stored in liquid condition under relatively low pressure, 0.87 MPa under 20 °C of ambient temperature. Hence, it can be stored with inexpensive pressure vessels, which have usually been used for LPG (Varisli and Kaykac, 2016). NH_3 is widely used as intermediate and end products, including fertilizer (about 60 %), energy carrier and fuel, pharmaceutics, and explosive compounds (Edrisi et al., 2014). Currently, NH_3 synthesis is performed mainly

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through Haber-Bosch, electrochemical, and membrane separation processes (Giddey et al., 2013). Unfortunately, both electrochemical and membrane separation processes are still immature for the application. The 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 to metal catalysts. Although the research to reduce these conditions has been carried out (Vojvodic et al., 2014), 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 partial oxidation, coal gasification, and water electrolysis using electricity.

High pressure and temperature conditions lead to the high demand of energy input during NH_3 synthesis. In addition, production of N_2 is also very energy intensive which finally reduces the total energy efficiency during conversion of H_2 into NH_3 (Aneke and Wang, 2015). Therefore, several research studies related to the efforts to intensify the process and improve the energy efficiency have been conducted. A coupled system consisting of the Haber-Bosch reactor, solid oxide electrolyzer, and pressure swing adsorption for N_2 production has been proposed and evaluated by Cinti et al. (2016) using electricity generated from renewable energy. Moreover, Frattini et al. (2016) evaluated the combined steam methane reforming and Haber-Bosch process. However, they only coupled several processes without extensive process intensification, resulting in low total energy efficiency. Smith and Klosek (2001) reviewed the integration of air separation with various energy conversion processes, including power generation and gas-to-liquid process. However, those reviewed processes only integrated the available technologies without paying intensive attention to the energy-efficient process integration.

To the best of authors' knowledge, there is almost no study focusing on the effort to effectively integrate N_2 production and NH_3 synthesis, 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 total energy efficiency.

2. Process design and calculation

2.1 Integrated system

Process integration 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 process is initially circulated intensively. These principles have been sufficiently described in (Kansha et al., 2013) and applied in several systems, including drying (Liu et al., 2013). In addition, the latter deals with the utilization of unrecoverable heat in any process to other processes, hence, minimize further the total exergy loss throughout the combined system.

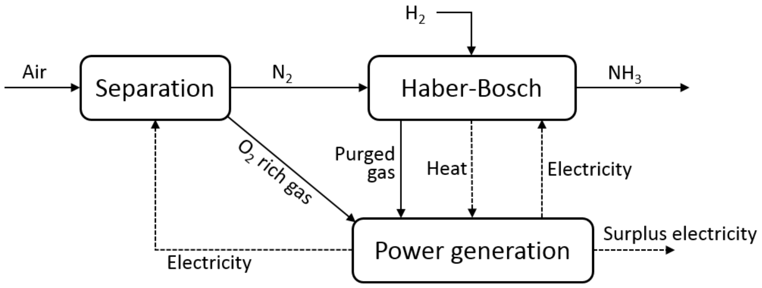

Figure 1: Schematic diagram of the integrated system

Figure 1 shows the basic schematic diagram of the combined system for NH_3 production. Three main processes are involved: N_2 production (separation), NH_3 synthesis (Haber-Bosch process), and power generation. In N_2 production, air is separated into the high purity of N_2 and O_2-rich gas streams. N_2 stream is utilized as a feed stream in NH_3 synthesis and reacted with H_2 to produce NH_3. On the other hand, O_2-rich gas is utilized as a reactant for combustion of the purged stream from NH_3 synthesis. Furthermore, the generated heat from power generation and NH_3 synthesis are recovered for power generation through the combined cycle.

Figure 2 shows the process flow diagram of the proposed integrated system. Cryogenic N_2 production is adopted with consideration of applicability for large scale and high purity of produced N_2 stream (Smith and Klosek, 2001). Air is compressed in multistage compressors (CP1, CP2, and CP3) and split into two streams, which are fed into the distillation column (COL1) in different stages. Air is then cooled down using the separated N_2 and O_2-rich streams through several heat exchangers. An expander (EX1) is installed to recover the compression work brought by the produced N_2 stream (S13) and provide sufficient cold heat for the stream fed to the column (S6), leading to a self-heat exchange.

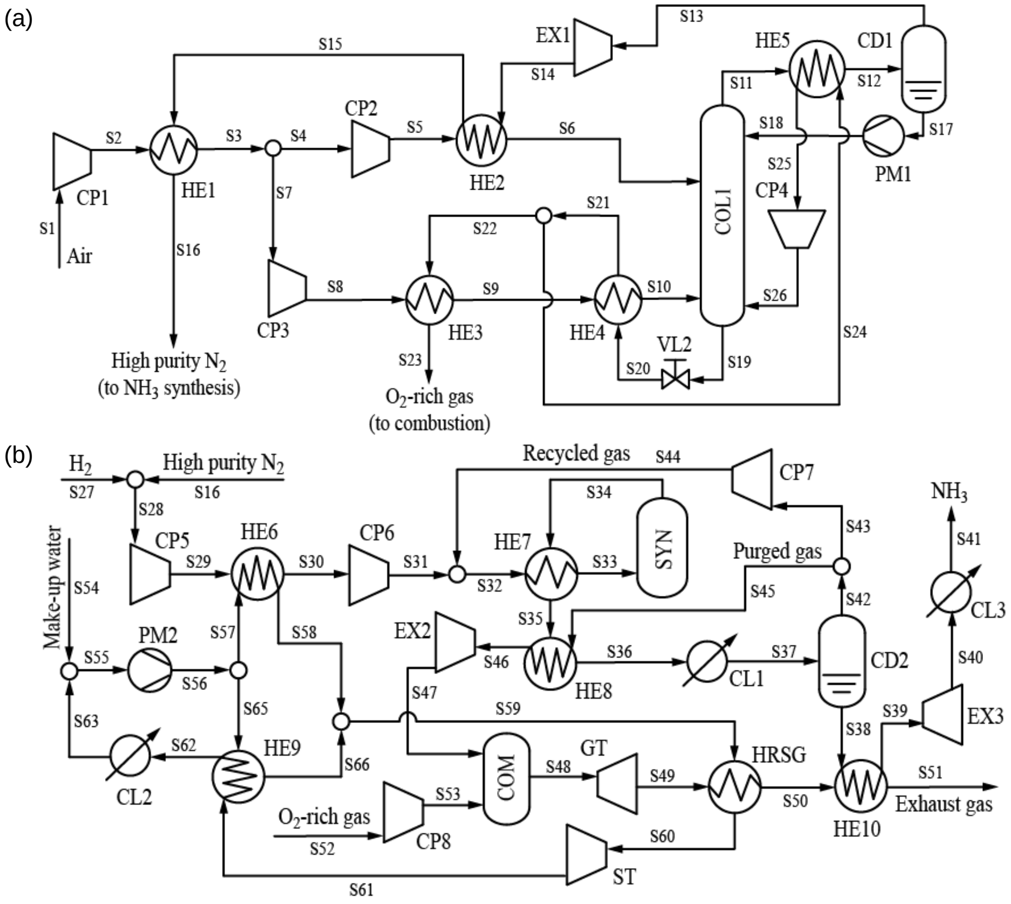

Figure 2: Process flow diagram of the proposed integrated system: (a) N_2 production, (b) NH_3 synthesis and power generation

A single distillation column (COL1) is adopted in this study with consideration of N_2 as the main product (not O_2), and also the advantages in system simplicity and low installation cost. To improve the energy efficiency, similar to VRC technology, reboiler and condenser are eliminated and changed with a heat exchanger (HE5). To facilitate condensation and re-boiling of overhead and bottom (refed) streams, respectively, the separated bottom stream (refed stream; which is in liquid condition) is at first expanded by a valve (VL1) to drop its temperature. Therefore, it can supply the cold heat to the overhead stream to condense in HE5. Furthermore, the refed stream is then compressed (using CP4) to the designated pressure and refed to the distillation column. By applying this system, the self-heat exchange among the streams can be achieved, leading to lower exergy loss and, hence, higher energy efficiency can be achieved. The produced highly pure N_2, and the rest of O_2-rich gas are going to NH_3 synthesis and power generation modules, respectively.

As the feed stream in NH3 synthesis, H_2 and N_2 gases are mixed and compressed through multi-stage compression (CP5 and CP6). NH_3 synthesis occurs in reactor SYN, and the mixture of produced NH_3 and unreacted gas is used for preheating in HE7.

The mixture of NH_3 and unreacted gas is cooled down in cooler (CL1) and separated in condenser (CD2). The unreacted gas is split into recycled and purged gases. The former is recycled and mixed with the fresh feed stream containing N_2 and H_2, while the latter is utilized for power generation. Because a complete conversion per pass cannot be achieved (fractional conversion rate per pass in the reactor is about 10–30 % (Liu, 2013)), the synthesis 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. The purged stream also includes H_2, N_2, and a small amount of gaseous NH_3. In the proposed system, the purged stream is utilized for power generation supplying the electricity consumed internally, including N_2 production.

HE7 is the preheater installed before NH_3 synthesis reactor to heat up the feed stream for reaction. In addition, reheating of the produced NH_3 after condensation is conducted in HE10 in order to recover the compression energy brought by condensed NH_3. For this purpose, EX3 is installed after HE10 to produce additional electricity. On the other hand, also to recover the compression work (due large pressure gap between NH_3 synthesis and combustion) brought by the purged gas (S45), a reheater (HE8) and an expander (EX2) are installed.
For power generation, four expanders are employed for power generation: purged gas expander (EX2), gas turbine (GT), steam turbine (ST), and NH_3 expander (EX3). At first, as the pressure of the purged gas is still high, it is expanded to the designated combustion pressure. The O_2-rich gas from N_2 production module is utilized as the reactant for combustion. In order to suppress the NO_x formation, combustion temperature is also controlled using the flowrate of O_2-rich gas.

2.2 Process calculation

Table 1 shows the calculation conditions in N_2 production, NH_3 synthesis, and power generation. In addition, modeling and process calculation are conducted using a steady state process simulator SimSci Pro/II (Schneider Electric Software, LLC.). The input flowrates of H_2 and N_2 in NH_3 synthesis module are 9 and 3 tmol h^{-1}, respectively. The heat exchangers involved in the system is considered in counter-current mode with a minimum temperature approach of 10 °C. In addition, the ambient pressure and temperature are assumed at 101.33 kPa and 20 °C, respectively. The outlet pressure of NH_3 expander (EX3) is set at 1 MPa; therefore, the produced NH_3 is ready for storage and transportation.

Table 1: Assumed calculation conditions

Module	Specifications	Value	Note
N_2 production	Number of stages	48	
	Feed stages	20, 47	
	Top pressure (kPa)	540	
	Refed stream ratios (%)	0.5, 0.6, 0.7	
	Bottom feed ratios (%)	0.7, 0.8, 0.9	
	Number of stages	48	
NH_3 synthesis	Operating pressure (MPa)	15	(Liu, 2013)
	Operating temperature (°C)	450	(Liu, 2013)
	Catalyst	$Fe_{1-x}O$	(Liu, 2013)
	Conversion rate per pass (%)	15, 20, 25, 30	
	Purged stream ratio	0.2, 0.25, 0.3, 0.35, 0.4	
Power generation	Max. gas turbine inlet temperature (°C)	1,500	
	Gas pressure (MPa)	2	
	Max. steam turbine inlet temperature (°C)	600	
	Steam pressure (MPa)	20	
	Min. outlet vapor quality (-)	0.9	

3. Results and discussion

3.1 N_2 production module

Figure 3 shows the calculation results on the performance of the proposed N_2 production module for production of 1 tmol-N_2 h^{-1}. Two operating parameters are evaluated: bottom feed and refed stream ratios. The former is defined as the mass ratio of air fed into the bottom of the column (S10) to the total air fed to the same column (S1). The latter is described as the mass ratio of the circulated stream to the bottom (S22) to the total stream exhausted from the bottom (S17).
Figure 3(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, Figure 3(b) shows the purity of produced N_2 in correlation with both refed stream and bottom feed ratios. Higher refed stream ratio is demanded to achieve a 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 0.70, 0.80, and 0.90 to achieve purity higher than 99.0 % are 3.16, 3.20, and 3.27 MW, with N_2 purities of 99.20, 99.68, and 99.94 %, respectively. The largest work in N_2 production module is the power consumed for compression by CP1 and followed by CP3.

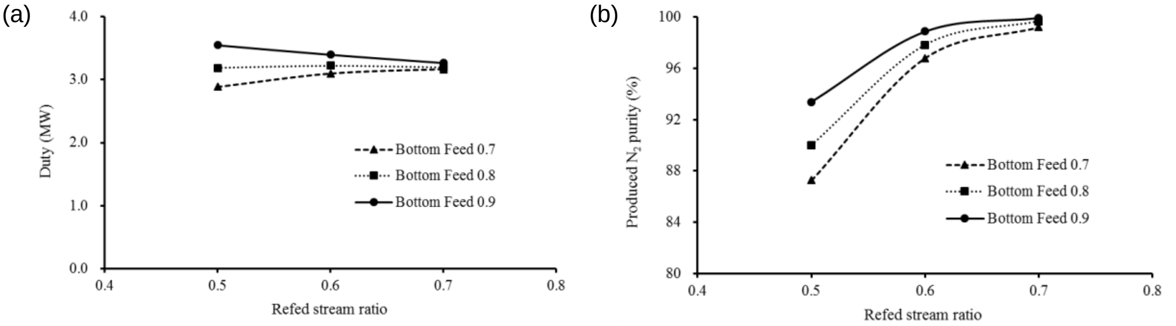

Figure 3: Calculation results on the performance of N_2 production module (the effects of refed stream and bottom feed ratios): (a) total duty, (b) produced N_2 purity

3.2 Energy efficiency of the integrated system

To perform the calculation and evaluation of NH_3 synthesis and power generation modules, the calculation results of N_2 production with the bottom feed and refed stream ratios of 0.9 and 0.7, respectively, are employed. Figure 4 shows the total energy efficiency achieved by the integrated NH_3 synthesis and power generation module under different conversions per pass and purged stream ratios. Generally, lower purges stream ratio leads to higher total energy efficiency, which is the total of NH_3 conversion efficiency and power generation efficiency. In addition, conversion rate per pass shows no significant influence on the total energy efficiency. Lower purged stream ratio results in higher total energy efficiency, mainly due to higher NH_3 production efficiency. It seems that conversion rate per pass during synthesis has no significant influence on both produced work and consumed duty, except the compression work performed by CP7 to recirculate the recycled stream (S43). As the flowrate of recycled stream increases in lower conversion rate per pass, the compression duty by CP7 increases accordingly; therefore, the net generated power decreases in lower conversion rate per pass.

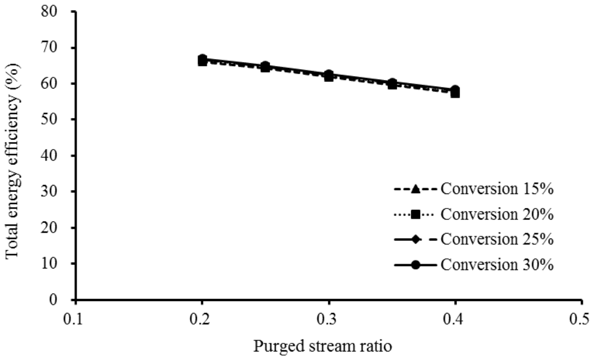

Figure 4: Energy efficiency of the total integrated system

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 an additional power supply from outside. The highest total energy efficiency achieved by the integrated system (including N_2 production) is 66.92 %, which is the sum of NH_3 production and power generation efficiencies of 66.69 % and 0.23 %, respectively. It can be realized under the conditions of conversion rate per pass and purged stream ratio of 30 % and 0.2, respectively.

From the results, higher conversion rate per pass and lower purged stream ratio are considered as essential objective parameters in NH_3 synthesis. In addition, since the maximization of the amount of produced NH_3 or NH_3 production efficiency is more important than power generation, lower purged stream ratio is demanded for the proposed H_2 to NH_3 conversion system.

4. Conclusions

An integrated system converting H_2 to NH_3 is designed in this study based on exergy recovery and process integration technologies. The integrated system includes N_2 production, NH_3 synthesis, and power generation.

First, N_2 production module shows very high energy efficiency and purity. In addition, the integrated system has relatively high total energy efficiency, including NH_3 synthesis and power generation. The achievable total energy efficiency of the integrated system is 66.92 %, including NH_3 production efficiency of 66.69 % and power generation efficiency of 0.23 %. From the energy point of view, the proposed system is considered promising as the currently available technologies for N_2 production and NH_3 synthesis consumed very large energy input.

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