

MONETIZATION OF STRANDED GAS THROUGH AMMONIA AND UREA  
PRODUCTION

A Thesis

by

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## ABSTRACT

The world demand for total fertilizer nutrients will reach 200 million metric tons in 2018. In the meantime, 6.3 trillion cubic feet per year natural gas are vented, flared and reinjected worldwide. Ammonia and urea production are promising routes to monetize these stranded gas resources. Greenhouse gas reduction through the incorporation of CO<sub>2</sub> generated in the reforming section into urea production is a plus for this process. This study examines and optimizes the ammonia and urea processes by process analysis, economic analysis, and process intensification. A case study is carried out on deploying the technology in Corn-Belt (an area with a thriving agricultural sector and heavy demand for fertilizers). A medium gas reserve size of 10 MM SCFD is chosen to maintain the flexibility of the process. The process includes a reforming section, high-temperature shift, low-temperature shift, CO<sub>2</sub> recovery, methanation, ammonia synthesis, refrigeration, ammonium carbamate condensation, urea generation and gas recycle. Kinetic models are used to set the rate while equilibrium criteria are chosen to build the boundary in this simulation. Two process intensifications – combined reformer and combined urea reactor – are proposed to increase the mobility of the system.

DEDICATION

To

My Parents

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## CONTRIBUTORS AND FUNDING SOURCES

### **Contributors**

This work was supervised by a thesis committee consisting of Professor Mahmoud M. El-Halwagi, my advisor, and Professor M. Sam Mannan of the Department of Chemical Engineering and Professor Hisham Nasr-El-Din of the Department of Petroleum Engineering.

All work for the thesis was completed by the student, under the supervision of Professor Mahmoud M. El-Halwagi of the Department of Chemical Engineering.

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# CHAPTER I

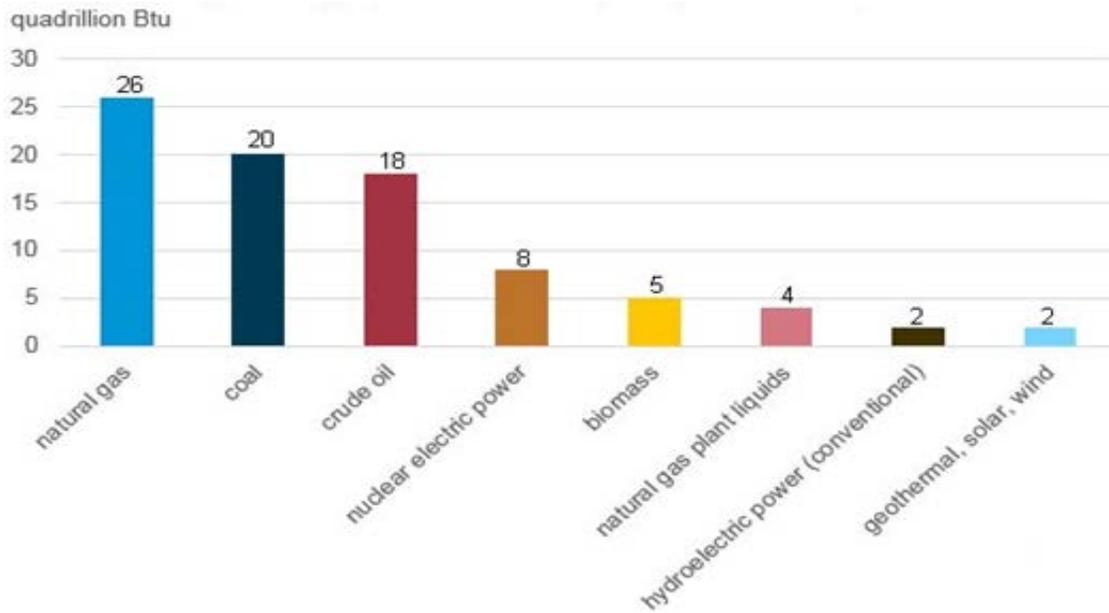
## INTRODUCTION

In this chapter, the background of the study is stated. The shale gas boom, huge fertilizer demand, case study region, and comparison between different natural gas monetization routes are discussed in the sections below.

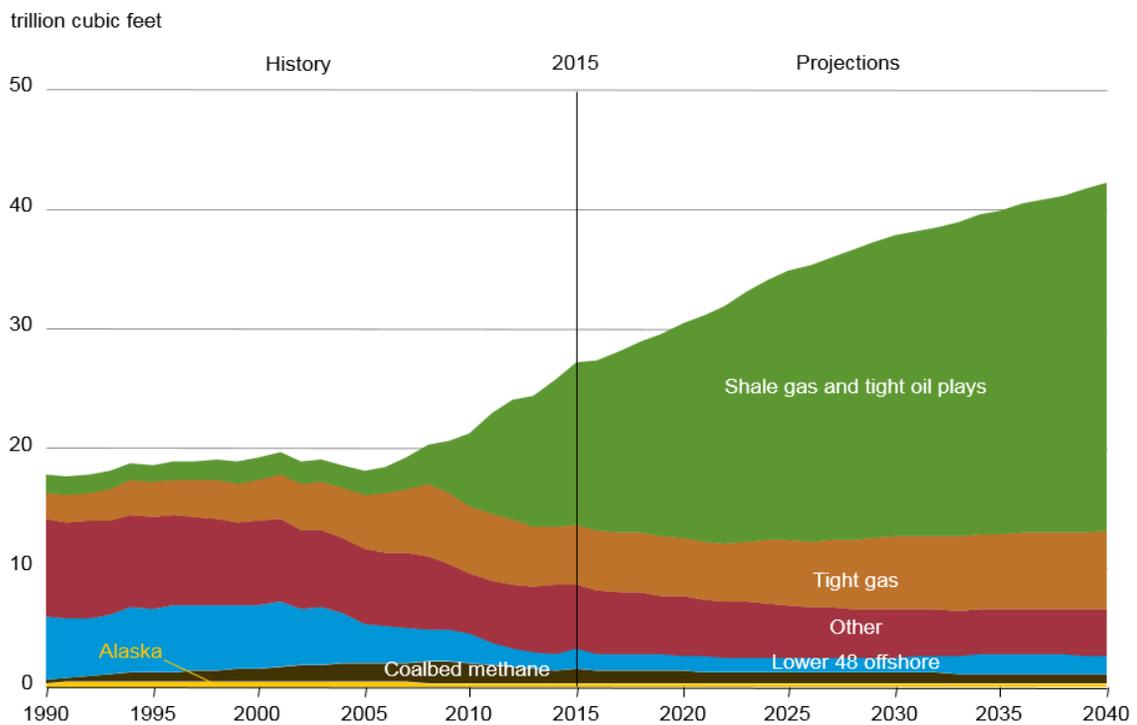
### I.1 Shale Gas Boom

In 2015, total U.S. primary energy consumption was about 97.7 quadrillion Btu. Among all sources, natural gas ranks 1<sup>st</sup> with a percentage of 32. Petroleum follows it, accounting for 28% of annual energy consumption. And in 2016, natural gas surpasses coal for the first time in electricity generation. So natural gas plays an important role in American energy usage. Detailed energy production data can be seen in the Figure 1.

With the rapid development of hydraulic fracture and horizontal drilling, the shale gas becomes an important part in natural gas sector. In 2000 shale gas provided only 1% of US natural gas production. In 2012, The U.S. government's Energy Information Administration predicts that by 2035, 46% of the United States natural gas supply will come from shale gas. However, in 2015 shale gas and tight oil plays already became the largest contributor, with 13.6 Tcf production in that year. The shale gas and tight oil play shared 50% of total U.S. dry natural gas production in 2015. And the share is expected to increase by 15.4 Tcf to 29 Tcf in 2040 (EIA, 2016a). In Figure 2, dry natural gas production by different sources are shown.

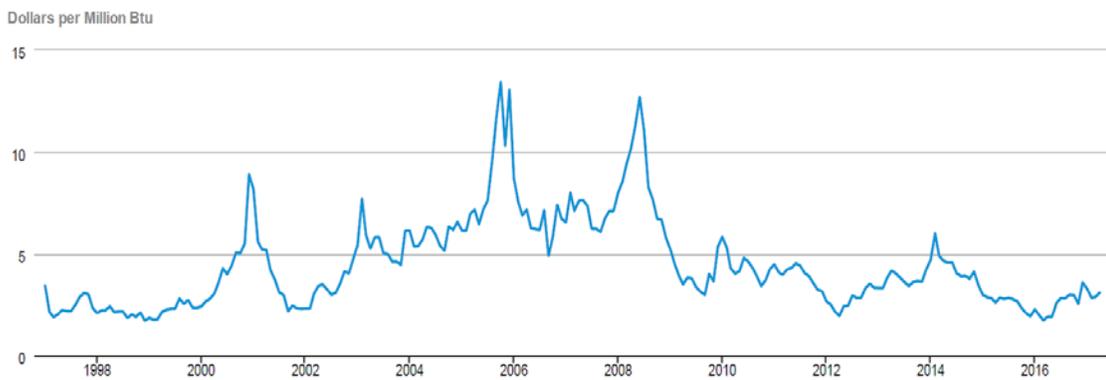


**Figure 1 U.S. Primary Energy Production by Major Source (EIA, 2015)**



**Figure 2 U.S. Dry Natural Gas Production by Source (EIA, 2016a)**

The large increase in natural gas production floods the market with cheap feedstock. Although the gas price bounds back recently, it is still at a historic low. Then the questions we want to ask are, how shall we use these abundant sources efficiently and where shall we focus on. The ample gas resources can be a opportunity and challenge at the same time. The trend of one standard natural gas price – Henry Hub Spot Price are illustrated in Figure 3.



**Figure 3 Henry Hub Natural Gas Spot Price (EIA, 2016b)**

## I.2 Vast Fertilizer Demand Globally

World population reached on March 12, 2012 according to the United States Census Bureau (U.S. Census Bureau, 2011). As of August 2016, the global population was estimated at 7.4 billion (Population Reference Bureau, 2016). The United Nations estimates it will further increase to 11.2 billion in the year 2100, based on the historical data of global population annual increases above 1.8% (United Nations, 2016). Total annual births are expected to remain essentially constant at their 2011 level of 135 million (United Nations, 2011).

The World Food Situation, released by the Food and Agriculture Organization of the United Nations in July 2014 forecasts an improved situation for global cereal supplies in the 2014/15 marketing season. The world cereal production in 2014 is estimated to reach 2,498,000,000 tonne, this is mainly due to improved production prospects in coarse grains and wheat crops in the United States, the European Union and India (FAO, 2015).

**Table 1 Top Five Crops Produced in 2013, Thousand Tonnes**

<b>Crops \ Year</b>	<b>2000</b>	<b>2013</b>
<b>Sugar cane</b>	1 256 380	1 877 110
<b>Maize</b>	592 479	1 016 740
<b>Rice, paddy</b>	599 355	745 710
<b>Wheat</b>	585 691	713 183
<b>Potatoes</b>	327 600	368 096

The crops planted worldwide increased almost 40% in the first 13 years of 21<sup>st</sup> century. Sugar cane and maize production had a big leap, rice and wheat had a rather big increase, while the potatoes production didn't alter too much (FAO, 2015). Detailed crop production data are shown in Table 1. Generally speaking, the production growth shows the food demand rise in the whole world. This trend actually matches the fact recently published by World Food Situation. The FAO Food Price Index (FFPI) averaged 173.8 points in January 2017, up 3.7 points (2.1 percent) from the revised December value. At

this level, the FFPI is at its highest value since February 2015 and as much as 24.5 points (16.4 percent) above its level in the corresponding period last year.

Other than the crops shown above, other crops also have huge production capacity. One example is the production of cereals. The World Food Situation, released by the Food and Agriculture Organization of the United Nations in July 2014 forecasts an improved situation for global cereal supplies in the 2014/15 marketing season. The world cereal production in 2014 is estimated to reach 2,498,000,000 tonne, this is mainly due to improved production prospects in coarse grains and wheat crops in the United States, the European Union and India (FAO, 2015).

### I.3 Case Study Region-Corn Belt Region

In the United States, the Midwest is the agricultural powerhouse region. 40 % of all U.S. farms, 37% of America's farmland, 57% of its cropland are in this area. Corn accounts for 87% of nation's total acres. Soybean accounts for 84% of United States total acres. For the country's hogs, 78% of them are fed in this region (Laingen, 2017). The region contains nearly half of the market value of all agricultural products sold in the United States (51 percent of the market value of crops sold and 41 percent of the market value of livestock sold) (Laingen, 2017).

When discussed about the corn belt, I will talk about the definition and history of this area. The region we call the Corn Belt has been existed since the late 1800s, and could be referred to the Corn-Soybean Belt today (Laingen, 2017). In 1892, The Nation first printed the word "Corn Belt", and in 1903 it was first applied academically when

Harvard University economist T.N. Carver wrote of “a tolerably compact strip where corn is the principle crop, and which may properly be called the corn belt” (Laingen, 2017). Later in 1903 Carver again mentioned to the region as “the most considerable area in the world where agriculture is uniformly prosperous”. These earliest references most likely indicate regions of western Ohio and central Indiana, where the first evidence of what would be the contemporary Corn Belt were found.

In 1927, agricultural economist O.E. Baker created one of the earliest statistically generated maps picturing the Corn Belt as a region. His map contains climate-, soil-, and topographically- based thresholds that described the geographic extent of where corn grew best. In 1950 the U.S. Department of Agriculture used O.E. Baker’s previous work to draft a map of the country that put each county into one of ten regions, based mainly on the county’s most common agricultural practice. The Corn Belt, “Region V: Feed Grains and Livestock”, was quite like Baker’s 1927 version, with additions to the region extending northward into Minnesota and South Dakota’s spring wheat region, into Kansas’ and Missouri’s corn and winter wheat region, and a peninsula of newly contained counties in both Illinois and Indiana.

When it comes specifically to crop production, as is known to all, corn and soybeans growth is concentrated in the this Corn-belt region (Schnitkey, 2013). In the article, two density maps of corn and soybean productions in America are analyzed.

Those figures are generated by using the average of total corn and soybean production in 2010, 2011, and 2012 from the NASS. Based on the three-years average, counties were listed from biggest to smallest production. Then, production totals were

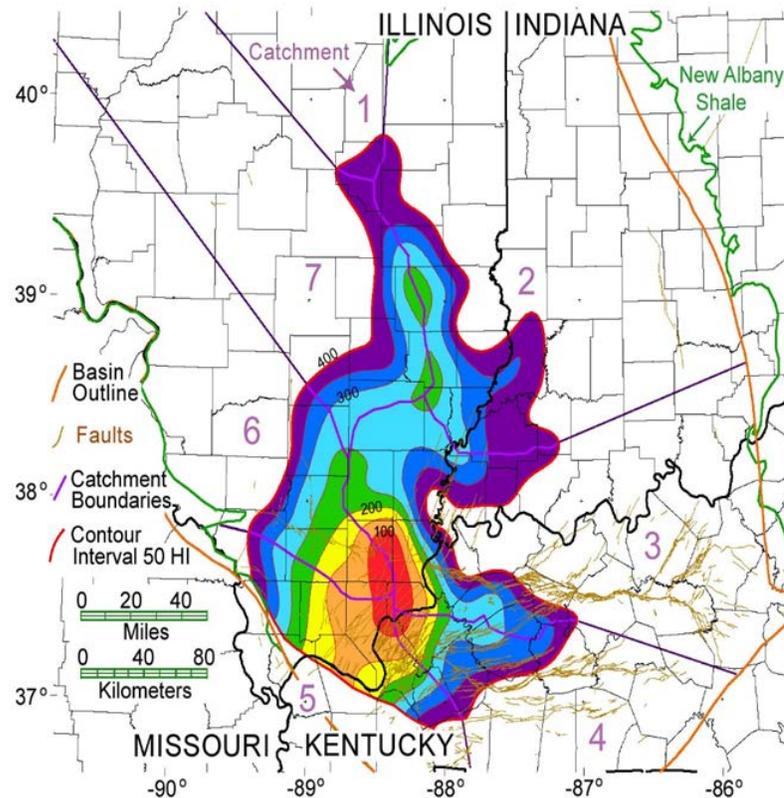
added up for the percentage. For instance, counties which have the first and second largest production were added together first to form the two largest counties. Then, counties which have the three biggest production was added together to form the three largest producing counties. This procedure was repeated until the production just exceeded 50% of total U.S. production in 2010, 2011, and 2012. These 220 largest counties are then drawn as dark green. It means the area accounts for around 50% of total U.S. production.

The same procedure was carried out for 75% of production and 90% of production. As a result, 456 counties are included in the light green and dark green counties. These areas are counties which account for 75% of total corn production. Adding another 291 largest counties, there are 753 counties in total with dark green, light, and yellow. These areas combined show the 90% of U.S. corn production.

When taking a closer look at the most dense area, the dark green area, which accounts for 50% of the total U.S. corn production, people can tell these counties are primarily located center of the Corn-belt. States by states data revealed Iowa (66 counties), Illinois (43 counties), Minnesota (37 counties), Nebraska (35 counties), South Dakota (11 counties), Indiana (7 counties) and North Dakota (6 counties) are the topmost counties in the top 50%. Other states that have counties in the 220 include Wisconsin (6 counties), Texas (2 counties), Kansas (3 counties), Colorado (3 counties), and Missouri (1 county).

The same methodology is used to evaluate soybean production distribution (Schnitkey, 2013). The dark green area shows 50% of total U.S. production.

In the same area, there is an organic-rich geologic formation of Devonian and Mississippian age. New Albany Shale located at the intersection between Illinois and Indiana. Recoverable shale gas in the shale is estimated to be about 10 trillion cubic feet. In Figure 4, as hydrogen index (HI) contours decrease, the thermal maturities of New Albany Shale source rocks increases. Contour interval is 50 HI. The 400 HI contour (red line) outlines the area of source rocks that are thermally mature for oil generation. These conditions show a great economic potential if these abundant gases are used for chemical conversion.



**Figure 4 Thermal Maturity of New Albany Shale Source Rocks within the Illinois Basin (Higley, Henry, Lewan, & Pitman, 2003)**

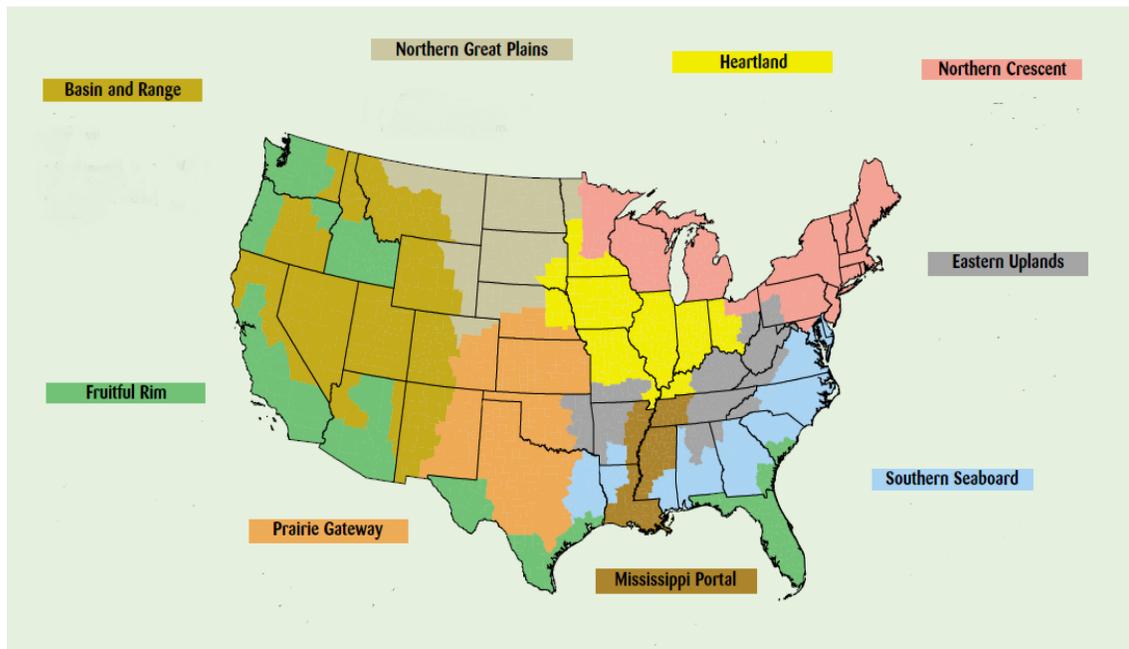
#### I.4 Comparisons Between Different Natural Gas Monetization Routes

With the luxuriant raw materials in hand, finding a commercial process for them can sometimes still be challenging. That is because we still need to make sure we have plenty of potential customers in the area. Or the gas will still be stranded due to margin issue. Market demand and present production amount are first things to consider for a monetization plan. Other things like capital investment, ROI, control safety and infrastructures are detailed matters to be considered further on. There are several methods to utilize the natural gas. Direct use like fuel, electric power and chemical production like methanol, nitrogen fertilizers are the major uses for natural gases. From the introduction above, fertilizer production seems to be viable route. I will further justify the answer with data and comparison.

**Table 2 Different Natural Gas Use in U.S.**

<b>Item</b>	<b>Production</b>	<b>Consumption</b>	<b>Surplus/Gap (%)</b>
<b>Total Natural Gas (2015)</b>	32.6 Tcf	27.3 Tcf	16.3
<b>Methanol (2016)</b>	6 MM tonnes	6.7 MM tonnes	-10.4
<b>Nitrogen Fertilizers (2014)</b>	8.6 MM tonnes	11.9 MM tonnes	-38.4

As we can tell from the Table 2, there are plenty of natural gases for direct use in United States of America. Production is 16% more than the consumption. For methanol, a little bit shortage was seen in 2016. And methanol capacity is rising quickly in past 3 years. US methanol capacity more than double in 2015 (Clark, 2016b).



**Figure 5 Farm Resource Regions**

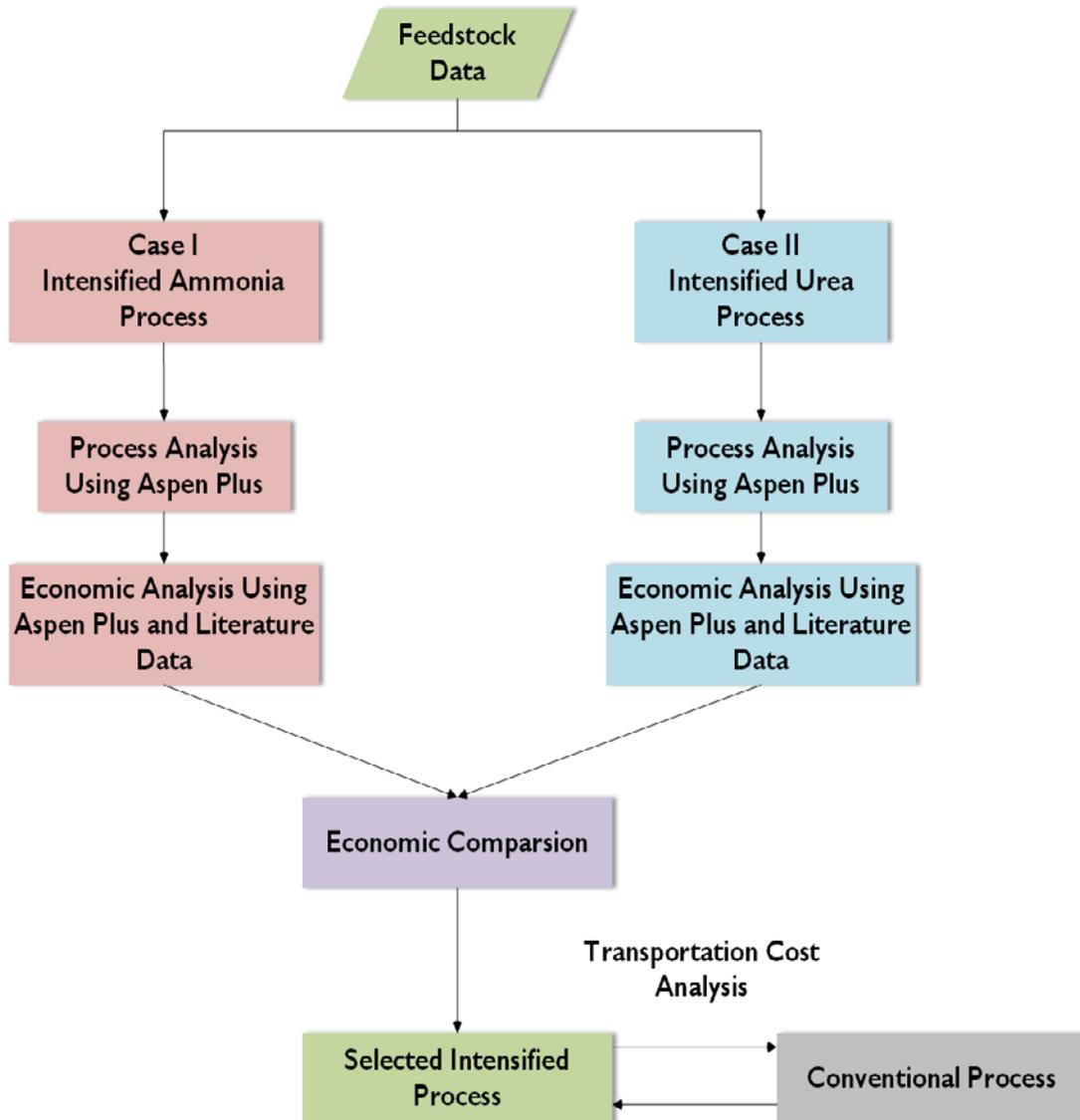
On the other hand, we can see that the nitrogen fertilizers production and consumption data is very promising. U.S. is scant of 38.4% nitrogen fertilizers. Up till today, U.S. is still a net importer of nitrogen fertilizers. In the Corn Belt region which overlaps USDA Heartland most, the need for nitrogen fertilizers is more urgent. In Figure 5, different farm resource regions are demonstrated based on USDA definition. In Table 3, N usage is calculated based on planted acres, share of acres that applied N and N rate (Wade, Claassen, & Wallander, 2015). The nitrogen fertilizers uasge of 3.09 MM tonnes accounts for more than a quarter of American N consumption. As we can see from Figure 5, Heartland occupy far less than a quarter of U.S. land. So the large demand in this area can be expected. And monetization via nitrogen fertilizer production can be a good solution for the ample natural gases.

**Table 3 N Rate and Usage in Heartland**

<b>Item</b>	<b>Planted Acres(MM)</b>	<b>Share of Acres That Applied N</b>	<b>N Rate (lbs per acre)</b>	<b>N usage (MM lbs)</b>	<b>N usage (MM tonnes)</b>
<b>Corn</b>	43.75	0.96	155	6510	2.95
<b>Cotton</b>	0.4	0.98	98	38	0.02
<b>Spring Wheat</b>	0.5	0.88	92	40	0.02
<b>Winter Wheat</b>	2.33	0.99	101	233	0.11
<b>Sum</b>	46.98	-		6822	3.09

Total natural gas data are acquired from EIA website. Methanol production is calculated from a ICIS report (Clark, 2016a). Methanol consumption in North America is collected from a IHS report (Alvarado, 2016). Some said U.S. demand for methanol depended on a GDP level (Clark, 2016a). So U.S. production is estimated based on its GDP portion of North America. Nitrogen fertilizers production and consumption data are collected from IFA.

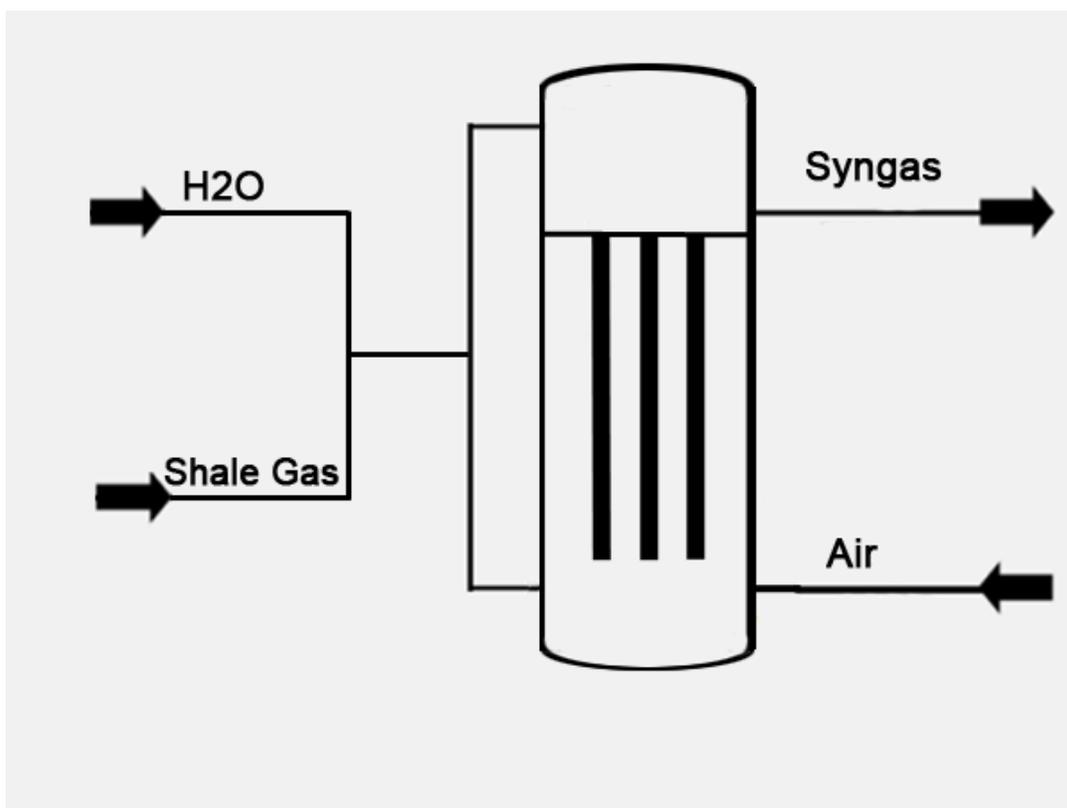
CHAPTER II  
PROBLEM STATEMENT



**Figure 6 Approach Flowchart of Ammonia and Urea Process**

The simulation and analysis flowchart of the whole thesis is shown in Figure 6. In this study, process intensification was used in two sections. First intensification

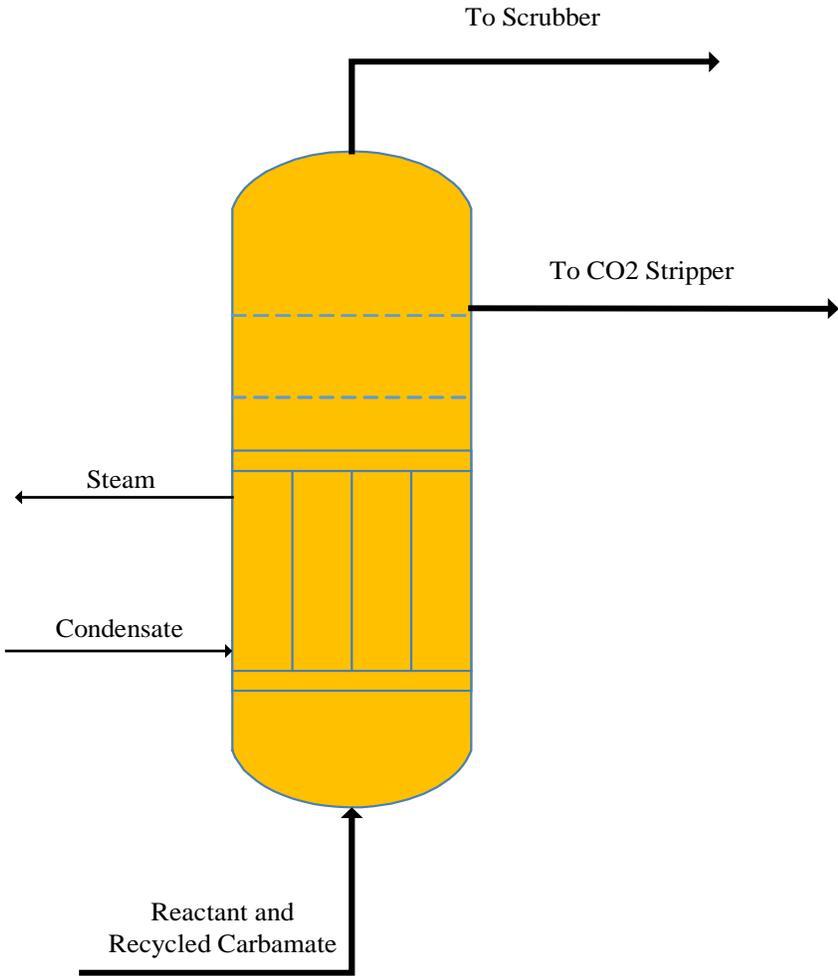
concept is a combined reformer at syngas production part. There are plenty options for the combined reformer setup (Radtke & Wulcko, 2015). In this ammonia and urea process, I applied a combined autothermal reformer. The schematic diagram of the equipment is shown in Figure 7.



**Figure 7 Combined Autothermal Reformer**

Second intensification concept is a combination of high-pressure carbamate condenser, urea reactor, and vapor-liquid separator at urea production part. For the urea production, several design layouts are shown in the ullmann's encyclopedia of industrial chemistry. In this thesis, a novel design is applied. The carbon dioxide and ammonia gases mixed carbamate solution enter the combined reactor at the bottom. With the

cooling utility, carbon dioxide and ammonia react and condense. Then the mixture enters submerged urea reactor part, urea is produced and water is formed. The unreacted gas leaves the column at the top and then goes to the scrubber. The liquid mixture is extracted from urea reaction part and then goes to the top of CO<sub>2</sub> stripper. The schematic diagram of this equipment is shown in Figure 8. Besides these, other reactor section are discussed in the following text.



**Figure 8 Combined Urea Reactor**

For the inlet natural gas flow volume of the whole plant, distribution of gas by field size category for onshore and offshore stranded gas fields was used as reference (Attanasi & Freeman, 2013). The detailed distribution is shown in Table 4. In order to design a high-mobility plant and analyze the benefits of process intensification, a very small volume of 10 MMCF/day was chosen.

**Table 4 Distribution of Gas by Field Size Category for Onshore and Offshore Stranded Gas Fields (Attanasi & Freeman, 2013)**

Size Class	Reserves (BCF)	Field life (years)	Number of wells	Reserves per well (BCF)	Plateau flow rate (MMCF/D)
1	68	17	10	6.8	13.6
2	136	17	13	10.5	27.2
3	272	17	19	14.3	54.4
4	543	25	28	19.4	101
5	1086	23	41	26.5	201
6	2172	22	62	35.0	403

The capital cost reduction are estimated based on the literature summary (Harmsen, 2010). As can be seen in Table 5, the capital cost reduction for using process intensification ranges from 10-80%. Taking the customized design cost into account, a conservative value of 20% is used in this study.

**Table 5 Capital Cost Reduction for Using Process Intensification (Harmsen, 2010)**

Technologies	Innovation drivers				Commercial implementation
	Feedstock cost reduction	Capital cost reduction	Energy reduction	Inherently safe	
Reactive distillation	—	20-80%	20-80%	+	>150

**Table 5 Continued**

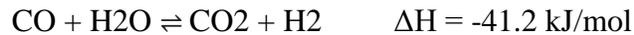
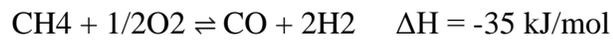
Technologies	Feedstock cost reduction	Capital cost reduction	Energy reduction	Inherently safe	Commercial implementation
DWC distillation	—	10-30%	10-30%	—	>100
Reverse flow reactor	—	>20%	Low	—	>100
Microchannels reactor	Yes	Yes for small scale	—	+	Only in fine chemicals sector
High gravity absorbers	Yes; case dependent	Yes; case dependent	—	—	A few
External field PI	—	—	—	—	—

(Reprinted with permission from Harmen, 2010)

### CHAPTER III

#### PROCESS ANALYSIS

All the feedstocks first go through a combined reformer. In the reforming section, the possible chemical reaction of natural gas, water and air are:



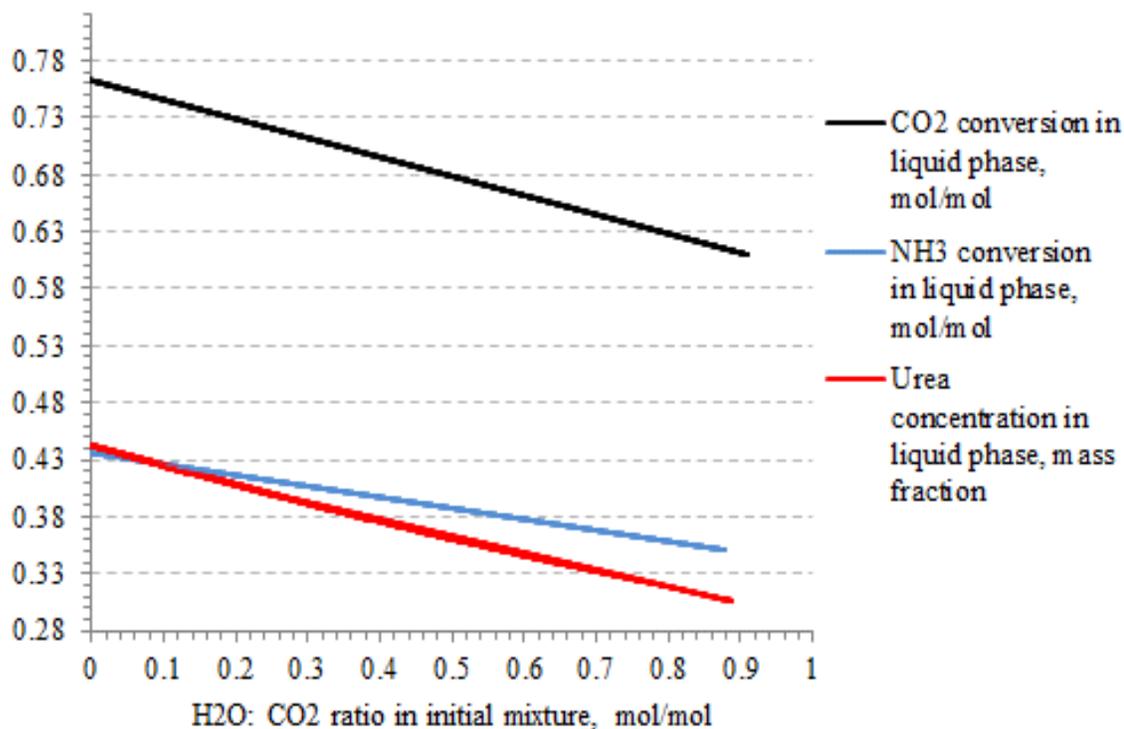
The first reaction produces the synthesis gas. But for the ammonia synthesis reaction, the generated hydrogen together with the imported nitrogen are the main components. Carbon monoxide doesn't contribute to the ammonia synthesis reaction. It also will poison the subsequent catalyst in the synthesis section. High temperature shift, low temperature shift and methanation are applied to eliminate the effect of CO in this paper.

The second and third reaction provide part of the heat for the reactor. However, O<sub>2</sub>/C mole ratio is around 0.55-0.75 in one similar combined reformer configuration. So the second reaction is unlikely to happen in this environment due to the scant of oxygen.

Carbon dioxide will still present in the reformer because of the fourth reaction-water gas shift. Since carbon dioxide is not useful in the ammonia synthesis and is poisonous to the following reaction, it must be separated before further processing. Conventional process for CO<sub>2</sub> removal is to absorb the gas from CO<sub>2</sub> containing syngas

under the pressure with a solvent. After absorption, the CO<sub>2</sub>-laden stream is heated in a column equipped with trays or packing. The CO<sub>2</sub> is released from the rich CO<sub>2</sub> stream and leaves the column at the top trays. The lean CO<sub>2</sub> solvent is enriched at the bottom and pumped back to the absorber column.

In the meantime, the urea production uses CO<sub>2</sub> as a feedstock to first generate ammonium carbamate. Then the compounds decompose to produce urea and water. So the urea production happens to be the process which can utilize the carbon dioxide. With the increasing concerns about the global warming, plenty countries proposed the carbon tax or carbon cap. This could also be a bonus for combining the urea production with the ammonia alone process. However, there also are challenges in incorporation with ammonia process. First, to use the CO<sub>2</sub> in urea production process, it needs to be separated from the mixer. The major impurity in the mixed stream is water. So a distillation column should be built to separate the water from the carbon dioxide. Furthermore, the maximum concentration of water allowed in the urea reactor must be determined. The influences on CO<sub>2</sub> conversion and NH<sub>3</sub> conversion are shown in Figure 9.



**Figure 9 Water : Carbon Dioxide Ratio Effect in Urea Reaction**

As we can see from the Figure 9, without the presence of water, the CO<sub>2</sub> conversion is about 75%. And at the same circumstance, the NH<sub>3</sub> conversion is around 43% (Meessen, 2010). There is a difference between two conversions. The reason behind this is that the experiment is carried out using arbitrary choice of material as key component. In other words, the initial NH<sub>3</sub>:CO<sub>2</sub> ratio is not stoichiometric. Chances are that at a certain concentration, one component will act as limiting/key component. So to avoid a faulty conclusion, the urea yield is used here to identify the maximum concentration of water.

In absence of water, urea mass concentration in liquid phase is 44% at 190 deg C and with NH<sub>3</sub>:CO<sub>2</sub> initial ratio 3.5mol/mol. At 0.1 mol/mol H<sub>2</sub>O:CO<sub>2</sub> ratio, the urea mass concentration in liquid phase stays at 42%. Taking the water generated by ammonium carbamate decomposition in the recycle loop into account, the 10 percent H<sub>2</sub>O:CO<sub>2</sub> ratio in initial mixture is reasonable for getting desired amount of urea. Second, the purged CO<sub>2</sub> must be compressed to pressure at which ammonium carbamate is formed. Hence a compressor is also required. Apparently, there is a tradeoff between advantage of free feedstocks and disadvantage of additional facilities. In order to view and analyze a big picture first, a succinct thought is applied for integrated ammonia–urea plant. The CO<sub>2</sub> used in urea production is assumed to be acquired outside the plant at the market price. The NH<sub>3</sub> is transported from ammonia plant and heated up by a heater.

Another advancement of this study is the use of process intensification. One is the combined reformer as a substitute of pre-reformer and autothermal reformer in the reforming section. The other is the combined reactor as a replacement of high-pressure carbamate condenser, urea reactor, and vapor-liquid separator. The intensified vessels occupy less space and use less construction material. And the deployment of this intensified plant near the stranded gas reserves eliminate the cost of pipeline construction. The only drawback is the potential technology cost for customized reactor. The trade-off in this case is the saved construction materials and reduced transportation cost versus potential technology improvement. In this chapter, some important sections and process diagrams are analysed. The fixed and operating costs are compared in the Chapter IV.

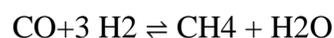
Further improvement potential lies in the water decanter section. The reformed gases first go through high temperature and low temperature shift reaction, then they are cooled to separate the water out. In the decanter 897 kmol water and 97 kmol CO<sub>2</sub> are emitted every hour. The pressure 35 bar is still enough for recycle. But the temperature 50 deg C is too low for reforming reaction. Thus, a heater is needed to heat the stream up to the initial feedstock temperature. H<sub>2</sub>O can undergo steam reforming and CO<sub>2</sub> can undergo dry reforming. So two components are both useful materials in this case. There is no impurity in this case. However, the mole fraction of water may have an effect on reactor heat duty and product gas composition. And dry reforming is a high endothermic reaction. Hence, more shale gas and air are required to provide the energy. In the circumstance in which separation is needed, a column should be considered for the fixed and operating cost.

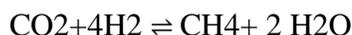
Detailed mechanism analysis of important sections are stated in III.1. Simulation results are summarized in III.2.

### III.1 Detailed Analysis by Section

The kinetics, chemical equilibrium limit, temperature and pressure condition, and simulation approaches of methanation, synthesis gas compression, and ammonia reaction unit are discussed in the following sections.

#### *III.1.1 Methanation*





After high temperature water gas shift, low temperature water gas shift and CO<sub>2</sub> scrubber, most carbon oxides are removed from the syngas stream. However, all oxygen-containing substances will poison the ammonia synthesis reaction catalyst (Allen & Yen, 1973). In industrial practice, the carbon oxides concentrations need to be reduced to a level of 10 ppm for further processing. Several processes namely methanation, the Selectoxo process, methanolation, dryers, cryogenic approaches, liquid nitrogen wash, pressure swing adsorption have been developed for this purpose. Among them, methanation is the simplest one and widely used one. Thus, this technique is further researched and applied in the Aspen Plus simulation.

This set of reactions can be viewed as the reverse reaction of steam reforming of methane. The reactions happen over a nickel catalyst. The temperature is around 250 - 350 Deg C. And the pressure is around 25 – 35 bar (Appl, 2011). In this process simulation, an intermediate value of temperature (300 Deg C) is selected. A pressure drop of 0 bar is used, so the pressure is the same with upstream pressure 33 bar. The RPlug reactor simulates this process with a residence time of 300ms suggested in a highly selective methanation (Görke, Pfeifer, & Schubert, 2005).

The first reaction implements a Langmuir-Hinshelwood type mechanism (Yadav & Rinker, 1993) based on a lab data program. Using the data reported by Yadav and Rinker at 503, 513 and 529 K, an Arrhenius equation is obtained as follows:

$$r = 0.314e^{(-1300[\frac{1}{T} - \frac{1}{513}])} \left( \frac{P_{CO}}{P_{H_2}^{0.5}} \right)$$

Where:

$r$  is the reaction rate in mol/(g\*s)

$P_{CO}$  is the partial pressure of carbon monoxide in kPa

$P_{H_2}$  is the partial pressure of hydrogen in kPa

$T$  is the temperature in K

To simulate the reaction better, the reactor model must include a backward reaction. Hence, the full version of the carbon monoxide reaction is as follows:

$$r = A_c 0.314 e^{(-1300[\frac{1}{T} - \frac{1}{513}])} \left( \frac{P}{P_{H_2}^{0.5}} \right) \left( y_{CO} - \frac{y_{CH_4} * y_{H_2O}}{y_{H_2}^3 * P^2 * K_{CO}} \right)$$

Where:

$r$  is the reaction rate in mol/(g\*s), which is converted to kmol/(m<sup>3</sup>\*s) using a bulk density of 1.2 g/cm<sup>3</sup>

$A_c$  is the catalyst activity factor

$T$  is the temperature in K

$P$  is the total pressure in kPa

$P_{H_2}$  is the partial pressure of hydrogen in kPa

$y_{CO}$  is the mole fraction of carbon monoxide

$y_{CH_4}$  is the mole fraction of methane

$y_{H_2O}$  is the mole fraction of water

$y_{H_2}$  is the mole fraction of hydrogen

$K_{CO}$  is the equilibrium constant of CO and H<sub>2</sub> reaction

$K_{CO}$  is determined by the equation below

$$K_{CO} = e^{(-38.4523 + 26270/T)}$$

Where:

$K_{CO}$  is the equilibrium constant of CO and H<sub>2</sub> reaction

T is the temperature in K

Due to the similarity of CO and CO<sub>2</sub> and the low concentration of CO<sub>2</sub> in the process stream, the kinetic for carbon dioxide use the same expression as carbon monoxide.

$$K_{CO_2} = e^{(-38.4523 + 26270/T)}$$

Where:

$K_{CO_2}$  is the equilibrium constant of CO<sub>2</sub> and H<sub>2</sub> reaction

T is the temperature in K

### *III.1.2 Compression*

Before 1950, gas generation and shift conversion operated at around 1 bar. Up to the mid-1960s, reciprocating compressors were widely used to compress the synthesis gas to the synthesis pressure, which was around 300 bar back then. The pressure was initially at 25 bar. At copper liquor scrubbing purification section, the pressure was further increased to 300 bar (Appl, 2011). Reciprocating compressors had as many as 7 stages, with CO<sub>2</sub> removal put between 3<sup>rd</sup> to 4<sup>th</sup> stages. This kind of compressor can take up to 15000 m<sup>3</sup> synthesis mixed gas at the first stage.

In 1963, M. W. Kellogg invented one of the most important technology in the modern energy integrated steam reforming ammonia plant, with the use of centrifugal

compressors for synthesis gas, recycle gas, process air and refrigeration (Appl, 2011). The centrifugal compressors are inherently less efficient than reciprocating compressors. But in the ammonia plant, there are plenty of excess heat which can be used to generate steam. Centrifugal compressors has a huge energy saving advantage of using these steam. Despite the use of excess, centrifugal compressors also avoid the losses in generation and transmission of electricity. Hence, overall efficiency of steam-driven centrifugal compressor surpasses the efficiency of electric power-driven reciprocating compressors. In this paper, multistage compressor are driven by excess high pressure steam. And an isentropic efficiency of 45% is assumed for steam turbine based on the literature (El-Halwagi, 2017). Other advantages of these equipments are low investment(single machines even for very large capacities) and maintenance cost, less frequent shutdowns for preventive maintenance, and high reliability (Williams & Hoehing, 1983).

One major limitation of centrifugal compressor is the size of outer impeller circumference. This causes a limit on minimum passage of gas in the compressor. The minimum width is 2.8 mm at present. The first single-train ammonia plants operated at 150 bar with a capacity of 600t/d. Modern plant usually operated at 145 bar with a capacity around 400 t/d. Newer ICI's LCA Process and Kellogg's KAAP can operate with a capacity of 220 t/d. For this paper, ammonia production is 445 tonne per day, which is beyond the lower bound of centrifugal compressor technology.

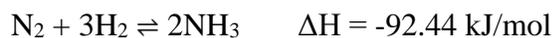
An isentropic efficiency of 75% is used for compressor. In practice, a compressor shaft must avoid vibration. So the impeller installed in the one compressor is limited.

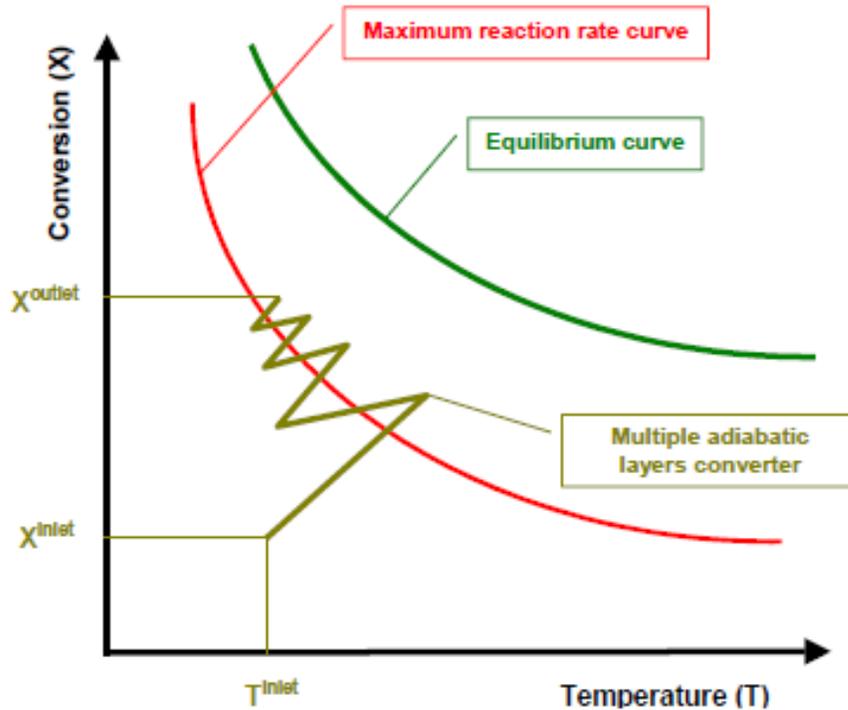
Generally, a compression ratio between 1.8 and 3.2 is selected in this process. Compression can render temperature rise of the stream. To avoid overheating stream, intermediate coolers are installed between to compressors.

### *III.1.3 Synthesis Unit*

Ammonia synthesis section is modeled by RPlug in Aspen Plus. The purified syngas is compressed to 300 bar by three stages compressors. An efficiency of 75% is chosen based on the description in Ullmann's Encyclopedia of Industrial Chemistry (Appl, 2011). Compression ratio 2.09 stays in the practical region from 1.8 to 3.2. All the compressors are followed by a cooler to reduce the gas temperature after the compression. The outlet temperature is set to 295 deg C which meets the inlet temperature of ammonia converter. Feed gas is first compressed to 68.8 bar, the temperature reaches 474 deg C. In the second compressor, the gas is compressed to 143.7 bar and it reaches a similar temperature of 468.8 deg C. In the third compressor, the target pressure is achieved, and the cooler inlet temperature is 470.4 deg C. The total work required is 10.02 MW. Net cooling duty is -9.89 MW.

The major synthesis reaction is shown as follow.





**Figure 10 Expected Thermal Profile of Catalyst Along the Converter (Filippi, Muzio, & Rizzi, 2006)**

As shown in the Figure 10, ammonia synthesis reaction are constrained by equilibrium limit. The process follows the line of highest reaction rate to obtain the maximum possible conversion per pass from a given catalyst volume. When the gas is first introduced into the catalyst bed, it reacts to a certain extent. The composition is very close to equilibrium line at this time, so the driving force is low. The gas cools to a temperature which has large driving force to react. Then the gas is introduced to the second catalyst bed. The process repeats several time until the mole fraction reaches the

target at about 20%. The number of commercial converters range from 2 to 4 catalyst beds. 3 catalyst beds are chosen to simulate for this study.

Nielsen *et al.* carried out an extensive kinetic study on a commercial triply promoted KMIR (K20, CaO, A1203) catalyst. It had been prereduced in the size range 3-6 mm but was tested in the size range 0.3-0.7 mm. The sample was reduced again at 150 atm up to 400 DC after which the pressure was increased to 300 atm and the temperature to 480 DC. The reactor had an internal diameter of 5 mm and was equipped with three thermocouples of 1 mm in outer diameter in the catalyst bed. Total catalyst volume was 2.5 cm<sup>3</sup>.

The operating conditions studied were as follows:

Pressure: 149-309 atm abs

Temperature: 330-495 Deg C

Space velocity: 13200-105600 vol/h

H<sub>2</sub>/N<sub>2</sub> ratio: 6.23-1.15

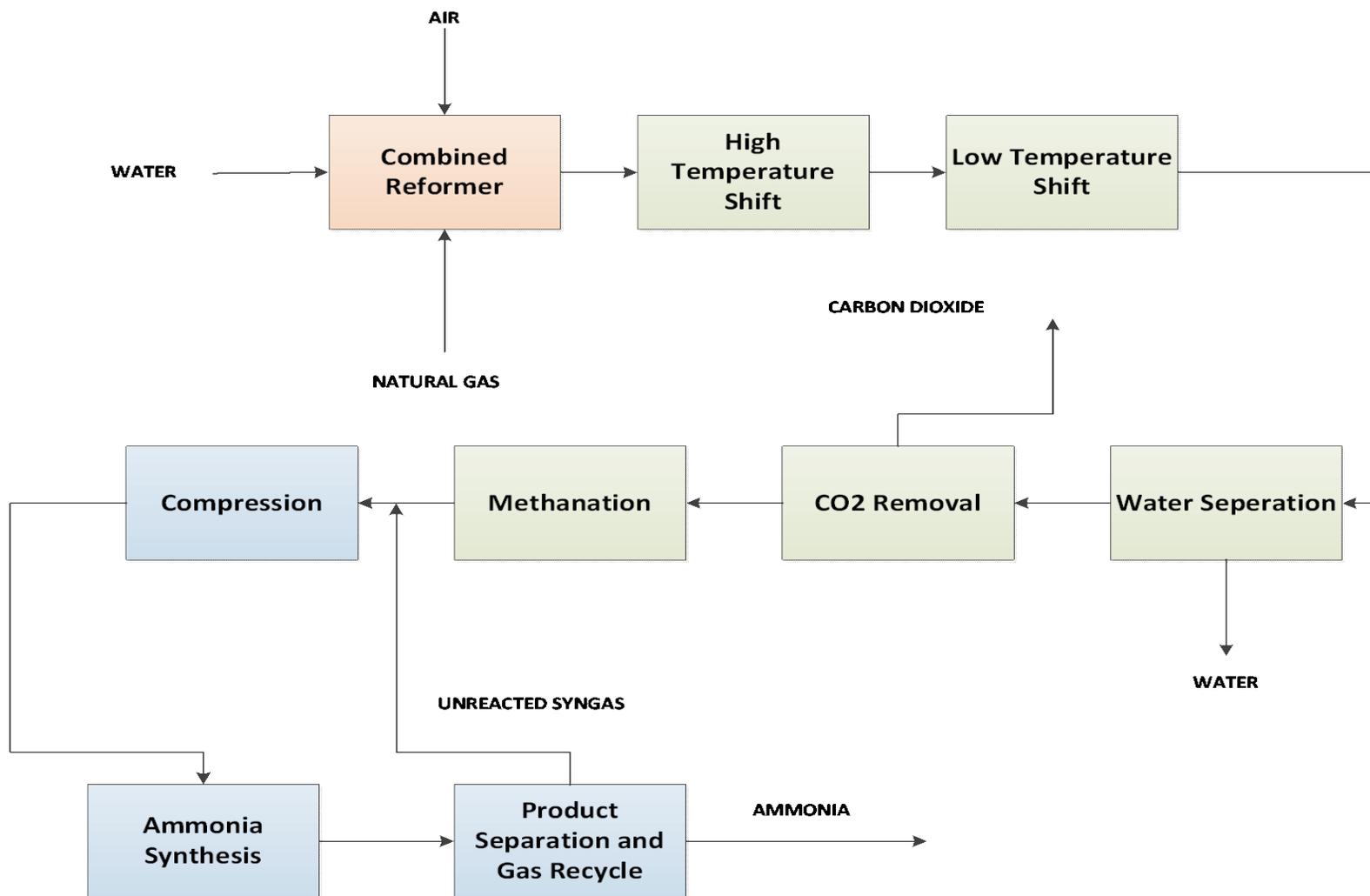
The ammonia synthesis units were simulated based on above conditions.

### III.2 Simulation Summary

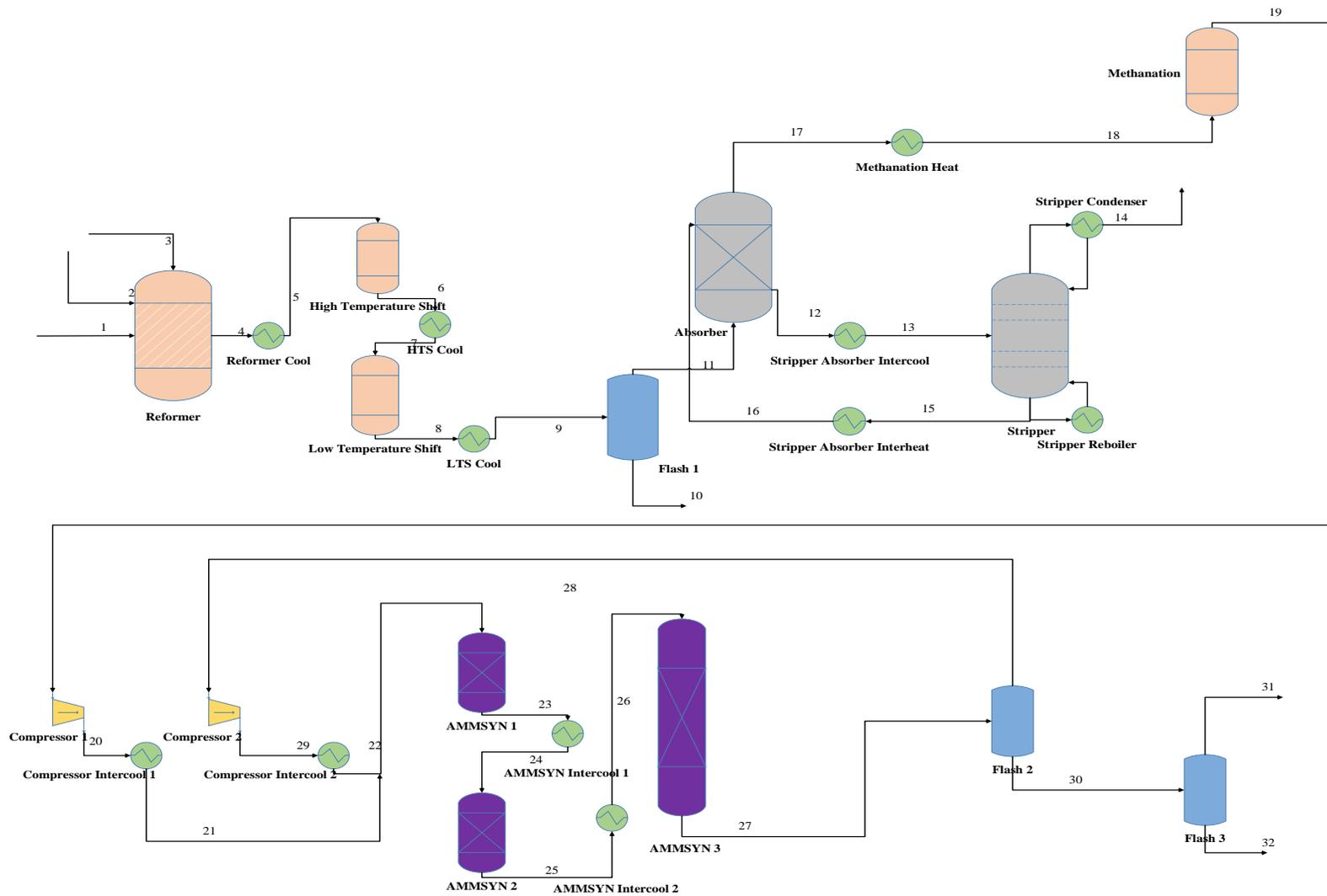
In section III.2.1 and III.2.2, detailed simulation results of two processes are discussed. Block diagrams and process flow diagrams of ammonia and urea process are illustrated in the following sections. The yield data, annual production rate, product purity, energy consumption, and raw material consumption are also analyzed.

### *III.2.1 Ammonia Process*

Only major facilities in the ammonia process are considered for generating the process. ASPEN PLUS V10.0 was used to simulate the steady state plant. A screenshot of the aspen equipment and process are attached in the appendix. ENRTL-RK was used as the thermodynamic model for simulations. Combined reformer were simulated by RGibbs model. High temperature shift, low temperature shift, methanation, ammonia synthesis reactors were simulated by RPlug model. All separation column were simulated by using RadFrac expect flash drums were simulated using Flash2. Block diagram of ammonia production process is shown in Figure 11. Process flow diagram of ammonia production process is illustrated in Figure 12.



**Figure 11 Block Diagram of Ammonia Production Process**



**Figure 12 Process Flow Diagram of Ammonia Production Process**

The whole ammonia process are simulated in ASPEN PLUS using the kinetics and specifications described in III.1. Detailed yield data are shown in the following tables for gas leaving combined reformer, water-gas shift, methanation, ammonia synthesis section. Reactor yield data after combined reformer are shown in Table 6. Yield data after water-gas shift section are shown in Table 7. Yield data after methanation are shown in Table 8. Yield data after ammonia synthesis section are shown in Table 9.

**Table 6 Reactor Yield Data after Combined Reformer**

Components	Reactor yield mass %
H2O	38.35
N2	27.43
CO	15.77
CO2	13.47
H2	4.79
CH4	0.19

**Table 7 Yield Data after Water-Gas Shift**

Components	Reactor yield mass %
CO2	37.57
H2O	28.45
N2	27.43
H2	5.89
CO	0.43
CH4	0.19
NH3	0.04

**Table 8 Yield Data after Methanation**

Components	Reactor yield mass %
N <sub>2</sub>	81
H <sub>2</sub>	17
CH <sub>4</sub>	1

**Table 9 Yield Data after Ammonia Synthesis**

Components	Reactor yield mass %
NH <sub>3</sub>	62.43
H <sub>2</sub>	28.27
CH <sub>4</sub>	4.72
N <sub>2</sub>	4.58

All the simulations ran smoothly without any errors. Adding the air as a direct oxidant and nitrogen source worked out in the simulation. The obtained simulation results are within the reasonable area compared to literature data. The reformer was operating at 1000 deg C, 35 bar. The air flow and water flow were manipulated by using Aspen Plus design spec. The final H<sub>2</sub>O/CH<sub>4</sub> ratio was 3.11. Air/CH<sub>4</sub> ratio was 0.62.

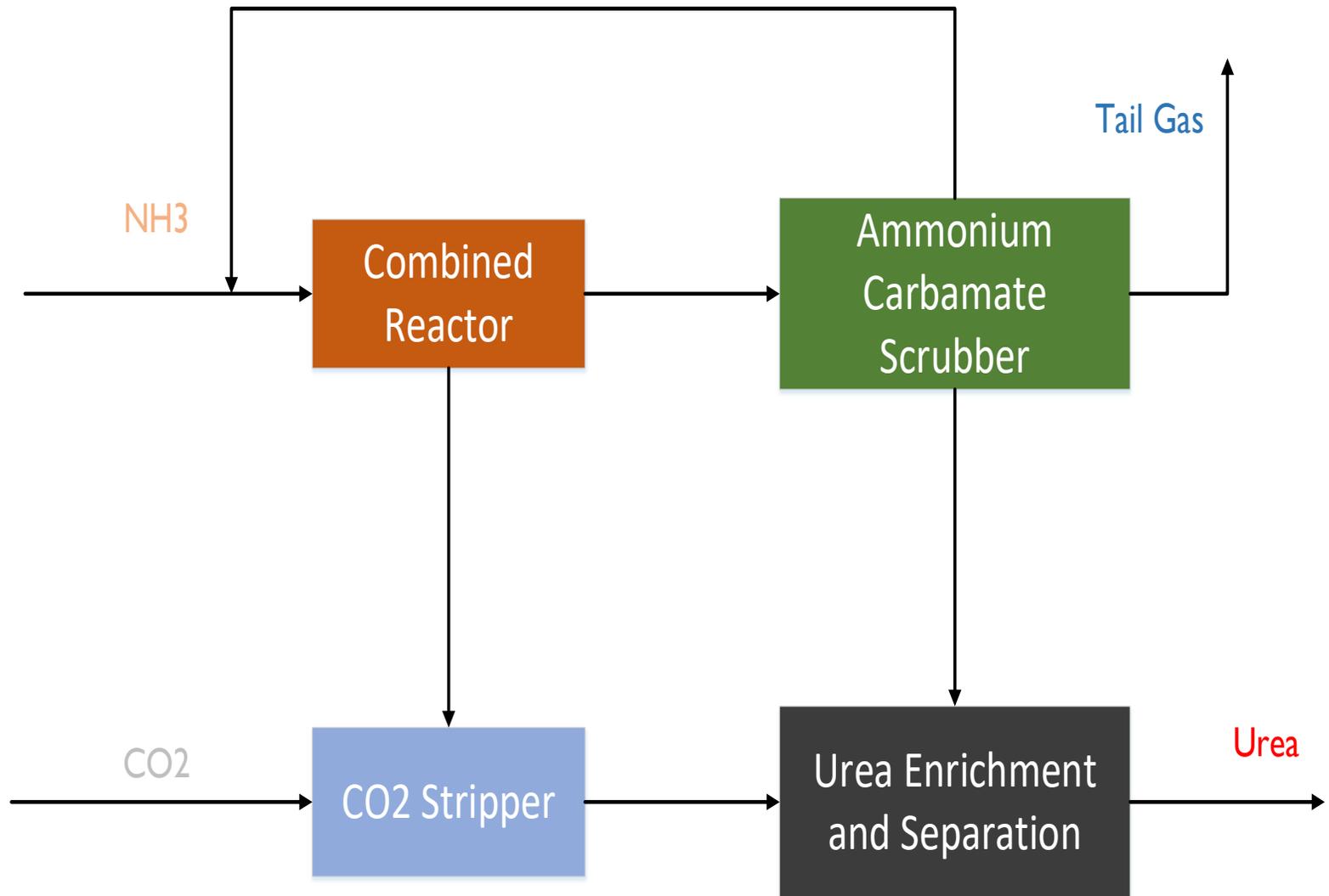
The summarized simulation results are shown in the Table 10 below. Because the economic analysis need to use detailed utility consumption and raw material consumption as a reference, so these analysis are analyzed in Chapter V with economic analysis for better view.

**Table 10 Summarized Simulation Results-Ammonia**

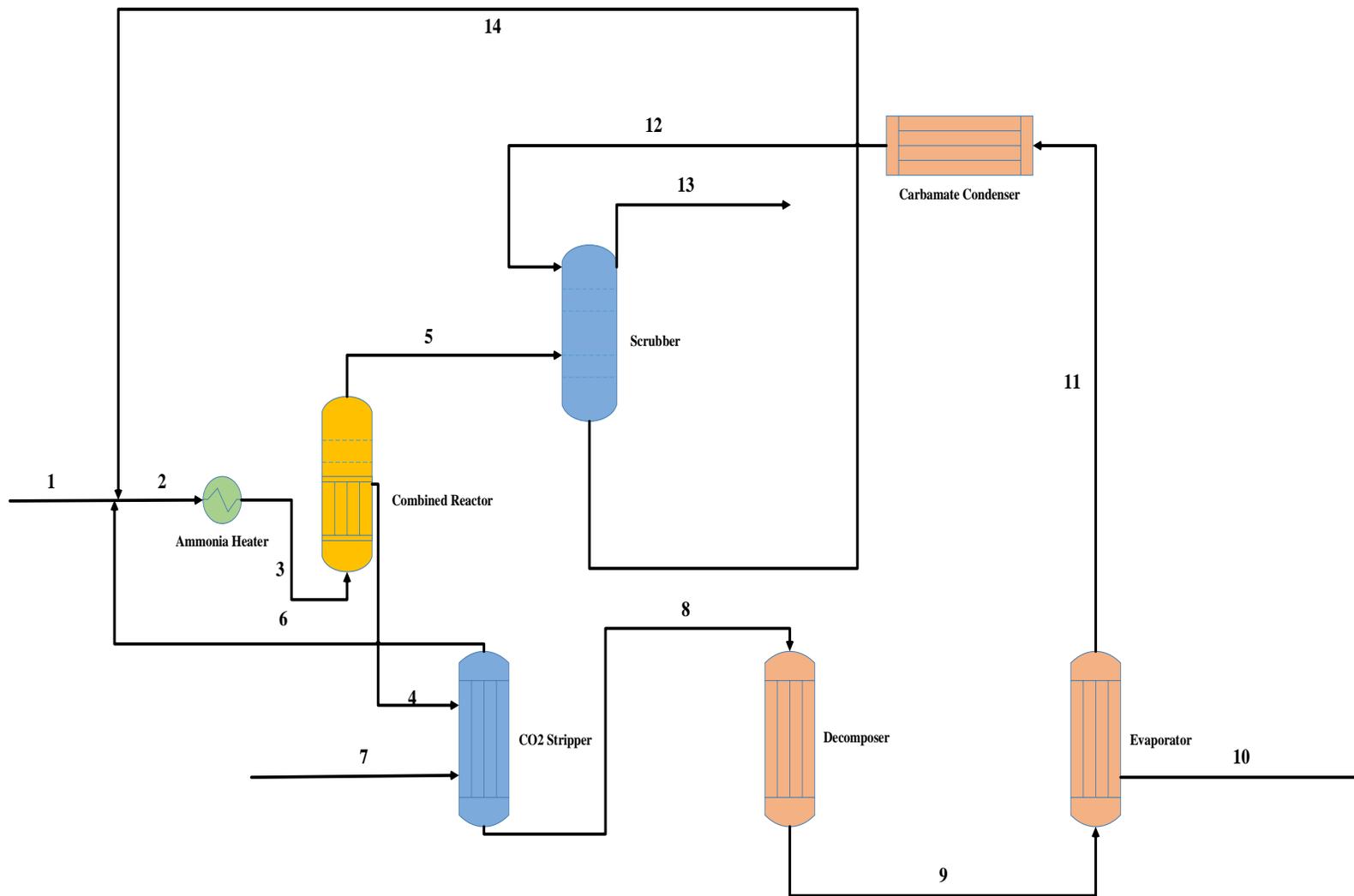
Parameter	Value	UOM
Annual Production rate of ammonia	136,246	Tonnes/yr
Product purity	99.6	wt %
Annual Methane Feed rate	64,796	Tonnes/yr
Actual energy requirements	899	MMBtu/hr
Specific Energy Consumption	52.8	MMBtu/tonne of ammonia
Specific consumption of raw material	2.1	Tonne of ethylene/ tonne of ethane

### *III.2.2 Urea Process*

Only major facilities in the urea process are considered for generating the process. ASPEN PLUS V10.0 was used to simulate the steady state plant. A screenshot of the aspen equipment and process are attached in the appendix. SR-POLAR was used as the thermodynamic model for simulations. Vertical combi-reactor and carbamate condenser was simulated by RGibbs model. CO<sub>2</sub> Stripper and scrubber were simulated by RadFrac model. Decomposer was simulated by using RStoic. While evaporator was simulated using Sep. Block diagram of urea production process is shown in Figure 13. Process flow diagram of urea production process is illustrated in Figure 14.



**Figure 13 Block Diagram of Urea Process**



**Figure 14 Process Flow Diagram of Urea Production Process**

The whole urea process are simulated in ASPEN PLUS using the kinetics and specifications described in III.1. Detailed yield data are shown in the following tables for gas leaving vertical combi-reactor and carbamate condenser. Reactor yield data after combined urea reactor is shown in Table 11. Reactor yield data after carbamate condenser is shown in Table 12.

**Table 11 Reactor Yield Data after Combined Urea Reactor**

Components	Reactor yield mass %
Stream 5	
NH3	77.27
CO2	17.59
H2O	5.07
UREA	0.07
Stream 4	
UREA	34
NH3	25
Ammonium carbamate	21
H2O	18
CO2	2

**Table 12 Reactor Yield Data after Carbamate Condenser**

Components	Reactor yield mass %
H2O	47.8
NH3	3.3
UREA	0.4
Ammonium carbamate	48.5

The simulation results were in line with the literature. All the simulation ran smoothly without any errors. Setting up a vertical combi-reactor worked out in the

simulation. The obtained simulation results are within the reasonable area compared to literature data. The feed of the vertical combi-reactor is at 149 deg C. The operating pressure is 142 bar.

The summarized simulation results are shown in the Table 13. Because detailed utility consumption and raw material consumption is needed when doing the economic analysis, so these analysis are analyzed in Chapter V with economic analysis for better view.

**Table 13 Summarized Simulation Results-Urea**

<b>Parameter</b>	<b>Value</b>	<b>UOM</b>
Annual Production rate of urea	218,526	Tonnes/yr
Product purity	77.4	wt %
Annual Ammonia Feed Rate	136,244	Tonnes/yr

## CHAPTER IV

### ECONOMIC ANALYSIS

Chemical plant is built to make profits, so an estimate of capital investment, operating cost, ROI and payback period is of vital importance before a plant is installed. In this chapter, economic analyses are applied to evaluate the economics of ammonia alone plant, urea plant without mass integration and urea plant with mass integration. The main purpose of this chapter is to identify the effect in cash flow and payback time when a new plant is added or waste material is reused. Economics of the plants are examined based on equipment cost, flow rate of the streams, raw material cost, utilities cost and product sales. The cost of workers hasn't been included in this study. The major utility costs are retrieved from Aspen Energy Analyzer V8.8. The price of raw materials are taken from Energy Information Administration and industrial water rates in Danville, VA. The price of products are fetched from industrial market source.

#### IV.1 Ammonia Plant

Fixed capital costs, raw material costs, utilities costs and product sales are the four major components discussed in this section. The types of utilities except reformer heat and electricity are first determined in Aspen Energy Analyzer. Operating conditions are shown in Table 14. And utilities prices are shown in the Table 15. Energy consuming equipment and their consumptions in ammonia plant are stated in Table 16. The fired heat price in Aspen Energy Analyzer is defined based on recent natural gas price. The

reformer heat is also based on the natural gas. The industrial electricity price are taken from Illinois power price in November 2016 on energy information administration website (EIA, 2016c).

**Table 14 Utilities Operating Conditions**

Utility	Inlet T(Deg C)	Outlet T(Deg C)
Air	30	35
Refrigerant	-40	-39
MP Steam	175	174
Fired Heat (1000)	1000	400
HP Steam	250	249
LP Steam	125	124
Cooling Water	20	25

**Table 15 Unit Utilities Cost - Ammonia Plant**

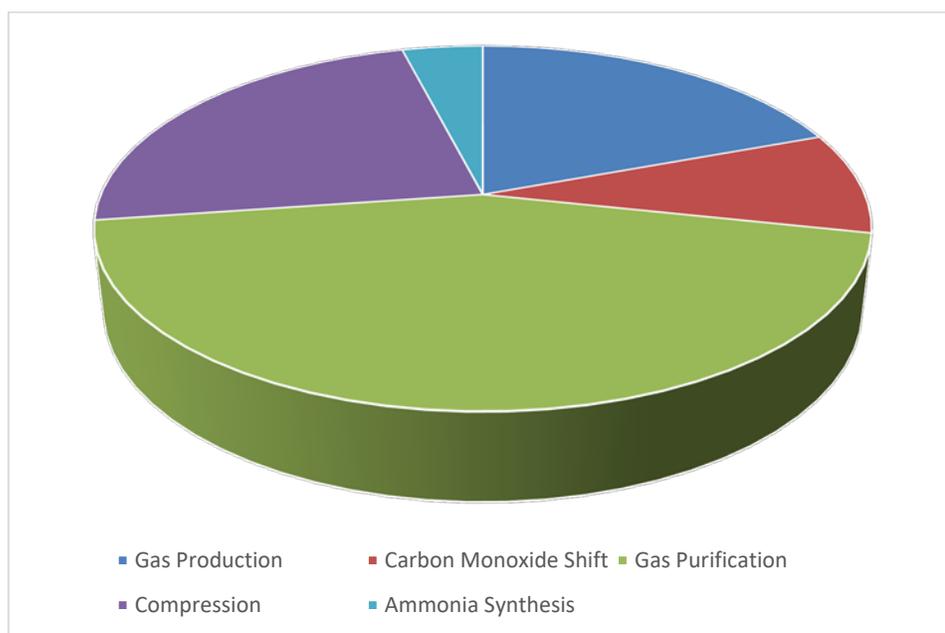
Type	Specification	Value	Unit
Heating	LP Steam	2.00	\$/MMBtu
	MP Steam	2.32	\$/MMBtu
	HP Steam	2.64	\$/MMBtu
	Natural Gas	2.82	\$/MMBtu
Cooling	Refrigeration	3.55	\$/MMBtu
	Cooling water	0.22	\$/MMBtu

**Table 16 List of Energy Consuming Equipment and Their Consumptions - Ammonia Plant**

Section	Name in PFD	Utility type	Heat Duty (MMBtu/hr)
Gas Production	Reformer	Natural gas	92
	Reformer Cool	Cooling water	-82
Carbon Monoxide Shift	HTS Cool	Cooling water	-24
	LTS Cool	Cooling water	-57
Gas Purification	Stripper Condenser	Cooling water	-51
	Stripper Reboiler	HP Steam	105

**Table 16 Continued**

<b>Section</b>	<b>Name in PFD</b>	<b>Utility type</b>	<b>Heat Duty (MMBtu/hr)</b>
<b>Gas Purification</b>	Stripper Absorber Intercool	Cooling water	-139
	Stripper Absorber Interheat	MP Steam	88
	Methanation Heat	Natural gas	16
<b>Compression</b>	Compressor 1	HP Steam Turbine	52
	Compressor Intercool 1	Cooling water	-53
	Compressor 2	HP Steam Turbine	53
	Compressor Intercool 2	Cooling water	-51
<b>Ammonia Synthesis</b>	AMMSYN Intercool 1	Cooling water	-18
	AMMSYN Intercool 2	Cooling water	-18
		<b>Total Energy Requirement</b>	<b>899</b>



**Figure 15 Specific Energy Consumption - Ammonia Process**

Specific energy consumption of ammonia Process is analyzed in Figure 15. If we analysed the specific energy consumption by section, we can see that gas purification accounts for about half the energy consumption. Compression part is the second largest energy consuming sector. Then the utility cost was calculated based on energy consumption and unit utility cost. The details are shown in Table 17.

**Table 17 Utility Cost of Equipment - Ammonia Plant**

Section	Units name	Cost (\$/hr)
Gas Production	Reformer	259
	Reformer Cool	18
Carbon Monoxide Shift	HTS Cool	5
	LTS Cool	13
Gas Purification	Stripper Condenser	11
	Stripper Reboiler	277
	Stripper Absorber Intercool	31
	Stripper Absorber Interheat	204
	Methanation Heat	45
Compression	Compressor 1	305
	Compressor Intercool 1	12
	Compressor 2	311
	Compressor Intercool 2	11
Ammonia Synthesis	AMMSYN Intercool 1	4
	AMMSYN Intercool 2	4
<b>Total</b>		1510

**Table 18 Raw Material Cost - Ammonia Plant**

Specification	Value	Unit
Unit price of water	2.4	\$/100 ft <sup>3</sup>
Density of water	62	lb/ft <sup>3</sup>
Price of water (cubic foot basis)	0.024	\$/ft <sup>3</sup>
Price of water (pound basis)	3.85x10 <sup>-4</sup>	\$/lb

**Table 18 Continued**

<b>Specification</b>	<b>Value</b>	<b>Unit</b>
Price of water (metric toone basis)	0.848	\$/tonne
Specific consumption of water to ammonia	1.56	tonne/tonne ammonia
Amount of water required	29	tonnes/hr
Price of water	24	\$/hr
Unit price of natural gas	2.82	\$/MMBtu
Heat content of natural gas	1032	Btu/ft <sup>3</sup>
Density of natural gas	0.05	lb/ft <sup>3</sup>
Price of natural gas (cubic foot basis)	2910	\$/MMft <sup>3</sup>
Price of natural gas (pound basis)	0.058	\$/lb
Price of natural gas (metric toone basis)	128	\$/tonne
Specific consumption of natural gas to ammonia	0.44	tonne/tonne ammonia
Amount of natural gas required	8	tonnes/hr
Price of natural gas	1037	\$/hr
Unit price of MEA	1341	\$/tonne
Amount of Makeup MEA required	1.2	kg/hr
Price of MEA	1.6	\$/hr
Unit price of makeup water	0.848	\$/tonne
Amount of makeup water required	1.7	tonnes/hr
Price of makeup water	1.4	\$/hr

After that, raw material cost was evaluated to hourly feedstock and other recycle material consumption. Raw material cost of ammonia plant is shown in Table 18. Different methods for evaluating purchased quipment cost were applied in this study based on data availability. For those equipments which have data in the Aspen Process Economic Analyzer (APEA), equipment cost are quoted directly from the software. For

those equipment lacking data in APEA, such as reformer, HTS, LTS, and compressor, the correlations in the chemical engineering design : principles, practice, and economics of plant and process design book (Towler & Sinnott, 2012) was used to get a preliminary estimates. The correlations are as follow

$$C_e = a + b S^n$$

Where:

$C_e$  = purchased equipment cost on a U.S. Gulf Coast basis, Jan. 2010 (CEPCI = 532.9, NF refinery inflation index = 2281.6)

a, b = cost constants in chemical engineering design

S = size parameter, units given in chemical engineering design

n = exponent for that type of equipment

**Table 19 Cost Curves Parameters (Towler & Sinnott, 2012)**

Equipment	S	a	b	n
Reactor	m <sup>3</sup>	61500	32500	0.8
Pressure vessels, Vertical	kg	11600	34	0.85
Centrifugal compressor	kW	580000	20000	0.6

**Table 20 Minimum Practical Wall Thickness (Towler & Sinnott, 2012)**

Vessel Diameter (m)	Minimum Thickness (mm)
1	5
1 to 2	7
2 to 2.5	9
2.5 to 3.0	10
3.0 to 3.5	12

In Table 19 and Table 20, cost curves parameter used in this study and minimum practical wall thickness list used to estimate the vessel wall thickness are shown. In order to validate difference between APEA and Ce correlation, several equipments are analysed using both methods.

**Table 21 Aspen Energy Analyzer Estimation Validation**

Units	Area/m <sup>3</sup>	Cost curves prices (\$)	Energy Analyzer prices (\$)	Relative difference
LTS Cool	233	65430	82000	0.2
Stripper Absorber Intercool	198	58789	64974	0.1
Stripper Absorber Interheat	285	75666	83590	0.09

As we can see from the Table 21, there is only 15% relative difference between different method. From engineering point of view, the result is quite acceptable. For all other equipments, a general six by tenth rule was used to estimate the equipment cost (Ward, 2001). The correlation for scale factor of equipment cost is:

$$\text{Equipment Cost}_B = \text{Equipment Cost}_A * (\text{Capacity of B} / \text{Capacity of A})^x$$

A general value of 0.6 is used in this case. Purchased equipment cost of equipment in ammonia plant is shown in Table 22.

**Table 22 Purchased Equipment Cost of Equipment - Ammonia Plant**

Section	Units name	Cost (\$)
Gas Production	Reformer	118086
	Reformer Cool	119266
Carbon Monoxide Shift	HTS	15313

**Table 22 Continued**

<b>Section</b>	<b>Units name</b>	<b>Cost (\$)</b>
<b>Carbon Monoxide Shift</b>	HTS Cool	103329
	LTS	14141
	LTS Cool	82011
<b>Gas Purification</b>	Flash 1	36200
	Stripper Absorber Intercool	83589
	Stripper Absorber Interheat	64974
	Stripper	574800
	Methanation Heat	108200
	Methanation	41600
<b>Compression</b>	Compressor 1	7039841
	Compressor Intercool 1	84693
	Compressor 2	7104121
	Compressor Intercool 2	62100
<b>Ammonia Synthesis</b>	AMMSYN 1,2, and 3	389684
	AMMSYN Intercool 1	28588
	AMMSYN Intercool 2	32775
<b>Product Separation and Recycle</b>	Flash 2	182900
	Flash 3	38700
	<b>Total</b>	<b>16390611</b>

Lang factor was used to convert purchased equipment cost into fixed capital cost.

The formula is given by:

$$C = F(\sum C_e)$$

Where:

C = total plant capital cost (including engineering costs)

$\sum C_e$  = total delivered cost of all the major equipment items: reactors, tanks columns, heat exchangers, furnaces, etc.

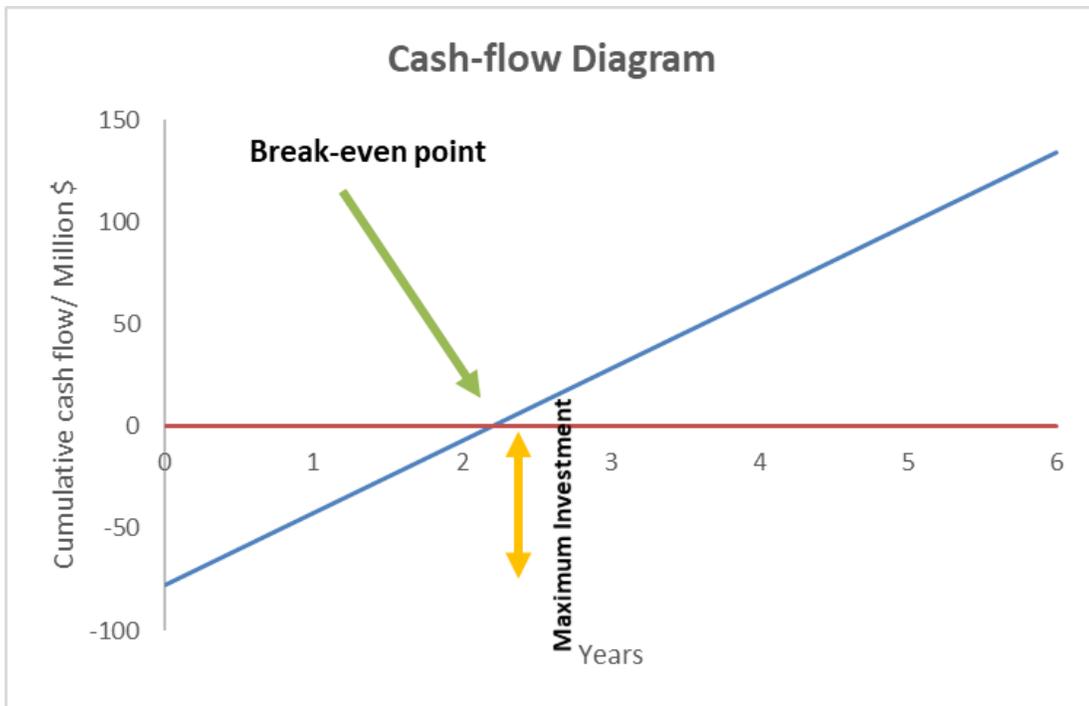
F = an installation facotr

F = 4.74 for fluids processing plant

After calculating utility cost, raw material cost, fixed capital cost one by one, I got the consolidated economic summary. Economic summary of ammonia plant is shown in Table 23. \$376/tonne was used for product price of ammonia based on ICIS data. Cash flow of an ammonia plant is shown in the Figure 16.

**Table 23 Economic Summary - Ammonia Plant**

Parameter	Value	Unit
Utility Cost	12.1	MM \$/a
Raw Material Cost	8.5	MM \$/a
Operating Cost	20.6	MM \$/a
Total Plant Capital Cost	77.7	\$ MM
Product Sales	55.9	MM \$/a
Economic Gross Potential	47.4	MM \$/a
Payback time	2.2	year



**Figure 16 Ammonia Process Cash Flow**

## IV.2 Urea Plant

Fixed capital costs, raw material costs, utilities costs and product sales of urea process are discussed in this section. The utilities types are first determined in Aspen Energy Analyzer. Operating conditions and prices are the same as the ammonia process the table below. Raw material cost of urea process is shown in Table 24. Purchased equipment cost of urea plant is shown in Table 25. The fired heat price in Aspen Energy Analyzer is defined based on recent natural gas price. The reformer heat price is also based on the natural gas. The industrial electricity price are taken from Illinois power price in November 2016 on energy information administration website (EIA, 2016c).

For this analysis, the utility cost are generated from APEA. The utility cost of this case is \$569,514/yr. Purchased equipment cost were calculated by the method in chemical engineering design : principles, practice, and economics of plant and process design book (Towler & Sinnott, 2012). Fixed capital cost was evaluated using the same Long factor 4.74. The consolidated summary of urea process are shown in Table 26. The cash flow analysis are expressed in Figure 17.

**Table 24 Raw Material Cost - Urea Process**

<b>Specifications</b>	<b>Unit</b>	<b>Value</b>
Unit Price of CO <sub>2</sub>	\$/tonne	9
Amount of CO <sub>2</sub> required	Tonne/hr	22
CO <sub>2</sub> Price	\$/hr	198
Unit Price of NH <sub>3</sub>	\$/tonne	376
Amount of NH <sub>3</sub> required	Tonne/hr	17
NH <sub>3</sub> Price	\$/hr	6392

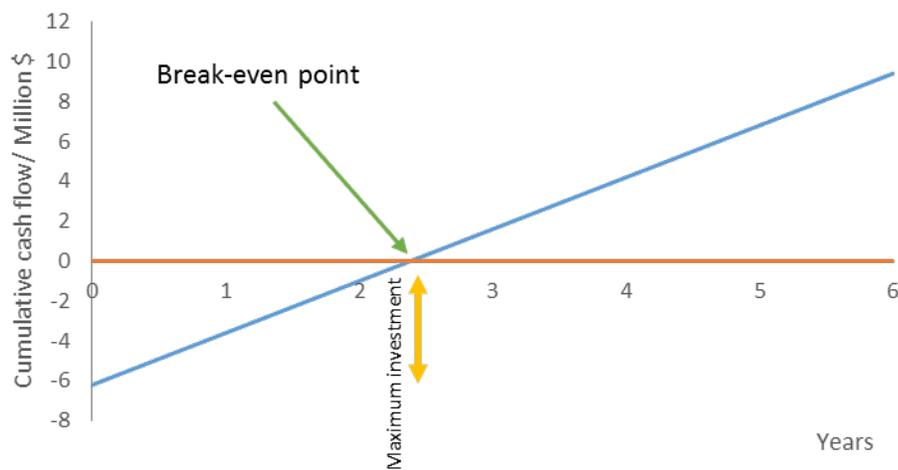
**Table 25 Purchased Equipment Cost - Urea Plant**

Section	Units name	Cost (\$)
Reactor	Ammonia Heater	11,100
	Combined Reactor	1,085,491
CO2 Stripper	CO2 Stripper	51,900
Ammonium Carbamate Scrubber	Scrubber	32,404
Urea Enrichment and Separation	Decomposer	29,034
	Evaporator	62,700
	Carbamate Condenser	35,345
<b>Total</b>		1307974

**Table 26 Economic Summary - Urea Process**

Parameter	Value	Unit
Utility Cost	0.57	MM \$/a
Raw Material Cost	57.7	MM \$/a
Operating Cost	58.27	MM \$/a
Total Plant Capital Cost	6.2	\$ MM
Product Sales	61.9	MM \$/a
Payback time	1.7	year

**Cash-flow Diagram**



**Figure 17 Urea Process Cash Flow**

### IV.3 Combined Plant

One analysis is done for ammonia alone plant combined with a urea plant. The consolidated economic summary is shown in the Table 27. There are several potentials for doing this, first is the heat integration. Hence the urea alone plant barely needs any cooling source, so it could a good sink to put heat in. Also, in the second process, the first purge mixture of water and CO<sub>2</sub> can be separated to use as feedstock.

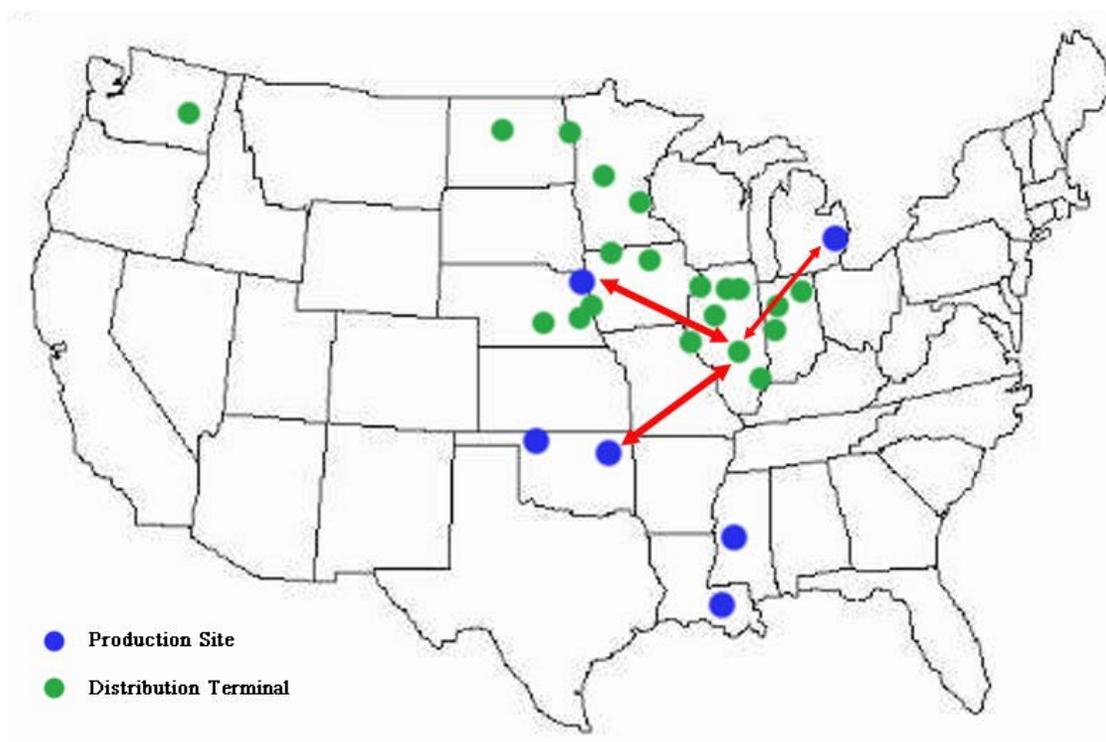
But several other factors like plant size needs to be considered, before one just simply connected the two processes. To avoid the repetition of calculation path, I just put a simple high-level analysis here.

**Table 27 Economic Summary - Combined Plant**

Parameter	Value	Unit
Utility Cost	12.67	MM \$/a
Raw Material Cost	10.1	MM \$/a
Operating Cost	22.77	MM \$/a
Total Plant Capital Cost	83.9	\$ MM
Product Sales	61.9	MM \$/a
Payback time	2.14	year

### IV.4 Transportation Cost

By using process intensification, the reactor size was reduced. Hence, there is opportunity for small volume stranded gas user to build fertilizer plant on site. This section is to analyze the effect of transportation cost on the whole project.



**Figure 18 Different Types of Sites in CF Industries**

CF Industries is one of the major fertilizer producer in North American market. In this section, a current sites map of CF Industries is used for the evaluation (CF Industries, 2017). First, the three closet production sites were chosen to calculate the average delivery length. Other production sites are not included in this analysis, so the actual saving for transportation can be even higher. The average distance from production sites to distribution facilities is 427 miles. If the manufacturers are using shale gas from Illinois, they need to first transport the raw material to production site. Then they still need to send the fertilizer products back to the place where most farmers reside. In this case, a round trip needs to be done. If they are using shale gas from other sources, that is a different scenario. Due to the scant information of feedstock source, the

raw shale gas are assumed to acquire from Illinois. The analysis is illustrated in Figure 18.

The transportation cost is estimated using a study on different natural gas product (Najibi, Rezaei, Javanmardi, Nasrifar, & Moshfeghian, 2009). The detailed data are shown in Figure 19. In all methods, PNG is the cheapest among all the methods when the distance is below 8,000km distance. Transportation distance of 687 kilometers (equal to 427 miles) is selected. \$0.0008/MJ transportation cost is applied in this study. \$0.5/MMBtu feed natural gas cost is subtracted to avoid calculation redundance. The economic summary when considering transportation cost is shown in Table 28.

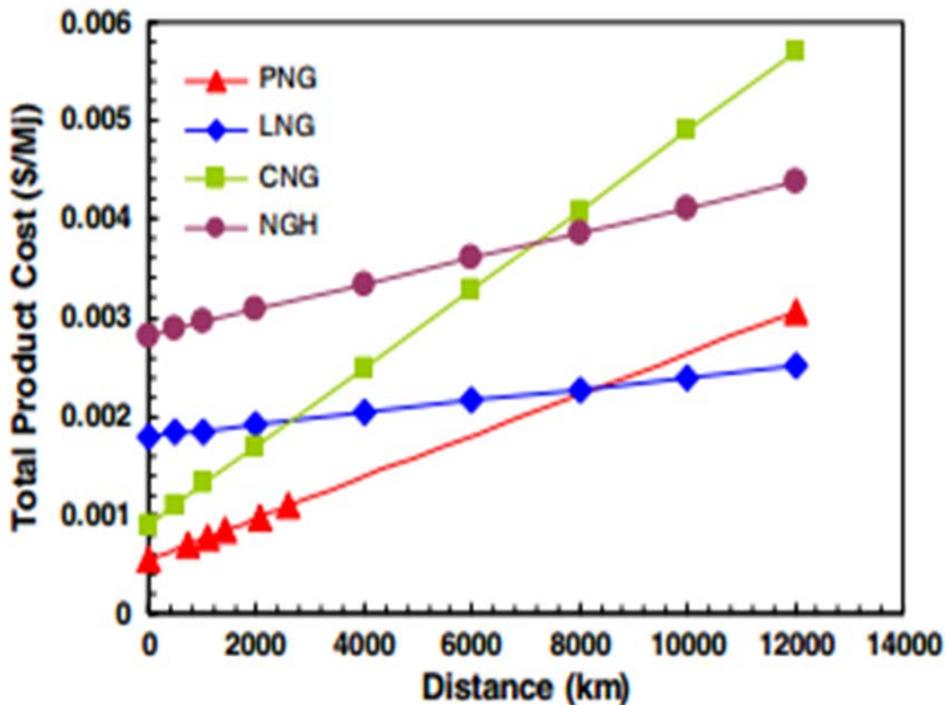


Figure 19 Different Product Transportation Cost vs Distance. (Reprinted with permission from Najibi *et al.*, 2009)

**Table 28 Economic Summary - Considering Transportation Cost**

Parameter	Value	Unit
Utility Cost	13.64	MM \$/a
Raw Material Cost	10.1	MM \$/a
Operating Cost	23.74	MM \$/a
Total Plant Capital Cost	85.1	\$ MM
Product Sales	61.9	MM \$/a
Payback time	2.23	year

## CHAPTER V

### CONCLUSIONS AND FUTURE WORK

As we can see from the analysis in the previous chapter, the ammonia alone plant has a payback period of 2.2 years. While the urea alone plant has a payback period of 1.7 years. If combined together, the whole plant will have a payback period of 2.14 years. In this case, both plants used the process intensification in one of the reactors, if take the transportation reduction into account. The cost saved is around 4% of total operating cost. If used the combined plant as an example, the payback period will slightly increase to 2.23 years.

For future work, heat integration can be applied to reevaluate the economic condition. Furthermore, safety standard can be used as additional approach for process selection.

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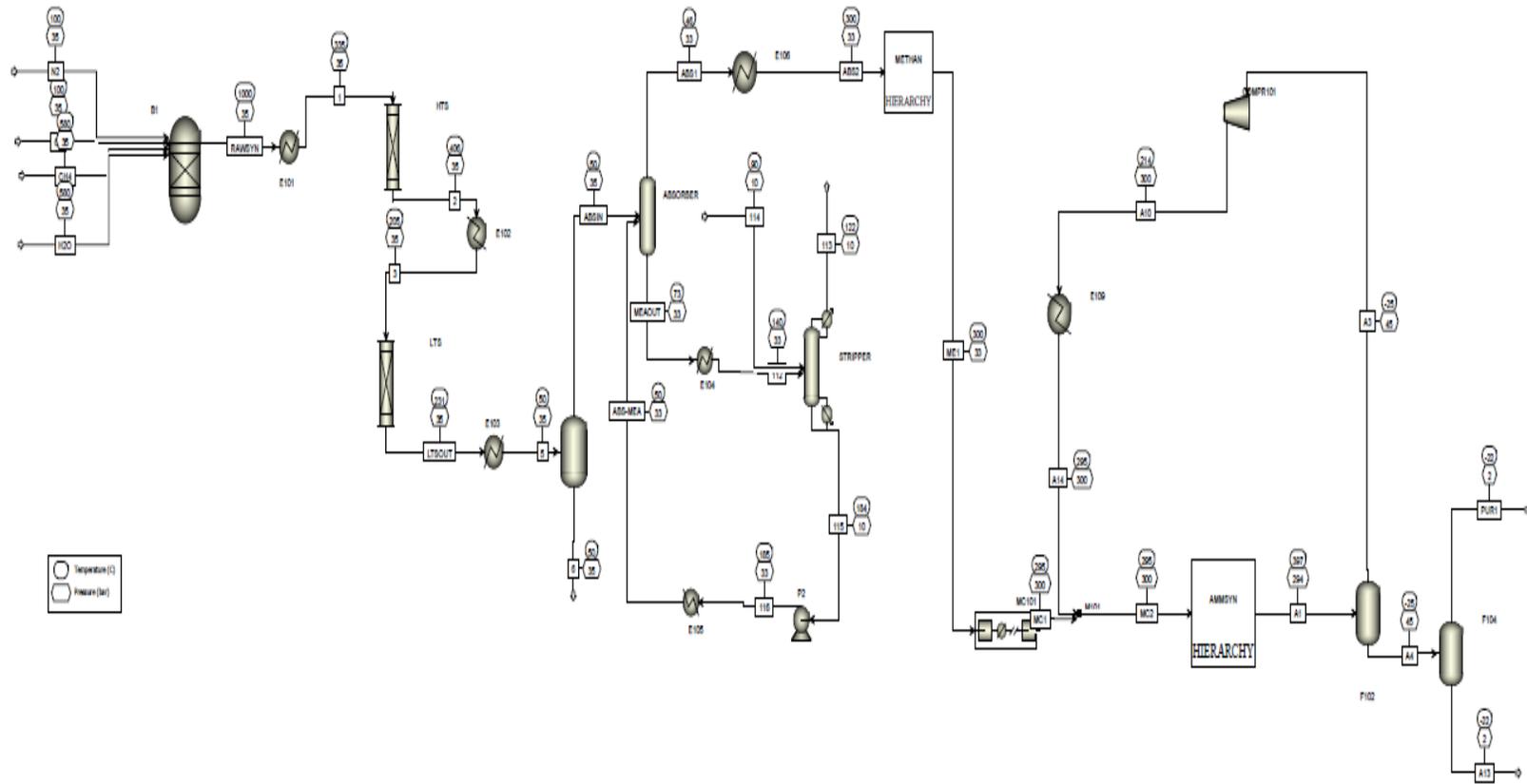
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## APPENDIX



**Figure 20 ASPEN Flowsheet - Ammonia Plant - Overall Process**

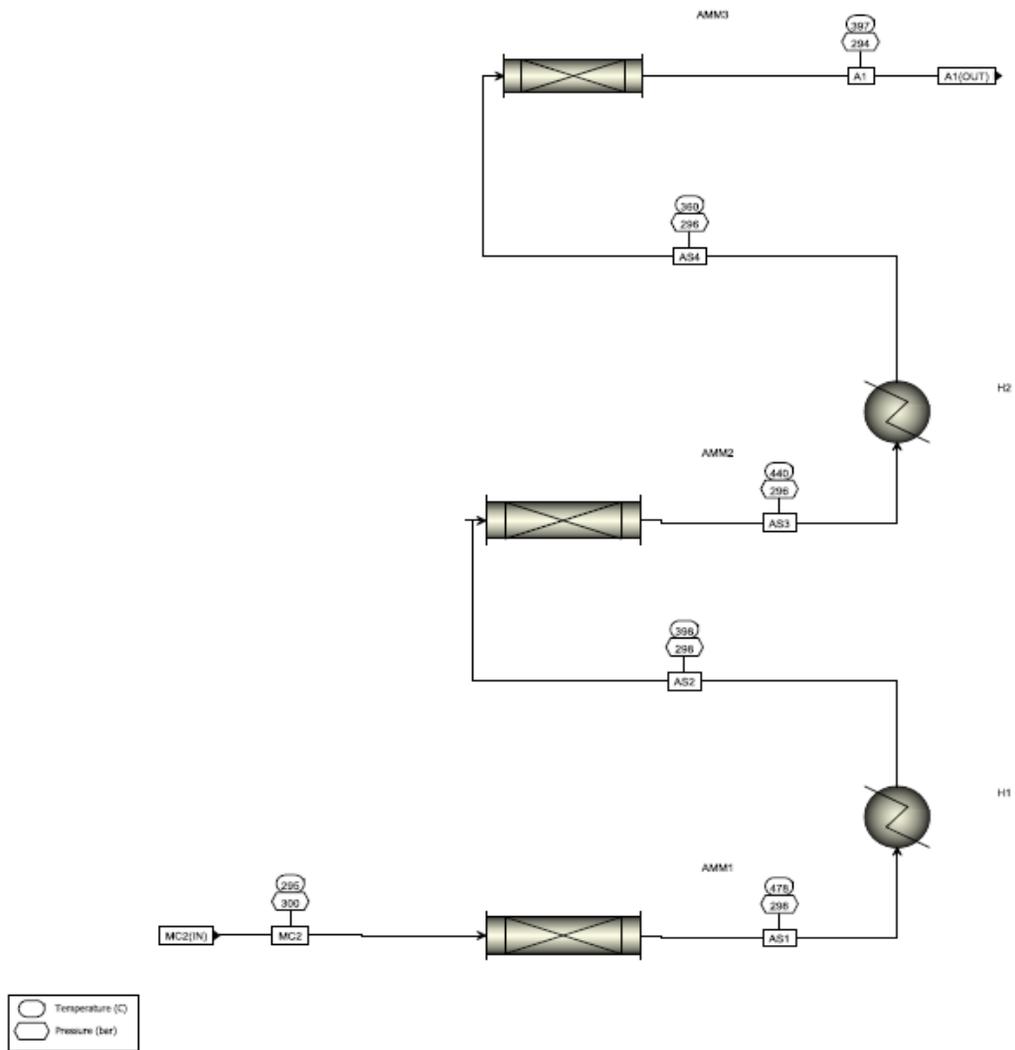


Figure 21 ASPEN Flowsheet - Ammonia Plant - Synthesis Section

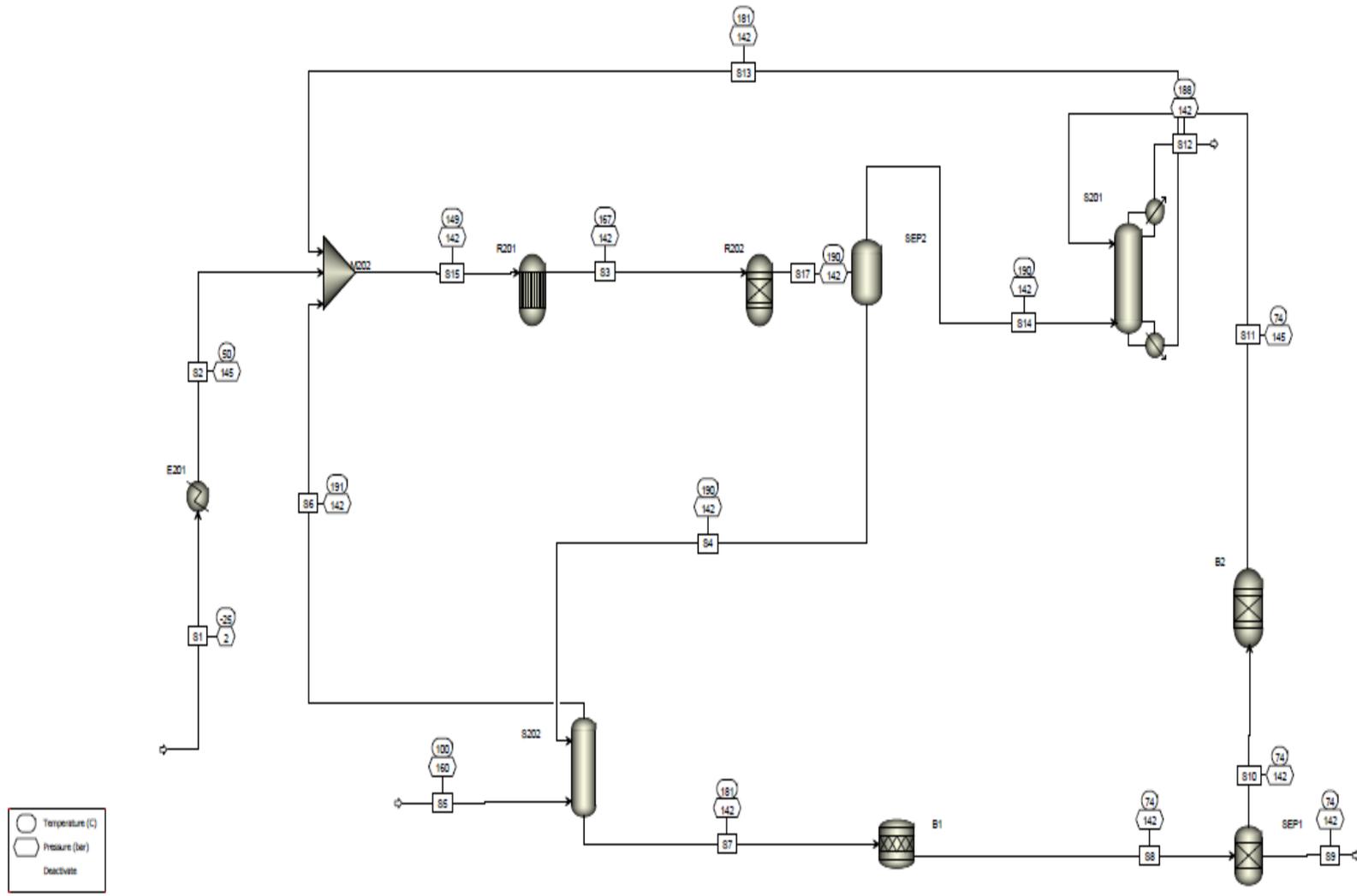


Figure 22 ASPEN Flowsheet - Urea Plant - Overall Process