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Research Article

Improving Mass Efficiency in Ammonia Production from Hydrogen and Nitrogen Through Optimizing Operating Condition

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Abstract

As one of the main raw materials in the fertilizer industry, global ammonia consumption continued to increase from 2010 to 2020, at a rate of about 1.81% per year. The ammonia production process is divided into four main stages: Feed Gas Pre-Treatment, Syngas Generation, Syngas Purification, and Ammonia Synthesis. The raw materials required for the ammonia production process include natural gas, steam, and air. To meet the increasing demand for ammonia, a production process with high efficiency is required in order to produce high conversion. One of the efforts to increase efficiency is through the addition of recycling, compressors, and TEE in the Aspen HYSYS simulation. With this increase in conversion, it is expected that the quantity of ammonia products produced will be greater, and the use of materials and energy will be more optimal. The method used to increase mass efficiency is by adding recycling, compressors, TEE, and adjusting the pressure in the separator. From this simulation, it can be concluded that our simulation shows an increase in mass efficiency compared to the simulation without the addition of compressors, recycle, and TEE in Aspen HYSYS. We can increase the mass conversion from 97% up to 99.09%. Net energy of the process can be reduced from 2.59e+8 to 1.64e+8 BTU/h.

Keywords: Ammonia production; syngas; optimization of operating conditions; Ammonia Synthesis

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1. Introduction

Syngas is a fuel made from a mixture containing hydrogen (H_2), carbon monoxide (CO) and methane (CH_4) [1]. Syngas also often contains argon (Ar) and nitrogen (N_2) that can be used to make ammonia, methanol and Fischer-Tropsch liquids (FTLs). Ammonia has a melting point -57.5 °C and a boiling point of 37.7 °C [2]. Gases that made up ammonia have specific nature, such as boiling point (-346 °F), melting point (-346 °F), critical temperature (-232.5°F) [3], meanwhile hydrogen (H_2) gas has the melting point of -259.2 °C and boiling point of -253 °C [4]. The production of syngas uses a partial oxidation process, an exothermic reaction that does not require high energy to start and needs to remove heat from the catalyst. Combined with the Haber-Bosch process (HB) that constitutes the dominant route for ammonia production, Although the reaction itself is exothermic, it requires significant energy input.

Nowadays, ammonia synthesis consumes 1%–2% of the total energy worldwide. The energy is primarily consumed for hydrogen production from the strongly endothermic steam-methane reforming (SMR) at 800 °C–1.000 °C equilibrium reaction. The reaction is as follows [5]:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H_{r,298\,K} = +206.1\ kJ.mol^{-1} \qquad (1)$$

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As well as reactant purification and compression. The effluents are subsequently fed to a shift reactor with excess steam at 350 °C–550 °C, to eliminate carbon monoxide and maximize hydrogen yield through the slightly exothermic water-gas shift (WGS) reaction [6]:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \ \Delta H_{r,298\,K} = +41.2 \text{ kJ.mol}^{-1} \tag{2}$$

The HBP, also known as the Haber process, is one of the most popular ways to produce NH3 [7]. Ammonia, produced via the Haber- Bosch (HB) process, is globally the leading chemical in energy consumption and carbon dioxide emissions. In ammonia plants, hydrogen is generated by steam-methane reforming (SMR) and watergas shift (WGS) and, subsequently, is purified for the high pressure ammonia synthesis [8]. Hydrogen extraction from the reforming compartment enhances the thermodynamically limited methane conversions, whereas 5%–14% of the pumped protons are converted to ammonia [6]. The reaction is exothermic and cooling is required to maintain reactor [1].

Ammonia is synthesized at atmospheric pressure by employing protons and electrons, then the thermodynamic restrictions of methane conversion at low temperatures (550 ℃–650 ℃) are surpassed through hydrogen extraction from the steam reforming chamber. Last, methane is directly converted to CO_2 instead of CO due to WGS dominance at these temperatures, thereby maximizing hydrogen yield in a single device and eliminating the need for a shift reactor downstream [6].

The main reaction that produces the product ammonia takes place in the gas phase and is exothermic. Nitrogen gas (N_2) reacts with hydrogen gas (H_2) to produce ammonia (NH_3) [9]. After the synthesis reaction in the reactor, the mixture, which includes unreacted nitrogen and hydrogen along with ammonia, undergoes cooling and separation. After the synthesis reaction in the reactor, the mixture, which includes unreacted nitrogen and hydrogen along with ammonia, undergoes cooling and separation [10]. In 1898, Adolph Frank and Nikodem Caro found that N_2 could be fixed by calcium carbide to form calcium cyanamide, which could then be hydrolyzed with water to form ammonia, but because this process required large amounts of energy, scientists focused their efforts on reducing energy requirements.

German chemist Fritz Haber performed some of the most important work in the development of the modern ammonia industry. He synthesized ammonia in the laboratory from N_2 and H_2, as follows [9]:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \ \ \Delta H_{r,298\,K} = -92.2 \text{ kJ.mol}^{-1} \tag{3}$$

The raw materials required for the ammonia production process include natural gas, steam, and air [11]. To improve the mass efficiency of ammonia during the production process, a new chemical looping process was designed for H_2 and NH_3 [12]. The updating of our study by adding recycling, a compressor, TEE, and increasing the pressure inside the separator in Aspen HYSYS simulation is very important. It can help study the improvement of mass conversion in ammonia production. We increased the mass conversion from 97.00% up to 99.09%.

2. Methods

2.1. Basic Process Flow Diagram

The basic flow diagram (Figure 1) is the basis of ammonia production considered in this study. Ammonia production is not maximized due to the presence of ammonia gas in the exhaust gas. In the ammonia production process, the property package used is the Peng-Robinson. The fluid package used in the process is the Peng-Robinson (PR) property package [13]. The selection of Peng-Robinson for this process is due to its involvement with hydrocarbon compounds and its suitability for analyzing gas-liquid, gas-liquid-liquid phase equilibrium, and phase equilibrium in multicomponent mixture systems. Hence, this equation is suitable for use in the ammonia production process [14].

2.2. Modification Method to Improve the Process

The Addition of Recycling, Compressor, and TEE: The addition of recycling is done after the process in the separator using the remaining ammonia vapor results that are directed towards the TEE. The addition of TEE is carried out to separate one percent of the purge, which is then directed to the recycle. Then after the recycle is flowed to the compressor to increase the pressure before entering the mixer so that the pressure is the same.

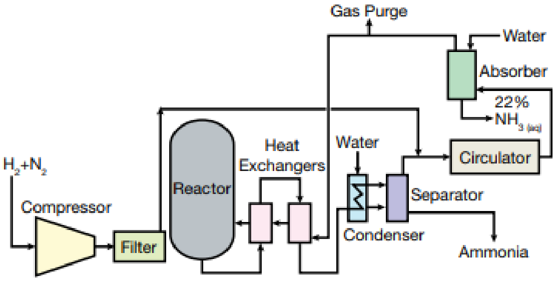

Figure 1. Basic process flow diagram (unmodified).

Changes in Pressure Within the Separator: the pressure in the separator undergoes a change from the initial pressure of 0 bar to 100 bars. This pressure change results in an increase in mass efficiency in ammonia production [15].

The review was conducted by measuring the resulting reaction conversion in ammonia production. The mole fraction of components were compared between before modification and after modification. Mass efficiency is a parameter that measures the extent to which a system or process can convert the mass of a particular substance into energy or perform work. It is often used in the context of engines or combustion processes, where fuel is transformed into energy. To calculate mass efficiency in the ammonia production process, we can use the general formula for mass efficiency:

$$\text{Mass Efficiency} = \frac{\text{Ammonia Production}}{\text{Mass of fuel}} \times 100\ \% \tag{1}$$

3. Results and Discussion

3.1. Ammonia Production Composition Comparison

It can be seen in Table 1 and Table 2 that after recycling is performed, there is an increase in the mol fraction composition of ammonia from 0.9754 to 0.9909. Thus, by optimizing the ammonia production process using recycling, the ammonia percentage can be increased, and the presence of residual ammonia vapor that is discarted can be minimized. The remaining ammonia vapor of 0.1272 is flowed to the recycle to be reacted again with the feed in the reactor.

3.2. Process Flow Diagram of Ammonia Production

For the first step (Figure 2), syngas that is used for the feed is set on the compressor to reach the needed requirement, such as temperature (280 ºC), pressure (25.5 bar_g), molar flow (7000 kgmol/h) and composition mole fraction H_2 (73.71%), N_2 (24.74%), CO (0.24%), Ar (0.27%), and CH_4(1.03%). Thus, the second step is that the

Table 1. Mole fraction composition of basic process (unmodified)

Component Mole Fraction	Syngas-2	Syngas terkompresi-2	Cooler feed-2	Reaktor feed-2	Produk V	Produk L	Produk dingin	V	L
Methane	0.0103	0.0103	0.0103	0.0103	0.0128	0.0129	0.0128	0.0147	0.0025
Ammonia	0.0000	0.0000	0.0000	0.0000	0.2446	0.2465	0.2446	0.1098	0.9574
Nitrogen	0.2475	0.2475	0.2475	0.2475	0.1857	0.1854	0.1857	0.2192	0.0041
CO	0.0024	0.0024	0.0024	0.0024	0.0030	0,0030	0.0030	0.0035	0.0001
Argon	0.0027	0.0027	0.0027	0.0027	0.0034	0.0034	0.0034	0.0034	0.0009
Hydrogen	0.7371	0.7371	0.7371	0.7371	0.5505	0.5489	0.5505	0.5505	0.0170

Table 2. Mole fraction composition of the modified process

Component Mole Fraction	Syngas-2	Syngas terkompresi-2	Cooler feed-2	Reaktor feed	Produk V	Produk L	Produk dingin
Methane	0.0103	0.0103	0.0103	0.0103	0.0128	0.0129	0.0128
Ammonia	0.0000	0.0000	0.0001	0.0001	0.2447	0.2466	0.2447
Nitrogen	0.2475	0.2475	0.2475	0.2475	0.1857	0.1853	0.1857
CO	0.0024	0.0024	0.0024	0.0024	0.0030	0.0030	0.0030
Argon	0.0027	0.0027	0.0027	0.0027	0.0034	0.0034	0.0034
Hydrogen	0.7371	0.7370	0.7370	0.7370	0.5504	0.5488	0.5504
Component Mole Fraction	V	L	Recycle	Purge	Recycle ke kompresor	Recycle mixer	
Methane	0.0147	0.0012	0.0147	0.0147	0.0147	0.0147	
Ammonia	0.1272	0.9909	0.1272	0.1272	0.1272	0.1272	
Nitrogen	0.2147	0.0015	0.2147	0.2147	0.2147	0.2147	
CO	0.0034	0.0001	0.0034	0.0034	0.0034	0.0034	
Argon	0.0038	0.0004	0.0038	0.0038	0.0038	0.0038	
Hydrogen	0.6362	0.0059	0.6362	0.6362	0.6362	0.6362	

compressed syngas enters the mixer with a mixer temperature condition of 934.6 °C. Then, the syngas goes into the cooler to lower its temperature to 482 °C before entering the conversion reactor. The operating conditions in the reactor employ the reaction in Equation (3) [16].

The temperature in the reactor is maintained at 482 °C, the reactor temperature is elevated to facilitate the reaction and align with the Haber-Bosch method. The resulting steam exiting the reactor will be passed to the cooler with a pressure drop of 100 bars, and the temperature of the exiting product is 26.8 °C so

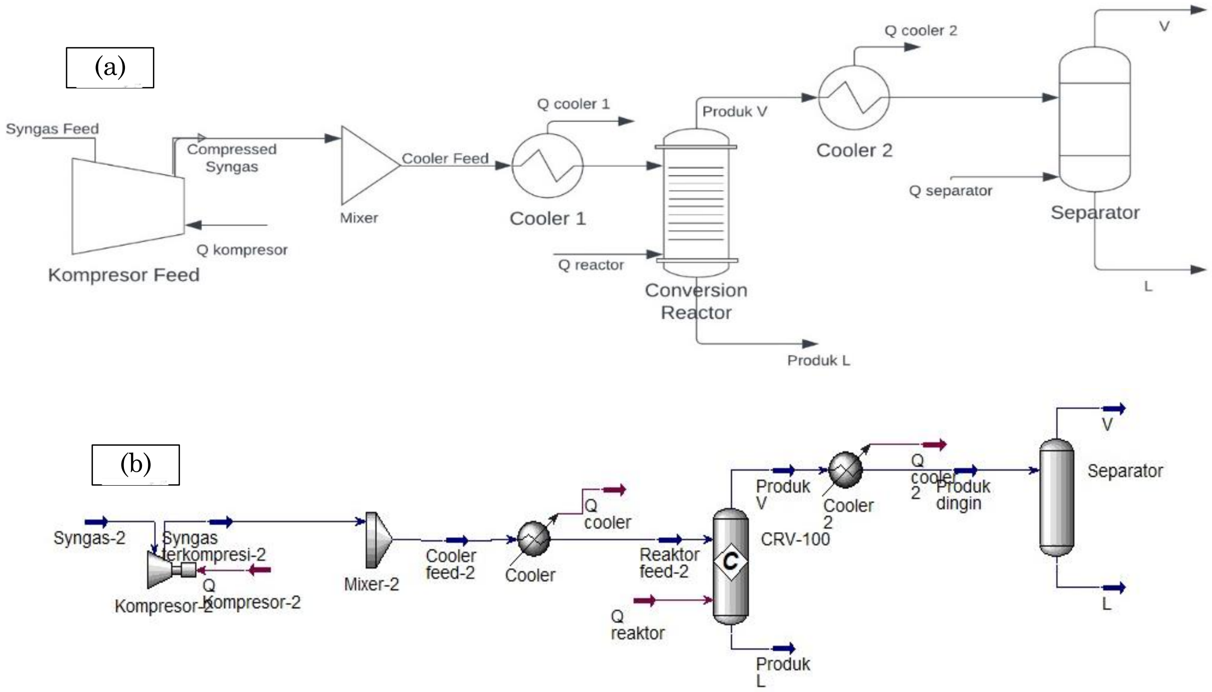

Figure 2. Basic Process Flow Diagram of ammonia production (a) and its HYSYS simulation (b)

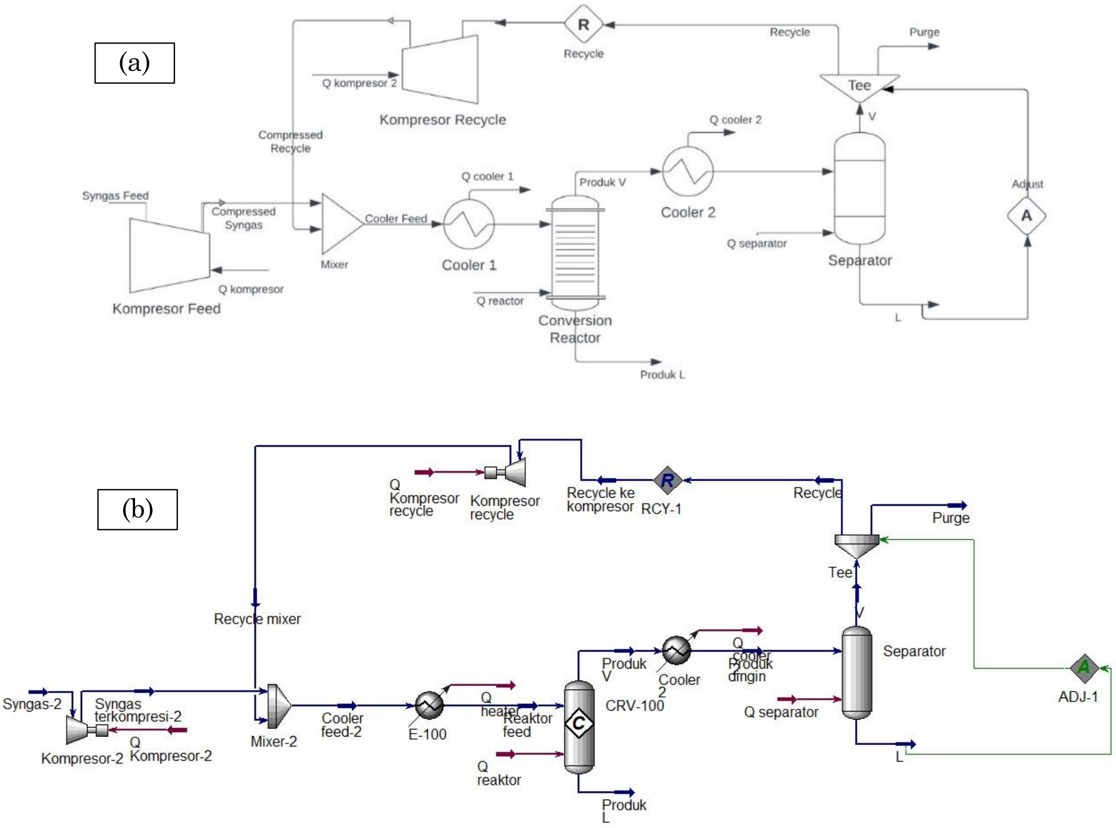

Figure 3. Process Flow Diagram of ammonia production with recycling (a) and its HYSYS simulation (b)

that liquid ammonia product can be obtained, which will later be separated by a separator. The vapor separator's output still contains ammonia that can be reused by recycling. The ammonia vapor from the separator is directed towards the TEE to have one percent discharged as a purge, and the remainder is directed to the recycle. The output from the recycle is compressed to match the pressure of the compressor output (Figure 3). Lennon's patent application (2017) include that compressing the recycle gas is an essential step in the ammonia production process, as it helps manage pressure, optimize energy consumption, reduce emissions, and prepare the gas for further processing, which is 274 bar_g. The effect of realtive evaporation in the separator is influenced by differences in vapor pressure, the upper results in the separator produce greater levels of hydrogen and nitrogen than in the lower results, while ammonia levels in the lower results of the separator are greater than in the upper results. The separator temperature of 14 °C makes the percentage of hydrogen content in the upper results greater, while the ammonia content in the lower results is greater than in the upper results. The pressure in the separator is 74 bar_g, this affects the ammonia content of the lower yield which is greater and the upper yield of hydrogen with greater nitrogen.

3.3. Thermodynamic Analysis

The change in enthalpy for the reaction in Equation (3) ($N_2 + 3H_2 \rightleftharpoons 2NH_3$) is -92.2 kJ/mol 298 K, while the enthalpy of formation for 1 mol of ammonia can be determined by dividing the equation by two, resulting in the heat of formation of ammonia (ΔH) being -46.1 kJ/mol. Based on Tables 3-5, we can compare that the effect of our process modification makes the vapour output

Table 3. Material balance streams before modified with recycling

Parameters		Syngas-2	Syngas terkompresi-2	Cooler feed-2	Reaktor feed	Produk V	Produk L	Produk dingin	V	L
Vapour Fraction		1.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.8442	1.0000	1.0000
Temperature	C	280.0	934.6	934.6	481.9	481.9	481.9	26.85	26.85	26.85
Pressure	Bar_g	25.50	274.0	274.0	274.0	274.0	274.0	174.0	174.0	174.0
Molar Flow	Kgmole/h	7000	7000	7000	7000	5624	0.0000	5624	4748	876.3
Mass Flow	Kg/h	6.132e+4	6.132e+4	6.132e+4	6.132e+4	6.132e+4	0.0000	6.132e+4	4.656e+4	1.476e+4
Liquid Volume Flow	gpm*	3.752e-6	3.752e-6	3.752e-6	3.752e-6	2.956e-6	0.0000	2.956e-6	2.530e-6	4.263e-7
Heat Flow	Btu/h	4.250e+7	1.796e+8	1.796e+8	8.476e+7	1.341e+7	0.0000	-8.516e+7	-3.127e+7	-5.389e+7

Table 4. Material balance streams after modification with recycling

Parameters		Syngas-2	Syngas terkompresi-2	Cooler feed-2	Reaktor feed	Produk V	Produk L	Produk dingin
Vapour Fraction		1.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.8441
Temperature	C	280.0	934.6	934.1	481.9	481.9	481.9	26.85
Pressure	Bar_g	25.50	274.0	274.0	274.0	274.0	274.0	174.0
Molar Flow	Kgmole/h	7000	7000	7000	7005	5628	0.0000	7005
Mass Flow	Kg/h	6.132e+4	6.132e+4	6.137e+4	6.137e+4	6.136e+4	0.0000	6.136e+4
Liquid Volume Flow	gpm*	3.752e-6	3.752e-6	3.754e-6	3.754e-6	2.958e-6	0.0000	2.958e-6
Heat Flow	Btu/hr	4.250e+7	1.796e+8	1.796e+8	8.479e+7	1.340e+7	0.0000	8.526e+7
Parameters		V	L	Recycle	Purge	Recycle ke kompresor	Recycle mixer	
Vapour Fraction		1.0000	0.0000	1.0000	1.0000	1.0000	1.0000	
Temperature	C	14.21	14.21	14.21	14.21	14.21	181.4	
Pressure	Bar_g	74.00	74.00	74.00	74.00	74.00	274.0	
Molar Flow	Kgmole/h	4862	765.9	4.862	4857	4.862	4.862	
Mass Flow	Kg/h	4.837e+4	1.299e+4	48.37	4.832e+4	48.37	48.37	
Liquid Volume Flow	gpm*	2.586e-6	3.717e-7	2.586e-9	2.586e-6	2.586e-9	2.586e-9	
Heat Flow	Btu/h	-3.654e+7	-4.872e+7	-3.654e+4	-3.650e+7	-3.654e+4	-3.654e+4	

Table 5. Energy balance before and after modification with recycling

Energy Streams	Unit	Q Kompresor-2	Q Kompresor-Recycle	Q Reaktor	Q Cooler 2	Q Heater	Q Separator	Q Cooler	**Net Energy**
Before recycling	Btu/h	1.371e+8	2.372e+4	-7.139e+7	9.866e+7	9.476e+7	1000	-	**2.59e+8**
After recycling	Btu/h	1.371e+8	-	-7.139e+7	9.858e+7	-	-	9.481e+7	**1.64e+8**

molar flow larger compare to the basic process. Thus the molar flow of liquid on separator be decreased after modification, but make it become more purify. On the other hand, the temperature and pressure conditions in the separator after being modified change the percent yield of ammonia liquid to be better and almost reach 100%. Net energy of the process can be reduced from 2.59e+8 to 1.64e+8 BTU/h.

4. Conclusion

Based on the simulation conducted with the addition of a compressor, recycle, and TEE, we succeed to increase the mass conversion from 97% up to 99.09%. Also by increasing pressure on the separator can lift up the conversion number on ammonia production. On this process we suggest to notice the increasing of the net energy in which Net energy of the process can be reduced from 2.59e+8 to 1.64e+8 BTU/h.

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