Ammonia Production Plant Design Project

By Alyeldin Helmy, Baihan Wang, Rajdeep Dev

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Chemical and Biological Engineering 201
University of British Columbia

December 14, 2019

An Investigation into the Design and Sustainability of the Ammonia Production Plant

Submitted to

Professor Michael Schoen, P.Eng, Dr. Jonathan Verret

CHBE 201:

Integrated Technical Communication

Submitted by

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December 14, 2019

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Professor Michael Schoen
Senior Instructor
Department of Chemical and Biological Engineering
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Subject: Submission of Ammonia Production Plant Design Report

Dear Professor Schoen,

Here is the final design report you requested on ammonia production plant.

This report analyzes the reaction catalyst used, energy balances, process description, process control, and safety and environmental analysis for the ammonia production process.

Please contact us if you have any questions.

Sincerely,
Alyeldin Helmy, Baihan Wang, Rajdeep Dev

Executive Summary

“An Investigation into the Design and Sustainability of the Ammonia Production Plant”

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This report analyses the design and sustainability of the ammonia production plant from a variety of various scopes.This report explains the design of a plant capable of producing 350,000 tonnes per year of ammonia. All data on the plant were obtained via research papers , articles, trusted websites and case studies. Sections mentioned below implement the simplest pathway in producing ammonia in an efficient and sustainable matter.

The ammonia production plant design consists of the reaction catalysts used, the separation train, energy balances, process description and process flow diagram (PFD), process control, safety and environment. Ammonia is produced using the Haber-Bosch process with the help of iron as a catalyst.Iron is the recommended catalyst considering cost and safety concerns. A condenser is used to separate ammonia from the unreacted gases (H_2 and N_2) and utility used to run the condenser is the very low temperature refrigerant (VLTR). VLTR is the simplest and least expensive way for separating the liquefied NH_3 at required temperature. All unreacted gases are recycled back to ensure that maximum yield of ammonia is obtained. Temperature is controlled in one of the heat exchangers to execute the reaction. a “What-if” analysis is made to establish the environmental and safety requirements.

Findings:

→ Iron catalyst has a low environmental impact.
→ The process does not have 100% conversion of product.

Recommendations:

→ Iron catalyst is chosen due to its cost effectiveness and environmental impact.
→ recycle unreacted gases to ensure maximum yield.

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1.0 INTRODUCTION

Ammonia is a naturally occurring compound that presents as a colourless gas or liquid. The chemical formula NH_3 reflects the central nitrogen atom surrounded by hydrogen bonds (fig.1). Ammonia plays a large role in fertilizer production as it is a readily available source of nitrogen; it is also used as a disinfectant and a refrigerant [1]. Annual global production of ammonia (2016) is at around 146,000,000 tonnes per year [2]. Based on the 2016 average price of ammonia in Illinois ($578 USD per tonne), the estimated value is $84,000,000,000 per year [3]. Currently, the largest ammonia plants can 1,000,000 tonnes per year (3000 tonnes per day) [2]. The market of ammonia is based on the global population. As the population grows, the demand of ammonia will follow an upward trend.

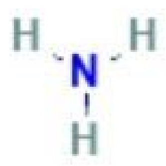


Figure 1: Chemical structure of Ammonia [1]

This report explains the design of a plant capable of producing 350,000 tonnes per year of ammonia. The plant will be located in Southern Manitoba near Winnipeg, where many chemical plants are located. The min (-40.0°C) and max temperature (36.1°C) vary greatly in Winnipeg area [4]. The manufacturing process requires a high temperature (450°C), high pressure (200 atm), and iron catalytic conditions. The Haber-Bosch process utilizes two raw materials. Nitrogen is acquired from the atmosphere, and hydrogen is obtained from natural gas and steam. A simplified input-output diagram shows the overall reaction (fig. 2). The formula for the reaction (1) is shown below. Table 1 provides molecular weights and costs.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H_r = -92.4 \text{ kJ mol}^{-1} \quad (\text{Reaction 1})$$

Overall Ammonia Production Reaction

Figure 2: Input-Output Diagram for Overall Reaction

Name	Formula	Molecular weight (g/mol)	Price ($USD/tonne)
Ammonia	NH3	17.031	578 [3]
Hydrogen	H2	2.016	13.99 [5]
Nitrogen	N2	28.014	25 [6]

Table 1: Common properties for compounds in ammonia manufacturing.

The design report will be submitted to both CHBE 201 and CHBE 220 course. The design process of the project follows the 12 step process. The source of materials are cited and referenced using IEEE format.

This report contains the following sections:

- Reaction catalysts

- Separation train
- Energy balance
- Process description and PFD
- Process control
- Safety and environment

2.0 REACTION CATALYSTS

2.1 Introduction

Three possible catalysts are considered for the Haber-Bosch reaction: Iron(Fe), Ruthenium(Ru), and Ruthenium Based Ba-Ca$(NH_2)_2$ catalyst. A functional decomposition is used to develop criteria that is applied quantitatively in an evaluative matrix to score and select the best catalyst. Iron catalyst is found to be the most suitable choice.

2.2 Iron (Fe) Based Catalyst

The formation of diazene (see mechanism 1) is the rate determining step for the complete reaction. The triple bond found in N_2 and single bond in H_2 must be broken, hence the high temperatures required. Once these temperatures are reached, an iron catalyst provides an ideal surface and the free electrons required for the breaking of these bonds.

(1) $N_{2\,(g)} + H_{2\,(g)} \rightarrow N_2H_{2\,(g)}$ (Mechanism 1)

(2) $N_2H_{2\,(g)} + H_{2\,(g)} \rightarrow N_2H_{4\,(g)}$ (Mechanism 2)

(3) $N_2H_{4\,(g)} + H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$ (Mechanism 3)

(4) $2NH_{3\,(g)} \rightarrow 2NH_{3\,(l)}$ (Mechanism 4)

2.3 Ruthenium (Ru) Catalyst

Ruthenium is a viable replacement for an iron catalyst. utilizing ruthenium significantly reduces the high temperatures and pressures required for the efficiency of the Haber-Bosch process [2]. However, using ruthenium comes with the drawback of uncertain costs and supply as it is a rare earth metal and hydrogen poisoning. Ruthenium based catalysts favour the production of single hydrogen atoms over single nitrogen atoms. Thus the presence of excess hydrogen severely limits the production of utilizable nitrogen.

2.4 Ruthenium Based Ba-$Ca(NH_2)_2$ Catalyst

Another catalyst is calcium amide with a small amount of added barium (Ba-$Ca(NH_2)_2$) [7]. Calcium amide increases the activity of Ru-based catalyst and the nanometer thin particle layer of barium forms a Ru-Ba core-shell structure to prevent hydrogen poisoning. This catalyst has 100 times greater activity than ruthenium catalyst at low temperatures below 300 °C, and obtains a six times higher synthesis rate than Fe-based catalyst (at 340 °C) [8]. The calcium amide catalyst requires far less energy than ruthenium and Fe-based catalysts, which makes on-site production possible [9].

2.5 Criteria for evaluation

Different attributes are described by order of importance and evaluated . They are used in an evaluative matrix to quantitatively compare and select the best catalyst used for this design project. Each criterion is assigned a weighted, numerical value (between 1 to 5) that is applied in a table to each of the pathways or catalysts to select the option with the highest score. Evaluation is based on 4 criteria : Cost of the catalyst, Energy Input, Efficiency, and Safety. The cost of catalyst greatly affect plants profit and is assigned 40% weight. Energy input is how the catalyst lowers the temperature or pressure needed in the reaction and efficiency is how the catalyst shorten the reaction time. Certain catalyst might be hazardous or require severe reacting condition, meaning larger investments in proper training operators of the plant. These three criteria are weighted 20% each.

	Weight	Iron	Ruthenium	Ba-$Ca(NH_2)_2$
Cost	40%	5	4	1
Energy	20%	2	3	5
Efficiency	20%	4	4	5
Safety	20%	2	2	3

Total	100%	3.6	3.4	3

Table 2: Evaluation of Catalysts

2.6 Recommended catalyst

An iron catalyst and the Haber-Bosch process are the recommended catalyst and reaction pathway. Calcium amide with high efficiency appears an attractive choice, but it is incredibly expensive. The iron catalyst scores the highest in the evaluation matrix and is a well-researched field and geared towards the dedicated large-scale production of ammonia.

The ideal reactor used in this procedure is the fixed bed reactor. This reactor operates at a temperature of 450°C and at 200 atm of pressure to decompose. The heat transfer coefficient in the reactor is 500 kcal/m^2hr°C. The conversion rate of the reactor is relatively low at 15%-20%. The Haber-Bosch process has no side product and all the unreacted reactants are recycled. The conversion rate can rise to 97% after multiple passes.

3.0 SEPARATION TRAIN

3.1 Introduction

The Haber-Bosch process is used to produce ammonia. Hydrogen and nitrogen gas are mixed under high temperature and pressure to synthesize ammonia. The reaction intermediates, diazene and hydrazine, are consumed instantaneously. The overall reaction has a conversion rate of 15% for a single pass, and a maximum of 97% after recycle the unreacted reactants for multiple passes [12]. The products in the exit stream need to be separated. The component of the stream are unreacted hydrogen and nitrogen and the desired product ammonia.

3.2 Selecting a separation unit

A condenser separates ammonia from the unreacted gases. A very low temperature refrigerant (VLTR) is used to separate product stream and obtain NH_3. Ammonia is collected as a liquid product because it has a higher boiling point than both hydrogen and nitrogen. Steam generation provides refrigeration in this process [13]. This separation is repeated throughout the process at very low temperature which is between ammonia boiling and melting point (-33.34°C → -77.7°C) at atmospheric pressure. These conditions allow ammonia to liquify. H_2 and N_2 remain gas phase, due to their extremely low temperature boiling points (-252.9°C and -195.8°C respectively) at atmospheric pressure.

Unreacted H_2 and N_2 is recycled to the reactor through a gas compressor. The yield of ammonia achieves 97% after recycling H2 and N2 for multiple passes. Figure 1 shows a block model for inputs and outputs of the separation unit.

Figure 3: Block figure of separation unit

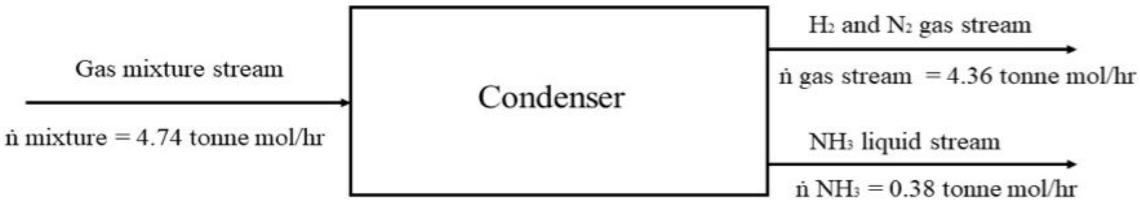


Table 3: Flows into and out of separation unit

Compound	**Flow into condenser (tonne mol/hr)**	**Flow out of condenser for single pass (tonne mol/hr)**
Hydrogen	N/A	3.27
Nitrogen	N/A	1.09
Ammonia	N/A	0.38
Total flow rate	4.74	4.74

Table 4:Physical properties for separation of each compound

Compound	Boiling Point (℃)	Heat of Vapourization (kJ mol^{-1})	Melting Point (℃)	Heat of Fusion (kJ mol^{-1})
Hydrogen	-252.9	0.4494	-259.2	0.05868
Nitrogen	-195.8	2.7928	-210.0	0.3604
Ammonia	-33.34	23.3500	-77.7	5.653

4.0 ENERGY BALANCE

4.1 Introduction

An energy balance is performed when ammonia and unused reactants enter the condenser. Ammonia has a much higher boiling point than the reactants in the product stream. Condensation is used for the separation technique. The boiling point of ammonia is -33.3°C. The stream is cooled to -43.3°C to ensure that all possible ammonia is condensed and to give a margin of safety.

4.2 Selecting a utility

A very low temperature refrigerant (VLTR) is used for the energy balance. This is the most suitable utility as the inlet and outlet temperature range satisfies the temperature of -43.3°C that is desired. This utility is also less expensive than an extremely low temperature refrigerant (ELTR). It is crucial to note again, the entire product stream containing unused reactants and products [M1] are cooled as a whole.

Table C: Utility energy values

Utility	Inlet T (°C)	Outlet T (°C)	P	Cost ($/GJ)
VLTR	-50	-35	N/A	13.11
ELTR	-100	-85	N/A	33.20

To cool the gaseous ammonia to a liquid state, the product stream is cooled from 450°C to -43.3°C. Appendix A shows The mass flow rate of each component and supporting calculations. The heat capacities (C_p) of ammonia, hydrogen, and nitrogen are 49.8 $Jmol^{-1}K^{-1}$ [14], 29.53$Jmol^{-1}K^{-1}$ [15], and 31.10$Jmol^{-1}K^{-1}$ [16], respectively. Thus, the amount of energy required to cool the stream is calculated from these respective values. The reactants are found in the product stream, cooling the entire stream is taken into consideration. The final energy value will be the sum of these three separate products. The final energy value is 73.79 $GJhr^{-1}$. Assuming a price of $13.11 GJ^{-1}, the hourly operating cost will be $967.39 hr^{-1}. Assuming a standard 8000-hour operating year, the yearly operational cost is $7,739,120.00 per operating year.

5.0 PROCESS DESCRIPTION AND FLOW DIAGRAM (PFD)

5.1 Introduction

The process flow diagram below focuses on the Haber-Bosch process. The main reactors are the fixed bed reactor (FBR) and the condenser, which separates ammonia from the reactants. The stream table listed below indicates all material balances related to the PFD.

5.2 Process flow diagram

V-102 Nitrogen Vessel	V-101 Hydrogen Vessel	C-101 Gas Compressor #1	E-101 Heat Exchanger	R-101 Fixed Bed Reactor
C-102 Gas Compressor#2	E-102 Condenser	P-101 Liquid Centrifugal Pump	TK-101 Ammonia Storage Tank	C-103 Gas Compressor #3

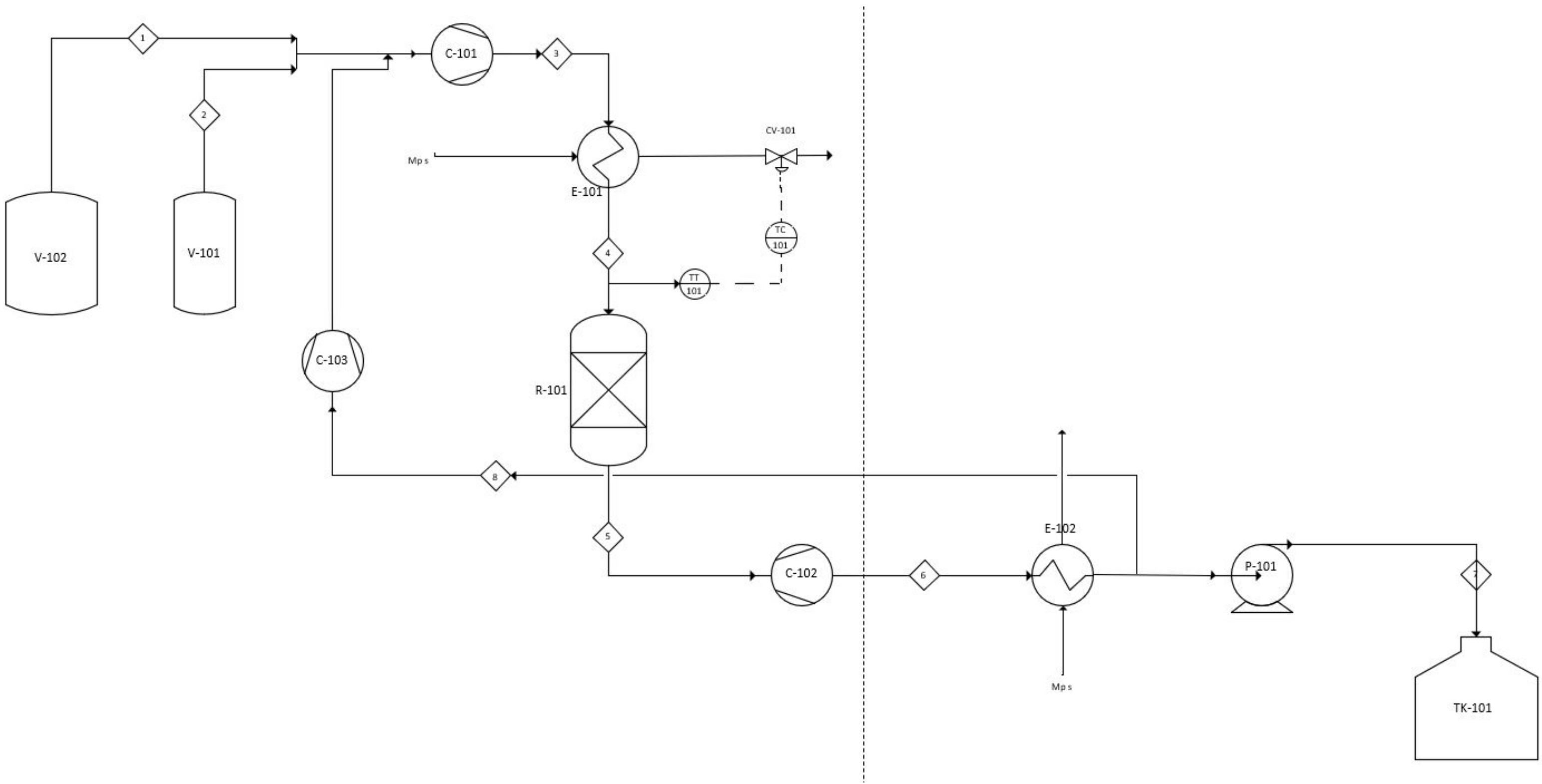


Table # Stream table

Stream number	1	2	3	4	5	6	7	8
Temperature (℃)	25	700	25	450	450	450	-43	-43
Pressure(atm)	1	3	200	200	200	1	1	1
Vapour fraction	1	1	1	1	1	1	0	1
Mass flow(tonne/hr)	35.98	7.77	43.75	43.75	43.75	43.75	42.37	1.38
Molar flow (tonne mol/hr)	1.28	3.85	5.13	5.13	4.74	4.74	2.49	0.15
Component molar flow (tonne mol/hr)								
Hydrogen	0	3.85	3.85	3.85	3.27	3.27	0	0.11
Nitrogen	1.28	0	1.28	1.28	1.09	1.09	0	0.04
Ammonia	0	0	0	0	0.38	0.38	0.38	0

5.3 Process description

Since the reaction is an equilibrium with a low conversion rate of 15%, ammonia is removed as it is produced in order to shift the equilibrium to the right. The reactants, H_2 and N_2, are isolated from natural gas and the atmosphere, respectively. The reactants are stored in vessels, (V-101 and V-102). Both reactants are mixed and pass through the compressor (C-101) where they are pressurized to 200 atm. the reactants are transported to the heat exchanger (E-101) and heated to 450°C with steam.

The reactants are fed directly into the FBR (R-101) which contains an extremely porous iron metal catalyst. H_2 and N_2 are converted into diazene (N_2H_2) which forms hydrazine (N_2H_4). hydrazine reacts with H_2 and forms NH_3. The reaction intermediates are consumed in the process and are not in the product stream exiting the FBR (R-101). the reactants are separated from the product stream. The product stream passes through a condenser (E-102) that cools the stream from 450°C to -43°C. Since the ammonia condenses at a much higher temperature than H_2 and N_2, the reactants remain as gases and the ammonia is pumped (P-101) from the condenser into the storage tank (TK-101) . The storage tank is kept at a temperature below -33.34°C and no less than -77.70°C to prevent the ammonia from evaporating or solidifying. This is achieved with the ultra-low temperature coolant. Remaining H2 and N2 are recycled back after the mixing point through the gas compressor (C-103) for further production of ammonia.

6.0 PROCESS CONTROL

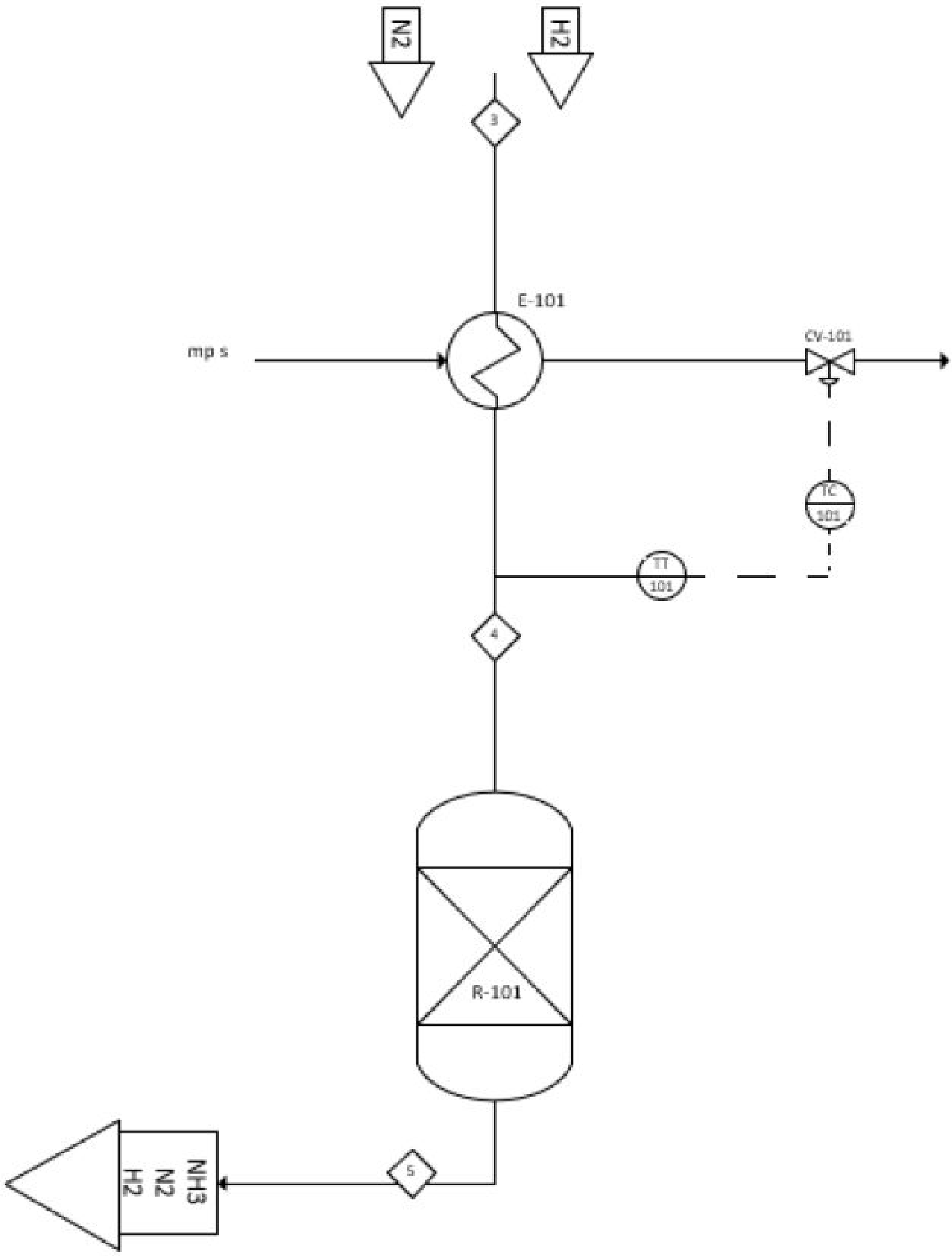
6.1 Introduction

In this section, the control strategy in the ammonia production plant is discussed. In the ammonia manufacturing process, high temperature is required for the Haber-Bosch process. Thus, a temperature control system is installed in the heating column (E-101) to ensure that hydrogen and nitrogen are heated to the desired temperature required to execute the reaction.

6.2 Control

The gas mixture of nitrogen and hydrogen is heated in the heat exchanger(E-101) to 450 °C before sent into the reactor(R-101). The temperature of gas entering the reactor are measured through a temperature transmitter(TT-101). A signal is sent to the temperature controller(TC-101) which controls the control valve(CV-101) connected to the heat exchanger(E-101). The valve controls the stream of high temperature steam which is the heating agent.

When temperature in stream 4 is higher than 450 °C, control valve(CV-101) closes, and the flow of high temperature steam used to heat the reactants will slow down, resulting in the decrease of temperature in the heat exchanger(E-101). When the temperature in stream 4 is lower than 450 °C, the control valve(CV-101) will open and allow more steam to heat the reactants, resulting in the increase of temperature in the heat exchanger(E-101).



E-101

Heat Exchanger

R-101

Fixed Bed reactor

7.0 SAFETY AND ENVIRONMENT

A Process safety and environment analysis for the heat exchanger E-101 is discussed in the section below. This analysis uses the “what-if” process hazard analysis strategy. Its purpose is to identify problems that could lead to terrible accidents. This process results in a list of potential problem areas and proposes mitigation methods.

“What-if” analysis of E-101

This “What-If” analysis focuses on the heat exchanger (E-101) which is shown in Figure 1:

Process Flow diagram. The “what-if” focuses on three deviations that are appropriate to E-101: 1) If condensate valve (CV-101) fails open, 2) If condensate valve (CV-101) fails closed, 3) If a leak develops in E-101.

Condensate valve (CV-101) fails closed

The flow of high temperature steam pass the heat exchanger quickly with relatively low steam pressure if the valve fails closed[17]. This lowers the heating temperature executing the reaction, which is compromised. The ammonia synthesis reaction equilibrium moves to the left side if gases with temperature below 450°C enter reactor R-101 as the reaction is reversible. It lowers ammonia production in the reactor. An emergency shutdown valve on the steam tube can solve the problem

Condensate valve (CV-101) fails open

The flow of heated steam exiting the heat exchanger slows down if the valve fails open. This causes increasing steam pressure in the steam tube thus the hydrogen and nitrogen in the heat exchanger will be overheated[17]. There is a risk of pressure buildup in the reactor if gases with a temperature higher than desired accumulated in the reactor. The gas compressor C-102 is overloaded and the equipment is damaged. Installing a pressure relief valve in the reactor R-101 as well as an emergency shutdown valve on the stream entering the reactor can solve this problem.

A leak develops in E-101

A leak in the tube leads to mixing of hydrogen, nitrogen, and ammonia gas with heated steam. Ammonia reacts with heated steam causing a decrease in final yield of ammonia[1]. The steam cools down after leaving the tube and exposes to the air. The leak of steam does not lead to any hazardous situation.

Recommendations

Addition of pressure relief equipment on the steam tube and the reactor is recommended to avoid any consequences if the condensate valve (CV-101) fails open. Installing an emergency shutdown valve on the stream entering the reactor is recommended to mitigate accidents if CV-101 fails close. Regular maintenance and operations are suggested to ensure no leakage in E-101.

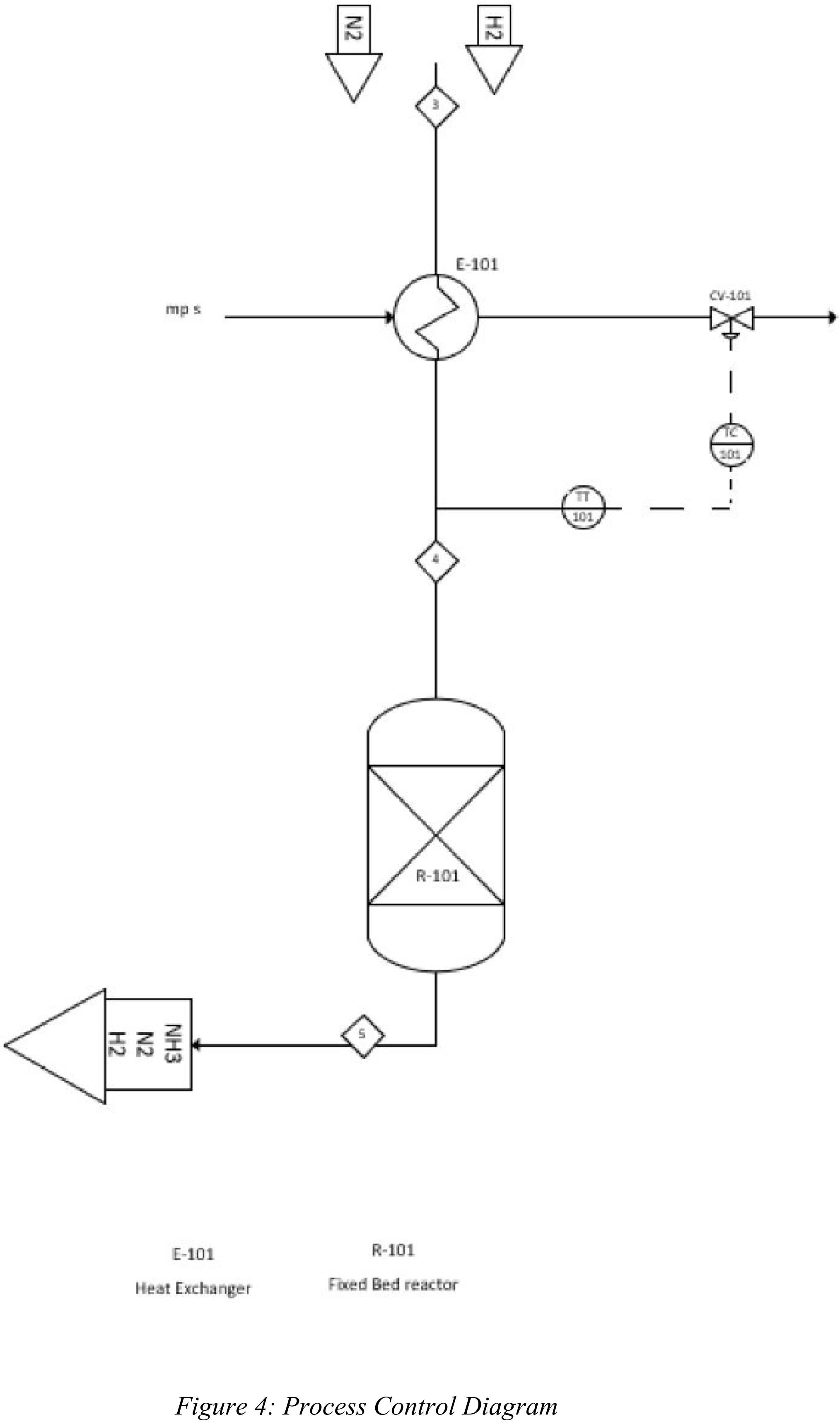


Figure 4: Process Control Diagram

8.0 CONCLUSION AND RECOMMENDATION

This report details the process design to produce 350,000 tonnes of ammonia per year. The ammonia production process uses nitrogen and hydrogen as reagents and iron as a catalyst. The overall cost of the process and the safety of the plant holds preference in each design decision.

Findings

Iron catalyst is compared to ruthenium and Ba-Ca$(NH_2)_2$ catalyst and found to be most suitable. The synthesis reaction has a low yield so a separation unit is required to recycle unreacted H_2 and N_2 to achieve a reaction yield of 97%. A process flow diagram outlines the general flow of the plant process and equipment. Three “what if scenarios” involving failure of condensate valves and a tube are analysed to recommend a solution.

Recommendations

Iron catalyst is recommended as it is the most cost effective with low environmental impact. A very low temperature refrigerant is used to separate unreacted H_2 and N_2 to obtain maximum yield. Installation of a pressure release valve and shutdown equipment helps to resolve any risk.

Appendix

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