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Name Surname

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
and Case Western Reserve University
2024

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Miss / Mr. Name Surname

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in Polymer Science / Petrochemical Technology
The Petroleum and Petrochemical College
Chulalongkorn University
Academic Year 2023

ชื่อเรื่อง

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
สาขาวิชาวิทยาศาสตร์พอลิเมอร์ / เทคโนโลยีปิโตรเคมี
วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2566

Title

Thesis Title	Aaaaaaaaa of Aaaaa Aaaaaaaaaaaa Aaaaaaaaaa for Aaaa Aaaaaaaaaa Aaaaaaaa for Aaaa Aaaaa Aaaaa Aaaaaaaa Aaaaa
By	Miss / Name Surname
Field of Study	Polymer Science / Petrochemical Technology
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สาขาวิชา วิทยาศาสตร์พอลิเมอร์
ปีการศึกษา 2566

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59xxxxxxxx : MAJOR POLYMER SCIENCE

KEYWORD: Bbbbbbbb/ Bbbbbbb bbbbbbbb/ Bbbbbb bbbbb/ Bbbbbbbbbbb/ Bbbbbbbbb/ Bbbbbbbb bbbbbb bbbbb/ Bbbbb bbbbbb bbbbbbb

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Field of Study:	Polymer Science	Student's Signature	....
Academic Year:	2023	Advisor's Signature	....
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ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Ammonia is one of important chemicals in the world. The use of ammonia to produce fertilizer has been increasing every year, relating to growing global population and increasing agriculture demand. Ammonia can be a feedstock to produce urea, the important chemical of nitrogen-based fertilizer and a widely used intermediate in the chemical industry. Ammonia can be used in various application such as solid ammonia energy carrier, liquid ammonia in cooling system, agriculture, chemical intermediate, polymer substance (synthesis fiber), etc.

Ammonia is a colorless, pungent smell gas and weak alkali which is very soluble in water. Ammonia is a compound of nitrogen and hydrogen with the formula NH_3. Mass production of Ammonia mostly uses the Haber–Bosch process, reacting hydrogen (H_2) and nitrogen (N_2) at a moderately-elevated temperature and high pressure.(Chisholm, 1911) Urea is an organic compound with the formula $CO(NH_2)_2$.

Urea is produced from ammonia and carbon dioxide. The urea synthesis process consists of two main equilibrium reactions. The first is call carbamate formation, that is exothermic reaction of liquid ammonia with gaseous carbon dioxide (CO_2) at high temperature and pressure. The second is called urea conversion, that is endothermic decomposition of ammonium carbamate into urea and water (Meessen and Petersen, 2000).

This research proposes the ammonia and urea synthesis process by using the PROII software to simulate workflow and estimate the energy consumption. This conceptual manufacturing process has production capacity about 3,000-4,000 ton per day for ammonia and 5,000 ton per day for urea, based on obtained data from Thailand’s industrial section. The feedstock of the process is methane from natural gas.

In the production process, it has many expenditures on feedstock which are from utilities, chemicals, equipment, operating cost and treatment unit. To be marketable and profitable to industrials, the techno-economic evaluation is considered in this work. Techno-economic evaluation is a methodology framework to analyze the technical and economic efficiency of a process, product or service. It normally combines process modeling, engineering design and economic assessment. The techno-economic evaluation is a key of feasibility study to estimate project expenditure and profitability. This technique represents the capital cost, the operating cost, net present value, and payback period.

For more benefit, this research also includes the stochastic analysis to design optimal supply chain with production rate of ammonia and urea from plant to markets. the stochastic analysis is a basic tool in probability theory and is used in many applied areas especially statistical mechanics. It has become particularly formula as a way of modelling financial markets and strategies. Stochastic programming model also be used in logistics network design under uncertainty. One of the most important and strategic issues in supply chain management is the configuration of the logistics network that has a significant effect on the total performance of the supply chain

CHAPTER 2
LITERATURE REVIEW

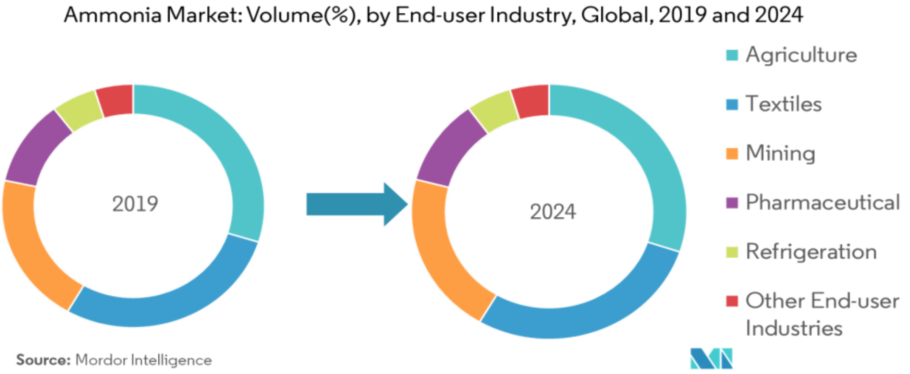
2.1 Ammonia, Urea Characteristic

Ammonia is a compound of nitrogen and hydrogen with the chemical formula NH_3. It is a colorless gas with a characteristic acrid smell. Ammonia is lighter than air, its density is 0.589 times that of air. It is easily liquefied due to the strong hydrogen bonding between molecules; the liquid boils at −33.3 °C (−27.94 °F), and freezes at −77.7 °C (−107.86 °F) to white crystals (Chisholm, 1911). Ammonia is a chemical found in trace amounts in nature, it is produced naturally in human body and being produced from nitrogenous animal and plants matter. Ammonia and the ammonium ion are vital components of metabolic processes.

Urea is an organic compound of amide and carbonyl group with chemical formula $CO(NH_2)_2$. It is also known as carbamide. It is a solid odorless white crystal and noncombustible. It is very soluble in water but insoluble in ether, with a melting point at 132°C. Urea is one of the most widely produced chemicals in the world and based on demand for crops and fertilizer has been increased. More than 90% of the production of urea in the world is used for a nitrogen-release fertilizer.(Meessen and Petersen, 2000).

2.2 Application of Ammonia, Urea

Ammonia can be used in various applications such as fertilizer, explosive, dyes, household cleaners, energy carrier, chemical intermediate, Polymer substance (synthesis fiber), etc. The agriculture industry dominates the global ammonia market, with an estimated market share of more than 80% in 2018. Ammonia is majorly used in fertilizers, and its usage has been increasing through the years, thereby, driving its usage in the agriculture market. Urea is a dry nitrogen material produced by reacting ammonia with carbon dioxide. Urea has the highest percentage of nitrogen among the commonly used dry fertilizers and is rapidly replacing ammonium nitrate in recent years.



Source: Mordor Intelligence

Figure 2.1 Ammonia Market by End-user Industry, Global, 2019 and 2024 (Mordor Intelligence, 2018).

From figure 2.1, it illustrates the major ammonia market is Agriculture section. The rest are textiles, mining, pharmaceutical, refrigeration, and other end-user industries. The forecast period of 2019-2024, the market's demand is increasing in the agriculture industry and the production of explosives (Intelligence, 2018).

M. Raihanul Islam Chowdhunry et al., (2002) researched effect of different methods of urea application on growth and yield in potato. The research was conducted to find out appropriate methods of urea application for maximizing the production of potato. There was a significant effect of different methods of urea application on plant emergence. The delay in plant emergence might be due to the accumulation of free ammonia and nitrites in the soil after the incorporation of urea. Application of urea as 50 % basal + 50 % top dressing produced the best result among the methods, and it was found to be the most cost effective. It might be concluded that split application of urea is the effective way to avoid the detrimental effect of urea on plant emergence and to maximize the tuber yield in Bangladesh (Chowdhury, 2002).

Debasish Chakraborty et al., (2009) studied for solid ammonia. This studied aim at the potential of 'solid' ammonia as a carbon-free energy carrier for mobile and transport applications, system integration and future opportunities. The result of this research illustrates that ammonia as a fuel cell for solid oxide fuel cell has some advantages over hydrocarbon fuels. The advantages include no desulfurization, and no pre-reforming requirement for ammonia. The combination of the direct ammonia fuel cell and the solid ammonia storage is very attractive for automotive applications, for several reasons. First, the operating temperature (400–600°C) of this type of fuel cell is ideal for ammonia decomposition So, there is a very good synergy between the reforming and fuel cell operation. Furthermore, the thermal desorption of ammonia from the solid storage materials can be achieved using the ‘waste’ heat from the stack, because the waste heat from a direct ammonia fuel cell stack operating at ~500°C will be of very good ‘quality’ to utilize for degassing ammonia. This will improve the overall system efficiency. Finally, the startup time much lower than the solid oxide fuel cell. This relatively lower operating temperature will also offer more options for materials selection (Chakraborty, 2009).

Sirinapa Santipanusopon, and Sa-Ad Riyajan (2009) studied the effect of ammonia treatment in field natural rubber latex with different storage period time on the properties of concentrated natural rubber latex and stability of skim latex. Fresh natural rubber latex was treated with various ammonia contents, 0.35, 0.60 and 0.80% w/w. The effect of storage time was observed with 0, 15, 30 and 45 days for concentrated natural rubber latex with different ammonia contents. This research demonstrated that magnesium content in field natural rubber latex and latex concentrate decreased with storage period times. The increasing ammonia content lead to the increment of the alkalinity content in both concentrated natural rubber and skim latex (Santipanusopon and Riyajan, 2009).

Zhe Han at al., (2015). The ammonia has been used as substrate for fertilizer such as ammonium nitrate. In this studied, the researchers focus on the alternatives to make ammonium nitrate safer as a fertilizer by reducing its explosivity. The effect of inhibitors, confinement, and heating rate on ammonium nitrate thermal decomposition has been studied. The results show that different types of additives, including sodium bicarbonate, potassium carbonate, and ammonium sulfate are good inhibitors for ammonium nitrate. The effect of confinement is concluded that confinement is dangerous to ammonium nitrate, which should be avoid in ammonium nitrate storage and transportation. The effect of heating rate shown that the lower heating rate lead to the lower the “onset” temperature detected (Han, 2015).

S. Seifi at al., (2016) studied Kaolin intercalated by urea for ceramic applications. They prepared Kaolinite-urea complexes by mixing and ball-milling at room temperature. Urea-intercalated kaolinite has potential applications in industry. This research found that the thermal transformations of intercalated kaolin with urea occur with several mechanisms depending on temperature. The expansion of kaolinite is involved to entering urea into inter-layers that confirms the occurrence of hydrogen bonding between urea and kaolinite. At expanded interlayers, bonds are formed between inner-surface hydroxyls of kaolinite and NH groups of urea that contribute to obtain physical properties of intercalated kaolinite similarly to delaminated kaolinite by intensive grinding that reduce the sintering temperature of more than 25^{O}C, accelerating the densification rate. It was sufficient to induce a significant reduction of the specific energy consumption during large scale manufacturing of clay ceramics for building (Seifi, 2016).

Orbel Barkhordarian at al., (2017) researched a novel ammonia-water cogeneration system that combined power and refrigeration cycle to produce power and refrigeration outputs simultaneously. This cycle has two evaporators that can produce refrigeration output in two different temperature levels and capacities. Ammonia was used in field regarding refrigerating application. One of the key parameters that effect on the cycle performance is ammonia concentration. The effect of evaporator outlet temperature is obvious that refrigeration output decreasing with increasing of basic solution ammonia concentration. They also investigated the effect of key parameters and It is shown that the cycle’s thermal performance is acceptable with exergy efficiency of 38.9%, effective exergy efficiency of 42.75% and thermal efficiency of 19% for the base case study (Barkhordarian, 2017).

Jiana Chen at al., (2017) studied effect of urea on nitrogen metabolism and membrane lipid peroxidation in Azolla pinnata. They reported the application of urea to Azolla pinata resulted in 44% decrease in nitrogenase activity, no significant change in glutamine synthetase activity, 660% higher glutamic-pyruvic transaminase, 39% increase in free amino acid levels, 22% increase in malondialdehyde levels, 21% increase in Na+/K+ levels, 16% in Ca2+ /Mg2+ ATPase levels, and 11% decrease in superoxide dismutase activity. Urea treatment of Azolla induced an increase in glutamic-pyruvic transaminase (GPT) and catalase (CAT) activity and free amino and Malondialdehyde (MDA) concentrations and a decrease in nitrogenase and superoxide dismutase (SOD) activity. These findings demonstrate that urea application promotes amino acid metabolism and membrane lipid peroxidation in Azolla pinnata. These studied estimated the associated urea demand for energy crops (Chen, 2017).

Kiyoshi Sakuragi at al., (2018) researched the application of ammonia pretreatment to enable enzymatic hydrolysis of hardwood biomass. Ammonia pretreatment majorly improved enzymatic hydrolysis of polysaccharides in birch and willow, but was less effective for acacia, eucalyptus, and poplar. The effectiveness of ammonia pretreatment increased with xylan content but decreased with lignin content of the hardwood species. This research present that a delignification process is unnecessary for at least some hardwood biomass, such as birch, prior to enzymatic hydrolysis. Ammonia pretreatment should be effective to improve production of biofuels and biochemicals from hardwoods with high xylan and low lignin contents, such as birch and willow (Sakuragi, 2018).

A Valera-Medina at al., (2018) reviewed highlights previous influential studies and ongoing research to use ammonia as a viable energy vector for power applications. The review presented that the original applications of ammonia were in the chemical and agriculture industries and it still finds its greatest application as a fertilizer for intensive crop farming. However, in addition to its traditional applications, ammonia is an energetic chemical energy store with favorable physical properties, especially when compare to other chemical energy storages media (Valera-Medina, 2018).

ArdaYapicioglu, IbrahimDincer (2019) Modified from this review shown the uses of ammonia in various engine practical applications are Fuel cells, Spark ignition engines, Compression ignition engines, Gas turbines, Boilers, Generators, Refrigeration systems. Also, Ammonia is used as a fuel source in engines and fuel cells for this research purpose. The main finding of this review in the field regarding influence of ammonia in dual fuel combustion is increasing the amount of ammonia used, the exhaust temperatures and efficiency of the engine decrease. However, this increase lead to a reduction in destructive emission which is the main motivation for the use of clean fuel sources for combustion (Yapicioglu and Dincer, 2019).

2.3 Feed Source of Ammonia, Urea

Ammonia can be produced form various feedstock such as naphtha, heavy fuel oil, coal, natural gas coke oven and refinery. Steam reforming of natural gas is the most used as feed source of ammonia production in the world, nearly 72% of ammonia production as represent in figure 2.2. The rest are coal, fuel oil, naphtha and others, respectively (Bicer, 2016).

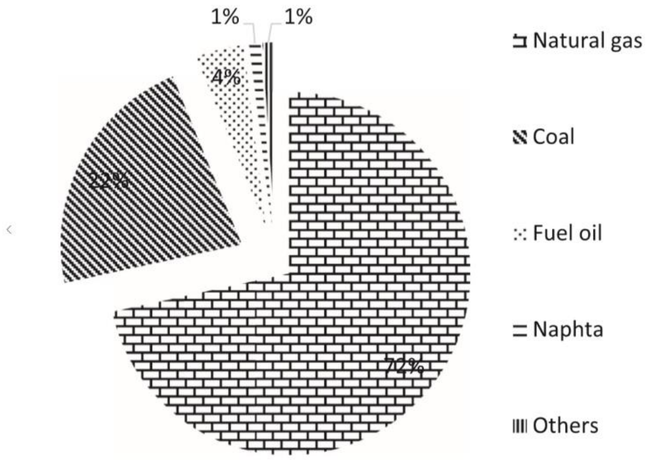


Figure 2.2 Feedstock sources of ammonia production in the world (Bicer,2016).

Cetinkaya et al., (2012) studied comprehensive life cycle assessment for five different methods of hydrogen generation including steam reforming of natural gas, coal gasification, water electrolysis via wind and solar, and thermochemical water splitting with a Cu-Cl cycle. They demonstrate that the most environmentally mind system is wind electrolysis-based hydrogen production, which is then followed by solar PV based electrolysis process. Both of the renewable energy methods can be utilized in suitable locations with low capacities (Cetinkaya, 2012).

Paul Gilbert at al., (2014) studied and assessed economically viable carbon reductions for the production of ammonia from biomass gasification. To reduce greenhouse gas emission from fertilizer, food supplies that support for growing population, biomass gasification are substituting natural gas reforming for ammonia production using techno-economic and life cycle assessment. The biomass 0.72 kg (35% moisture content) can produce 1 kg of syngas. It can be estimated that for 1 kg ammonia approximately 2.71 kg biomass (35% moisture content) is required (not considering biomass losses in the system). The assessment of economic illustrates that the biomass derived ammonia will be competing mainly with imported fossil fuel based ammonia. The cost of production of ammonia for both natural gas and biomass gasification systems is heavily influenced by the price of the feedstock, as well as by process scale. Producing ammonia from biomass gasification is economically viable at current biomass feedstock and ammonia prices, resulting in greenhouse gas reductions of 65% compared to conventional ammonia production from natural gas. Furthermore, the capital costs have high uncertainty to investor, lead to a very high risk investment (Gilbert, 2014).

Yusuf Bicer at al., (2016) present the result of comparative life cycle assessment of various ammonia production methods. They selected four different ammonia production methods for comparative assessment purposes. municipal waste-based ammonia production, nuclear high temperature-based ammonia production, biomass-based ammonia production, and hydropower-based ammonia production. They illustrate the energy efficiency for hydropower, nuclear high temperature, electrolysis, biomass-based electrolysis, and municipal waste-based electrolysis are calculated as 42.7%, 23.8%, 15.4%, and 11.7%, respectively. The exergy efficiencies of hydropower, nuclear, biomass and municipal waste-based ammonia production methods are yielded as 46.4%, 20.4%, 15.5% and 10.3%, respectively., respectively. They conclude that different resources-based ammonia production methods are thermodynamically analyzed and the energy and exergy efficiency values are comparatively assessed and renewable sources with their improved efficiency can reduce the overall environmental footprint. So, it can replace the current fossil fuel based centralized ammonia production facilities (Bicer, 2016).

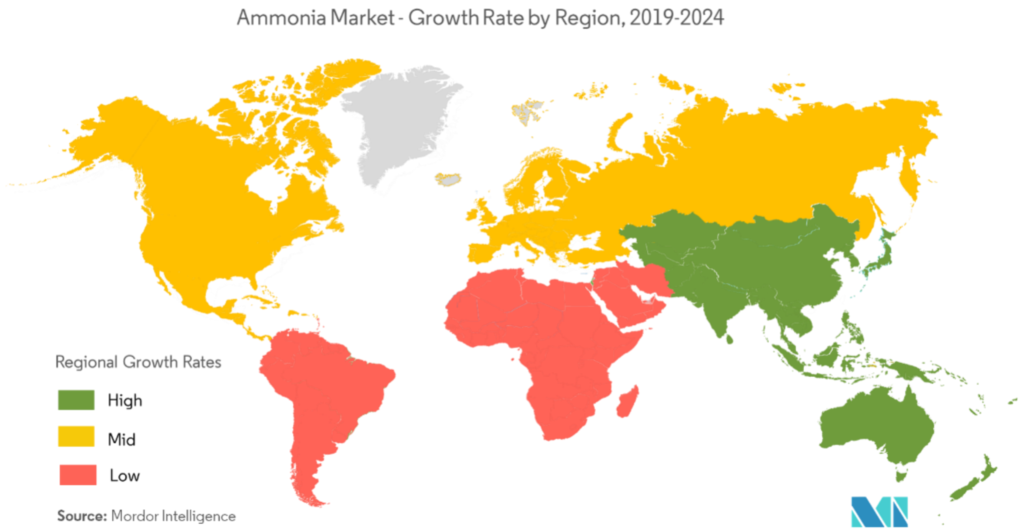
D. Frattini at al., (2016) researched a sustainable pathway for ammonia synthesis to reduce the use of fossil fuels of the Haber-Bosch process and, taking advantage of renewable sources. In field of use as a renewable energy system, hydrogen can be obtained from biomass gasification, biogas reforming or electrolysis of water with electricity generated by solar or wind energy. The Aspen Plus environment were used as the model development and operating parameters for simulations. The reactor block used to model units is “RGibbs” and the built-in NRTL property method is set as the thermodynamic model for the reforming and clean-up section. The authors reported that the model results are mainly in terms of gas and energy flows. Each of the three new concepts allows to produce ammonia in a novel way and simultaneously reducing the impact on the environment. This study demonstrates that ammonia can be produced in an efficient way from renewable using a thermochemical model developed in Aspen Plus (Frattini, 2016).

Maryam Akbari at al., (2018) studied the ammonia production from black liquor gasification and co-gasification with pulp and waste sludges. They investigated ammonia production though the gasification of three different feedstocks. The first case used black liquor, and in the other two cases pulp sludge and waste sludge are co-gasified with black liquor. The all of three cases process model in field of mass and energy balance were used to estimate the equipment size and estimate costs. The results indicated that ammonia production in all three cases cost decrease 10% competitive with current ammonia prices, there ranges from 743 to 748$/ton. The result of techno-economic assessment show that the cost of production is most sensitive to the capital cost, discount rate, electricity price and plant lifetime (Akbari, 2018).

Dong Xiang, Yunpeng Zhou (2018) studied a new design and techno-economic performance of hydrogen and ammonia co-generation by coke-oven gas-pressure swing adsorption technology integrated with chemical looping hydrogen process. This concept design process has two extreme configurations to produce hydrogen or ammonia only. The optimization of coke-oven gas utilization and maximize hydrogen and subsequent ammonia production desire the analysis of key operational parameters of system. The maximal ammonia and hydrogen productions are 4,784 and 7,126 kmol/h of 5,532 kmol/h coke–oven gas consumption for the extreme configurations, respectively. In this concept design process, switching between ammonia and hydrogen production have 68.5-73.6 % exergy efficiency and about 100% direct CO_2 efficiency. They also include the economic and sensitive analyses of this novel process in the studied (Xiang and Zhou, 2018).

2.4 The Market of Ammonia and Urea

In current, the demand in global market for fertilizer is rising modestly. In 2018, Asia-Pacific is the majority in ammonia market, accounting for more than half of the consumption globally. With the increasing population in countries such as China and India, increased agricultural activity has resulted in increased ammonia fertilizer usage, which will drive the market. China was the major consumer of ammonia in both the Asia-Pacific region and in the global market in 2018. Overall, the market for ammonia in Asia-Pacific region is anticipated to increasing significantly in the future (Intelligence, 2018).



Source: Mordor Intelligence

Figure 2.3 Ammonia Market – Growth Rate by Region, 2019-2024 (Mordor Intelligence, 2018).

From figure 2.3 that illustrate the growth rate of ammonia market by region. The forecast period is during 2019-2024 which have 3 regional growth rates.

Global production rates

Ammonia production has become one of the most important industries in the world. From figure 2.4, ammonia production has increased steadily since 1946 and it is estimated that the annual production of ammonia is worth more than $100 billion, with some plants producing more than 3,000 million ton per day of NH_3.

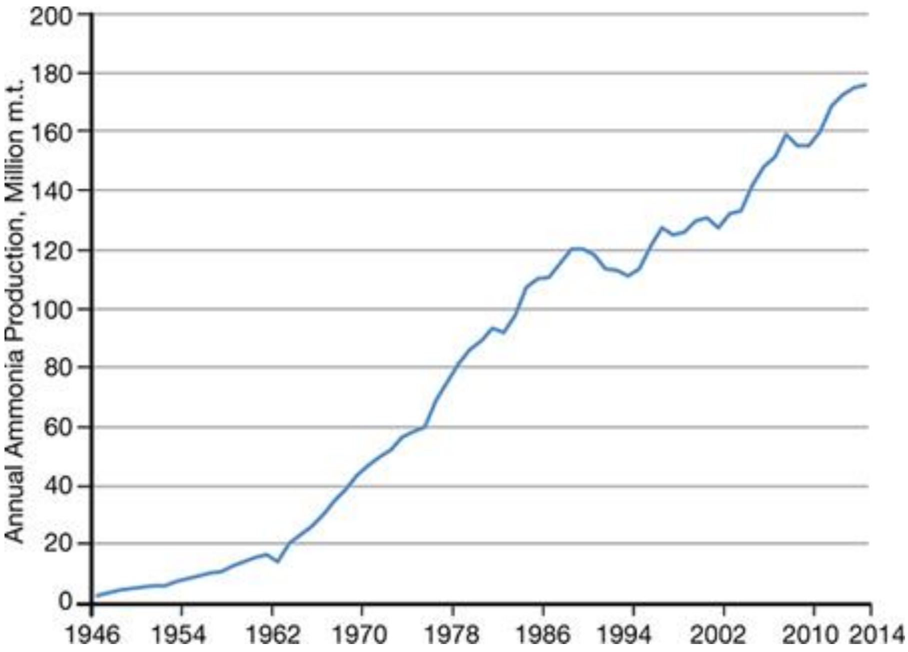


Figure 2.4 Worldwide ammonia production has continued increased from 1946 to 2014. (AlChE The Global Home of Chemical Engineers, 2016).

Patricia M. Glibert at al., (2006) reported the escalating worldwide use of urea and global contributing to coastal eutrophication. The review has shown in field of demand that global rates of urea-base fertilizer usage have increased rapidly, so that more urea is now used than any other nitrogen fertilizer. Global urea usage extends beyond applications; urea is also used extensively in animal feeds and in manufacturing processes. The use of urea around the world is expected to continue with the potential to increase coastal waters pollution world-wind (Glibert, 2006).

Patricia Carneiro dos Santos, Alexandre S. Szklo (2016) researched about urea imports in Brazil and the increasing demand pressure from the biofuels industry and the role of domestic natural gas for the country's urea production growth. Brazil is a major producer of liquid biofuels. These high production level require to use of fertilizer, and to put the pressure on the nitrogen fertilizer domestic market. This contributes to increasing level of imports and trade shortage in the chemical industry. The findings show that Brazil will stay a major importer of urea. Urea associated with the production of biofuels has sufficient magnitude to justify an expansion of production capacity through a greenfield facility. this study estimated the associated urea demand for energy crops. The data shown average import prices for ammonia and urea in Brazil, 511.83 and 315.113 US$ FOB/ton, respectively. However, the analysis of natural gas breakeven price to a greenfield urea project indicates that the project is not feasible (dos Santos and Szklo, 2016).

A Valera-Medina at al., (2018) reviewed highlights previous influential studies and ongoing research to use ammonia as a viable energy vector for power applications. The review shown that ammonia can be produced using renewable sources which not only contributes to reducing greenhouse emission, but also offers flexibility its utilization, allows fuel cells to be run effectively (using smaller, safer and economically viable configurations), enable combustion systems has the potential of operating at high power whilst producing tolerable levels of emissions, and enable advanced propulsion systems to be developed with smaller tanks. Thus, the ease of storages, transportation and use of ammonia make it an attractive candidate to act as the energy vector between sustainable energy harvesting and mobile and static energy demands (Valera-Medina, 2018).

2.5 Ammonia and Urea Production

Several processes of ammonia and urea have been invented for optimum production rate and product specification including energy conservation. A HEN optimization is a network to minimize the energy requirement of a conceptual ammonia/urea plants. Therefore, this work is focused not only on the energy consumption analysis but also economic feasibility of processes. The capacity of conceptual ammonia and urea plant is 3,264 and 2,000 ton per day (TPD), respectively. The methane from natural gas is used as feedstock of the production. The overall production design is shown in figure 2.5.

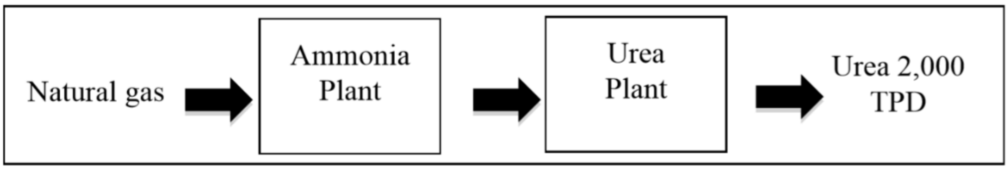


Figure 2.5 Overall production process for ammonia and urea plants.

2.6 Ammonia Manufacturing Process

Ammonia is synthesized from hydrogen (from natural gas) and nitrogen (from the air). The operating condition is operated with high temperature about 450-500 ºC and high pressure about 80-90 bar. The reaction mixture is cooled so that the ammonia liquefied and can be removed. The remaining nitrogen and hydrogen are recycled. Ammonia synthesis reaction is reversible. The overall reactions of ammonia production are shown as following equations.

The main reaction:

$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g)$ (reversible) ; $\Delta H_{298} = -92.43$ kJ/mol (1)

(Modak, 2002)

Desulfurization unit: to remove sulfur content. Natural gas contains some sulfurous compounds which damage the catalysts used in this process. These are removed by reacting them with zinc oxide, e.g.

$ZnO + H_2S \rightarrow ZnS + H_2O$; $\Delta H_{298} = 76.9$ kJ/mol (2)

(Giuffrida, 2010)

Primary reforming unit: methane (sweet dry gas) is converted to hydrogen and carbon dioxide, the reactions are:

$CH_4 + H_2O \leftrightharpoons 3H_2 + CO$ (synthesis gas) ; $\Delta H_{298} = 206.30$ kJ/mol (3)

$CH_4 + 2H_2O \leftrightharpoons 4H_2 + CO_2$; $\Delta H_{298} = 165.0$ kJ/mol (4)

(Ochoa-Fernández, 2005)

Secondary reforming unit: hot air is added, the reactions are:

$CO + H_2O \leftrightharpoons CO_2 + H_2$ (synthesis gas) ; $\Delta H_{298} = -41.15$ kJ/mol (5)

$2CH_4 + O_2 \rightarrow 2CO + 4H_2$; $\Delta H_{298} = -71$ kJ/mol (6)

$2O_2 + CH_4 \rightarrow 2H_2O + CO_2$; $\Delta H_{298} = -802.5$ kJ/mol (7)

(Azzaro-Pantel, 2018)

Shift conversion unit: carbon monoxide is removed by water gas shift reaction. Carbon monoxide is converted to carbon dioxide.

$CO + H_2O \leftrightharpoons CO_2 + H_2$; $\Delta H_{298} = -41.33$ kJ/mol (8)

(Lin and Wu, 2020)

Methanation unit: all carbon oxides are converted to methane by following equations:

$CO + 3H_2 \leftrightharpoons CH_4 + H_2O$; $\Delta H_{298} = -206.30$ kJ/mol (9)

$CO_2 + 4H_2 \leftrightharpoons CH_4 + 2H_2O$; $\Delta H_{298} = -164.90$ kJ/mol (10)

(Lin and Wu, 2020)

Ammonia synthesis unit: to produce final ammonia product

$N_2 + 3H_2 \leftrightharpoons 2NH_3$; $\Delta H_{298} = -46.14$ kJ/mol (11)

(Modak, 2002)

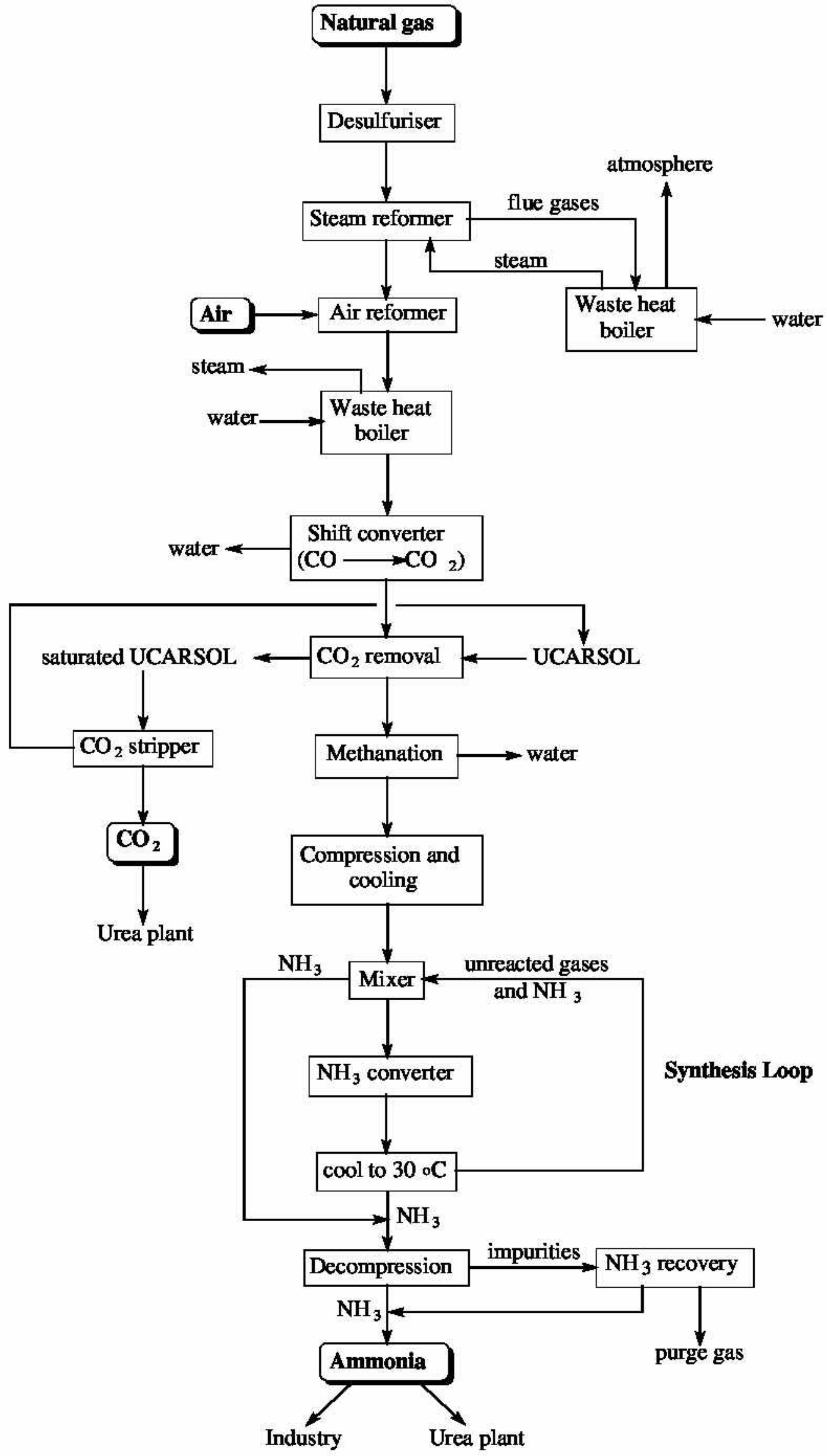


Figure 2.6 Schematic representation of the ammonia synthesis process (Copplestone and Kirk, 2008).

The ammonia manufacturing process is shown schematically in figure 2.6.

Schematic description

Step 1 - Hydrogen production: Hydrogen is produced by the reaction of methane with water. However, before this can be carried through, all sulfurous compounds must be removed from the natural gas to prevent catalyst damaging. These are removed by heating the gas to 400°C and reacting it with zinc oxide. The gas is sent to the primary reformer for steam reforming, where superheated steam is fed into the reformer with the methane. The gas mixture heated with natural gas and purge gas to 770°C in the presence of a nickel catalyst. The reaction converting the methane to hydrogen, carbon dioxide and small amount of carbon monoxide. This gaseous mixture is known as synthesis gas.

Step 2 - Nitrogen addition: The synthesis gas is cooled slightly to 735°C. It then flows to the secondary reformer where it is mixed with a calculated amount of air. The highly exothermic reaction between oxygen and methane produces more hydrogen. In addition, the necessary nitrogen is added in the secondary reformer.

Step 3 - Removal of carbon monoxide: Here the carbon monoxide is converted to carbon dioxide (which is used later in the synthesis of urea) in a reaction known as the water gas shift. This is achieved in two steps. Firstly, the gas stream is passed over a Cr/Fe3O4 catalyst at 360°C and then over a Cu/ZnO/Cr catalyst at 210°C. The same reaction occurs in both steps but using the two steps maximizes conversion.

Step 4 - Water removal: The gas mixture is further cooled to 40°C, at which temperature the water condenses out and is removed.

Step 5 - Removal of carbon dioxides: The gases are then pumped up through a counter-current of UCARSOL™ solution. Carbon dioxide is highly soluble in this solution, and more than 99.9% of the CO_2 in the mixture dissolves in it. The remaining CO_2 is converted to methane (methanation) using a Ni/Al_2O_3 catalyst at 325°C. The water which is produced in these reactions is removed by condensation at 40°C as above. The carbon dioxide is stripped from the UCARSOL and used in urea manufacture. The UCARSOL is cooled and reused for carbon dioxide removal.

Step 6 - Synthesis of ammonia: The gas mixture is now cooled, compressed and fed into the ammonia synthesis loop. A mixture of ammonia and unreacted gases which have already been around the loop are mixed with the incoming gas stream and cooled to 5°C. The ammonia present is removed, and the unreacted gases heated to 400°C at a pressure of 330 barg and passed over an iron catalyst. The outlet gas from the ammonia converter is cooled from 220°C to 30°C. This cooling process condenses more the half the ammonia, which is then separated out.

2.6.1 Ammonia Plant Design

Haldor-topsoe process is the process which depart form Haber's process. The residual gas of this process is wasted to atmosphere.

The advantages of this process are:

- It has a greater compactness, simplicity in case of converter design since under high-pressure gases have a smaller volume.
- This process is to eliminate expensive heat exchangers that are needed in processes that operate at low pressure.
- This process is removal of ammonia with water cooling alone.

The disadvantages of this process are:

- This process has a Shorter life of converters.
- High maintenance equipment in the high-pressure operation.
- There are about 20 % loss of gas production which is unconverted.

Haldor Topsoe process flow sheet of ammonia production is shown in figure 2.7

Process important sections:

1. Desulphurization Section
2. Reforming Section
3. CO Conversion Section
4. CO_2 Conversion Section
5. Methanation
6. Ammonia Synthesis Section
7. Refrigeration Section
8. Ammonia Absorption Section

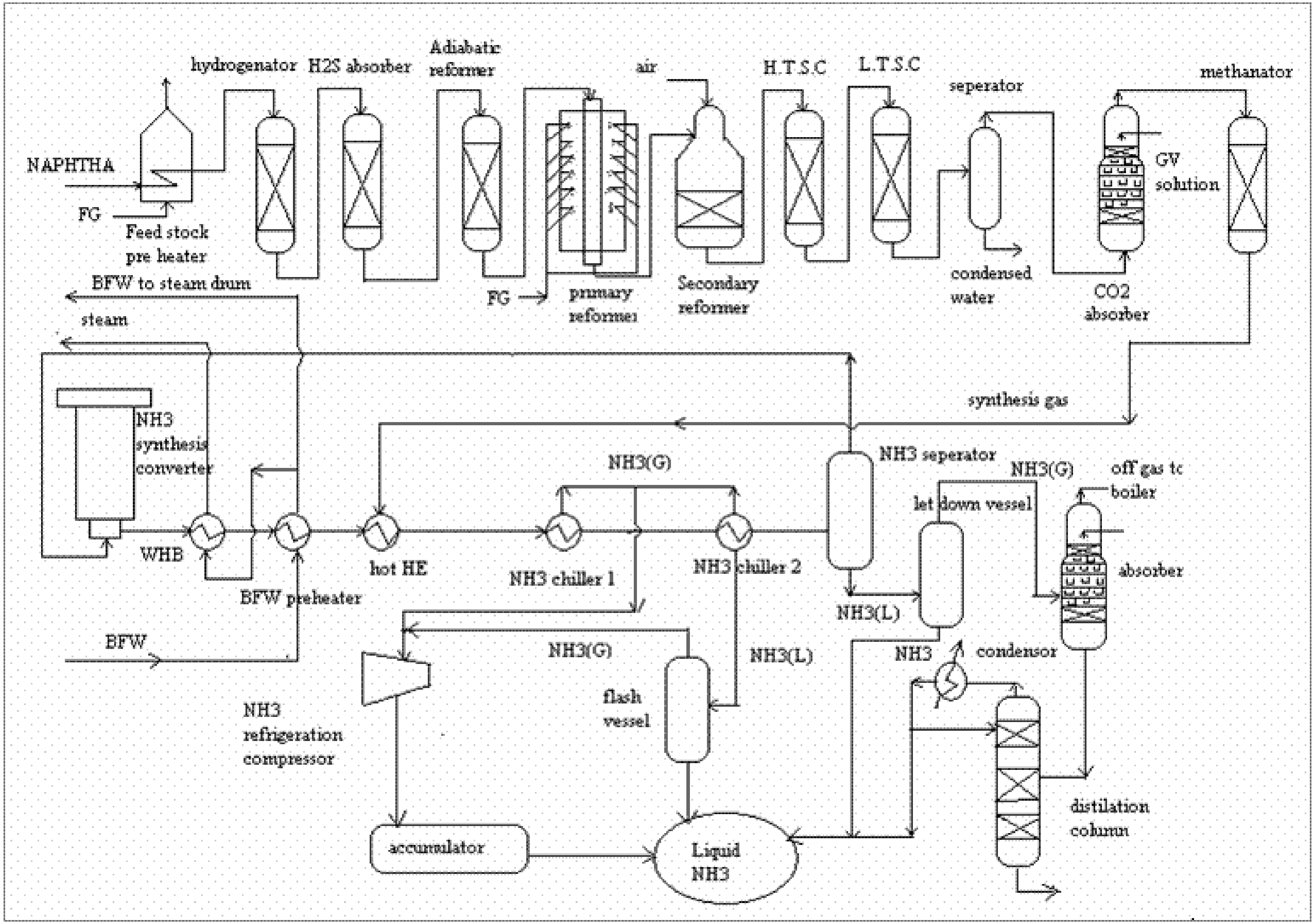


Figure 2.7 Haldor Topsoe Process Flow Sheet of Ammonia Production (Venkat Pattabathula, 2016).

Most of the global production of ammonia are produced from steam reforming of natural gas, significant quantities are produced by coal gasification; most of the gasification plants are in China.

The first commercial ammonia plant based on the Haber-Bosch process was built by BASF at Oppau, Germany with a production capacity of 30 million ton per day. The flow sheet of the first commercial ammonia plant by BASF is illustrated in figure 2.8.

2.6.2 Modern Production Processes

The demand for ammonia has increased considerably during the years 1950-1980, allowing plants to grow larger and save more energy.

In the mid-1960s, the American Oil Co. installed a single-converter ammonia plant engineered by M.W. Kellogg (MWK) at Texas City, TX, with a capacity of 544 million ton per day. The single-train design concept is illustrated in the figure 2.9.

Important differences between the MWK process and the processes used in previous ammonia plants included:

- using a centrifugal compressor as part of the synthesis gas compression
- maximizing the recovery of waste heat from the process
- generating steam from the waste heat for use in steam turbine drivers
- using the refrigeration compressor for rundown and atmospheric refrigeration.

Combined forms that use to balanced energy, energy production, equipment size and catalyst volume are combined throughout the plant.

2.6.3 Plant Designs in the 21st Century

During the first few years of the 21st century, there were many improvements in ammonia technology that helped existing plants increase production rates and new plants to be built with larger and greater capabilities.

Most of the ammonia plants recently designed by KBR utilize its Purifier process (figure 2.10), which combines low-severity reforming in the primary reformer, a liquid N_2 wash purifier downstream of the methanator to remove impurities and adjust the H_2:N_2 ratio, a proprietary waste-heat boiler design, a unitized chiller, and a horizontal ammonia synthesis converter. The energy consumption of this plant can be as low as 28 GJ per million ton. The primary reformer can be smaller than in conventional designs because the secondary reformer uses excess air.

The syngas generation section of a Haldor Topsøe-designed plant is quite traditional except for its proprietary side-fired reformer, which uses radiant burners to supply heat for the reforming reaction. More recent developments include the S-300 and S-350 converter designs. The S-300 converter is a three-bed radial-flow configuration with internal heat exchangers, while the S-350 design combines an S-300 converter with an S-50 single-bed design with waste-heat recovery between converters to maximize ammonia conversion. The Haldor Topsøe-designed plant is illustrated in figure 2.11.

The Linde Ammonia Concept (LAC) is an established technology process scheme with over 25 years of operating experience in plants with capacities from 200 million ton per day to over 1,750 million ton per day. The LAC process scheme, as shown in figure 2.12, replaces the expensive and complex front end of a conventional ammonia plant with two well-proven, dependable process units:

- production of ultra-high-purity hydrogen from a steam-methane reformer with PSA purification
- production of ultra-high-purity nitrogen by a cryogenic nitrogen generation unit, also known as an air separation unit (ASU).

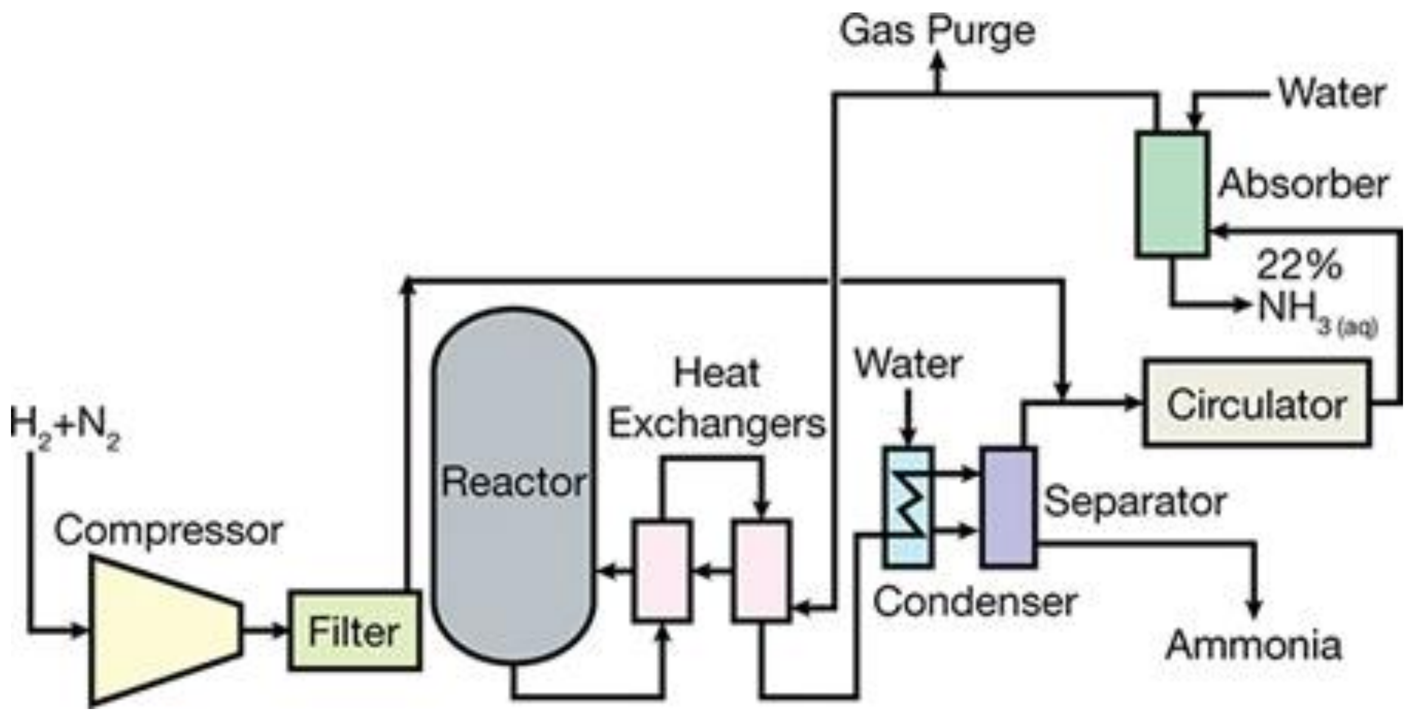


Figure 2.8 A simplified flowsheet of the first commercial ammonia plant by BASF (Venkat Pattabathula, 2016).

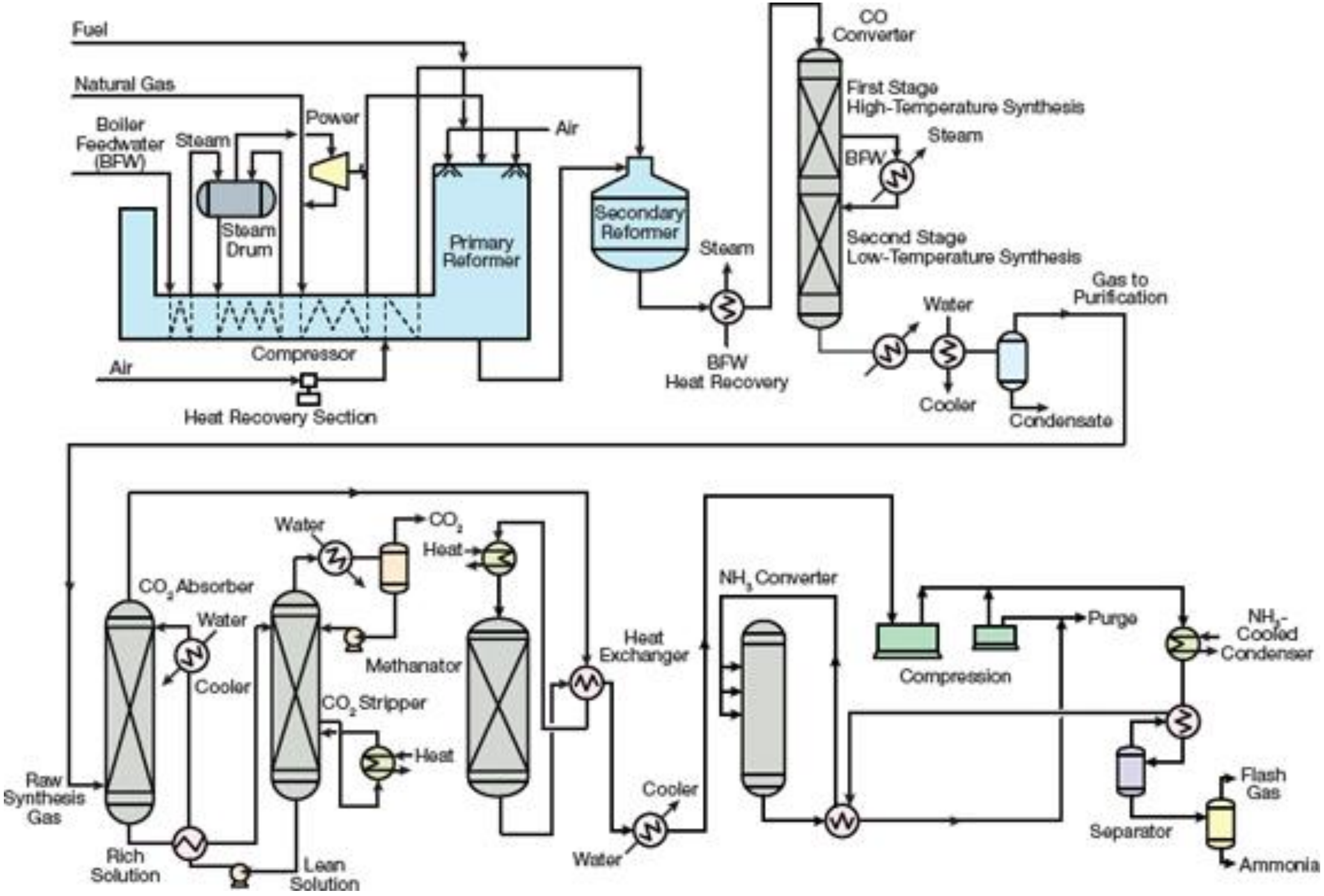


Figure 2.9 KBR designed one of the first single-train, large-capacity ammonia plants (Venkat Pattabathula, 2016).

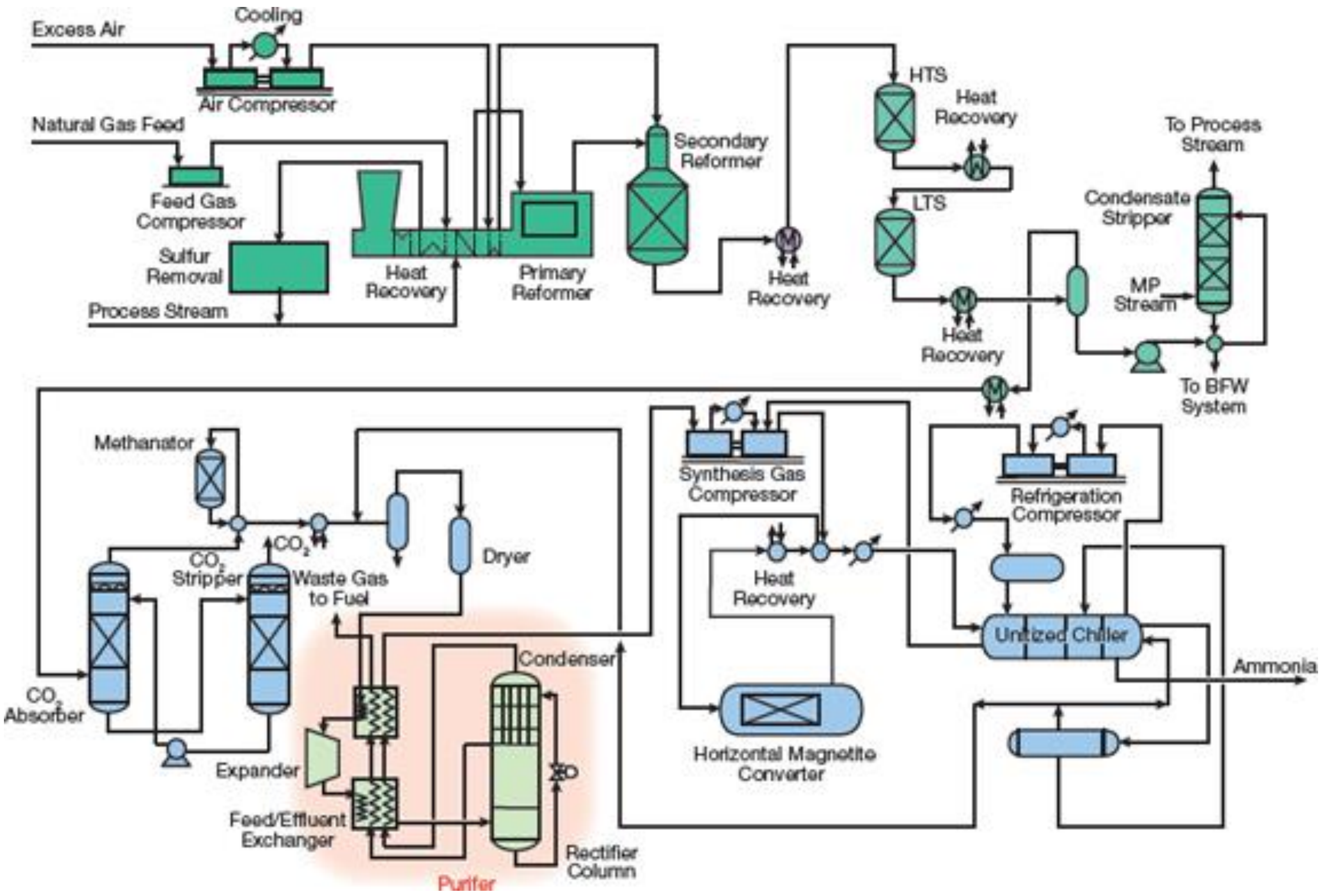


Figure 2.10 Modern ammonia plants designed by KBR employ its proprietary Purifier design (Venkat Pattabathula, 2016).

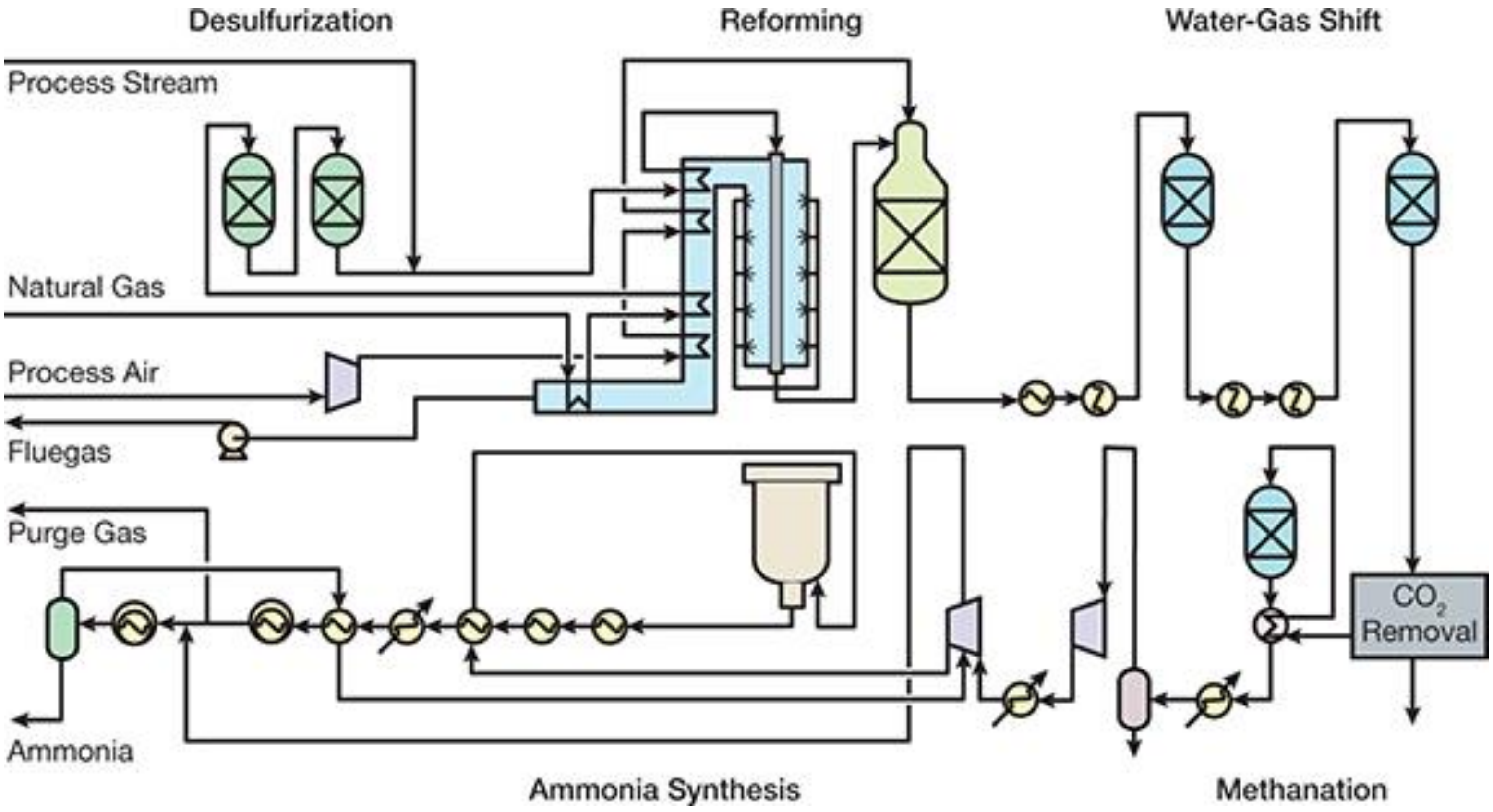


Figure 2.11 Haldor Topsøe offers an ammonia plant design that has a proprietary side-fired reformer in which radiant burners supply heat for the reforming reaction (Venkat Pattabathula, 2016).

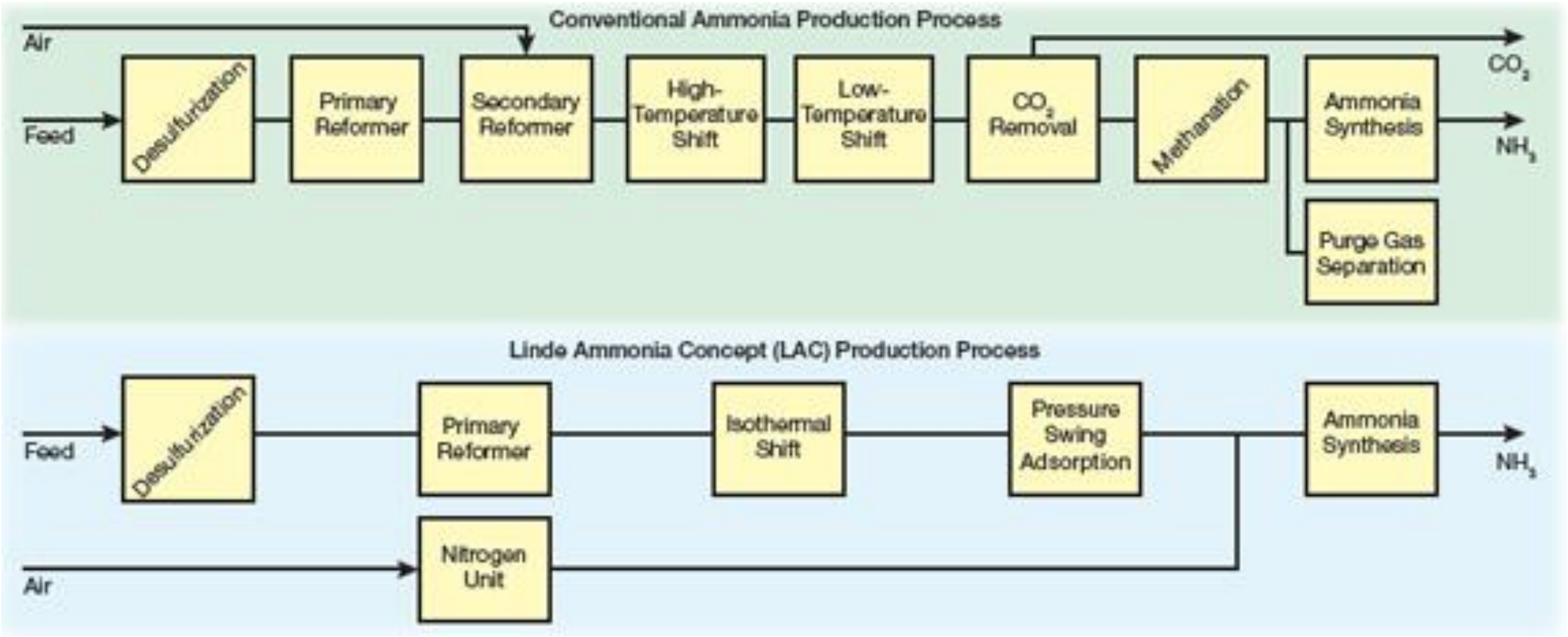


Figure 2.12 The Linde Ammonia Concept (LAC) features a pressure-swing adsorption unit for high-purity hydrogen production and an air separation unit for high-purity nitrogen production (Venkat Pattabathula, 2016).

2.7 Urea Manufacturing Process

As mentioned above, most of the ammonia is used on site in the production of urea. The remainder is sold domestically for use in industrial refrigeration systems and other applications that require anhydrous ammonia. The urea is used as a nitrogen-rich fertilizer, and as such is of great importance in agriculture, one of world's major industries. There are two main equilibrium reactions in the urea synthesis. The first reaction is highly fast exothermic in which ammonia and carbon dioxide are converted to ammonia carbamide. The second reaction is slow endothermic. The operating condition is operated at high pressure 20-25 bar with temperature 150-220 °C. Urea is produced from ammonia and carbon dioxide in two equilibrium reactions:

$$2NH_3(aq) + CO_2(g) \leftrightharpoons NH_2COONH_4(aq)\ ;\quad \Delta H = -72.32\ kJ/mol \qquad (12)$$

$$NH_2COONH_4 \leftrightharpoons NH_2CONH_2\ (urea) + H_2O;\ \Delta H = 15.5\ kJ/mol \qquad (13)$$

The urea manufacturing process, shown schematically in Figure 2.13, is designed to maximize these reactions while inhibiting biuret formation:

$$2NH_2CONH_2 \leftrightharpoons NH_2CONHCONH_2\ (biuret) + NH_3 \qquad (14)$$

This reaction is undesirable, not only because it lowers the yield of urea, but because biuret burns the leaves of plants. This means that urea which contains high levels of biuret is unsuitable for use as a fertilizer.

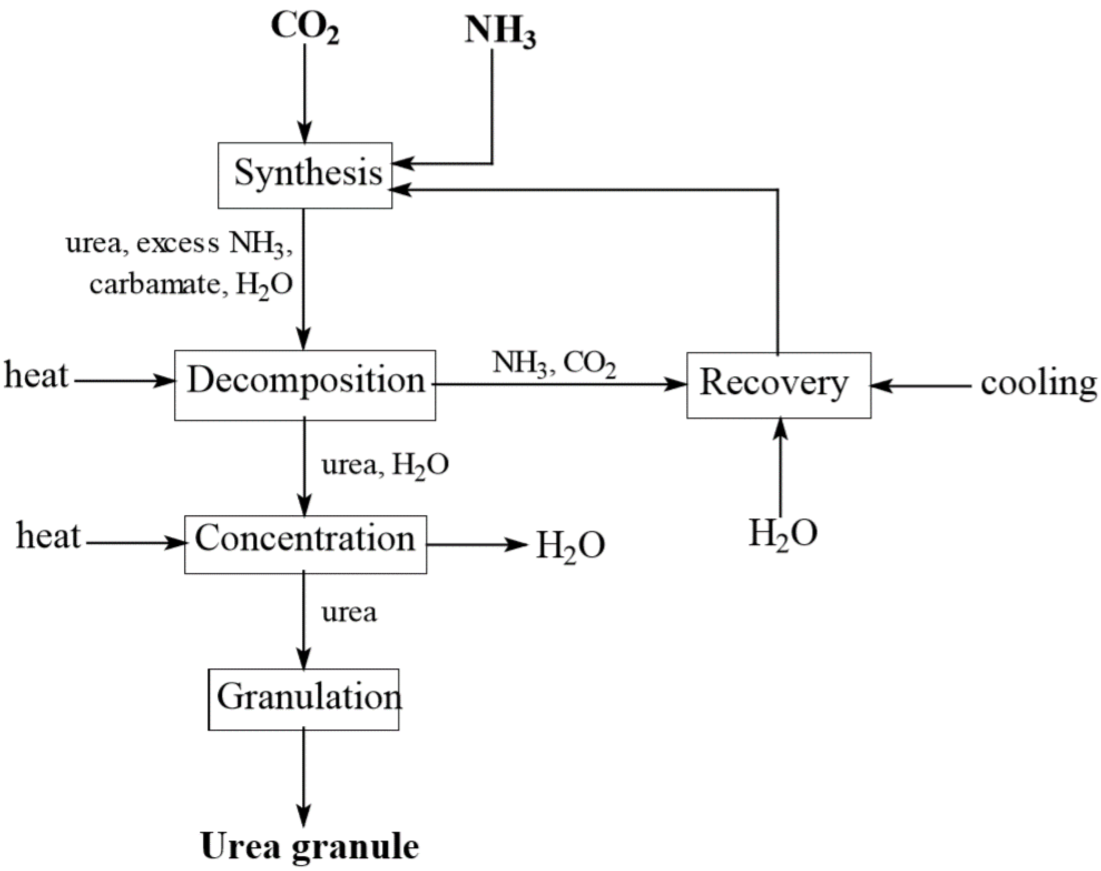


Figure 2.13 Schematic representation of urea synthesis (Copplestone and Kirk, 2008).

This reaction is undesirable, not only because it lowers the yield of urea, but because biuret burns the leaves of plants. This means that urea which contains high levels of biuret is unsuitable for use as a fertilizer.

Schematic description

Step 1 – Synthesis: A mixture of compressed CO_2 and ammonia at 240 barg is reacted to form ammonium carbamate. This is an exothermic reaction, and heat is recovered by a boiler which produces steam. The first reactor achieves 78% conversion of the carbon dioxide to urea and the liquid is then purified. The second reactor receives the gas from the first reactor and recycle solution. Conversion of carbon dioxide to urea is approximately 60% at a pressure of 50 barg.

Step 2 – Purification: The major impurities in the mixture at this stage are water from the urea production reaction and unconsumed reactants (ammonia, carbon dioxide and ammonium carbamate). The unconsumed reactants are removed in three stages. Firstly, the pressure is reduced from 240 to 17 barg and the solution is heated, which causes the ammonium carbamate to decompose to ammonia and carbon dioxide:

$$NH_2COONH_4 \leftrightharpoons 2NH_3 + CO_2$$

At the same time, some of the ammonia and carbon dioxide flash off. The pressure is then reduced to 2.0 barg and finally to -0.35 barg, with more ammonia and carbon dioxide being lost at each stage. By the time the mixture is at -0.35 barg a solution of urea dissolved in water and free of other impurities remains. At each stage the unconsumed reactants are absorbed into a water solution which is recycled to the secondary reactor. The excess ammonia is purified and used as feedstock to the primary reactor.

Step 3 – Concentration: 75% of the urea solution is heated under vacuum, which evaporates off some of the water, increasing the urea concentration. At this stage some urea crystals also form. The solution is then heated from 80 to 110°C to dissolve these crystals prior to evaporation. In the evaporation stage molten urea (99% w/w) is produced at 140°C. The remaining 25% of the 68% w/w urea solution is processed under vacuum at 135°C in a two series evaporator-separator arrangement.

Step 4 – Granulation: Urea is sold for fertilizer as 2 - 4 mm diameter granules. These granules are formed by spraying molten urea onto seed granules which are supported on a bed of air. This occurs in a granulator which receives the seed granules at one end and discharges enlarged granules at the other as molten urea is sprayed through nozzles. Dry, cool granules are classified using screens. Oversized granules are crushed and combined with undersized ones for use as seed. All dust and air from the granulator are removed by a fan into a dust scrubber, which removes the urea with a water solution then discharges the air to the atmosphere. The final product is cooled in air, weighed and conveyed to bulk storage ready for sale (Copplestone and Kirk, 2008).

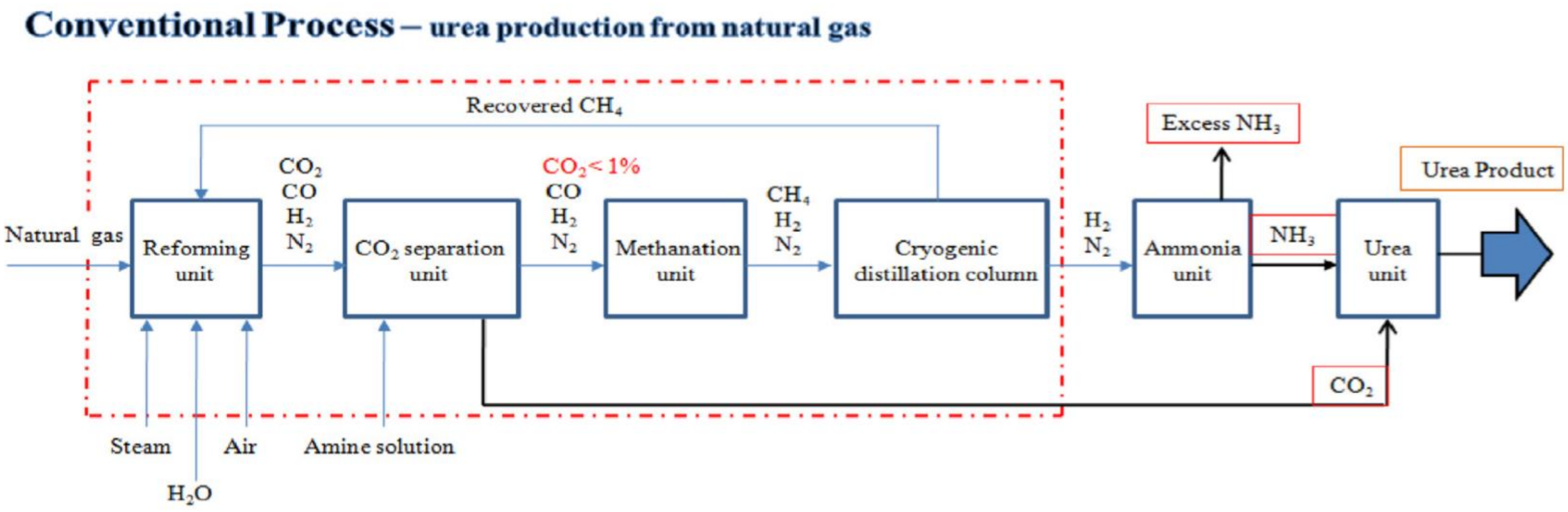


Figure 2.14 Scheme of the conventional process for urea production from natural gas (Edrisi, 2016).

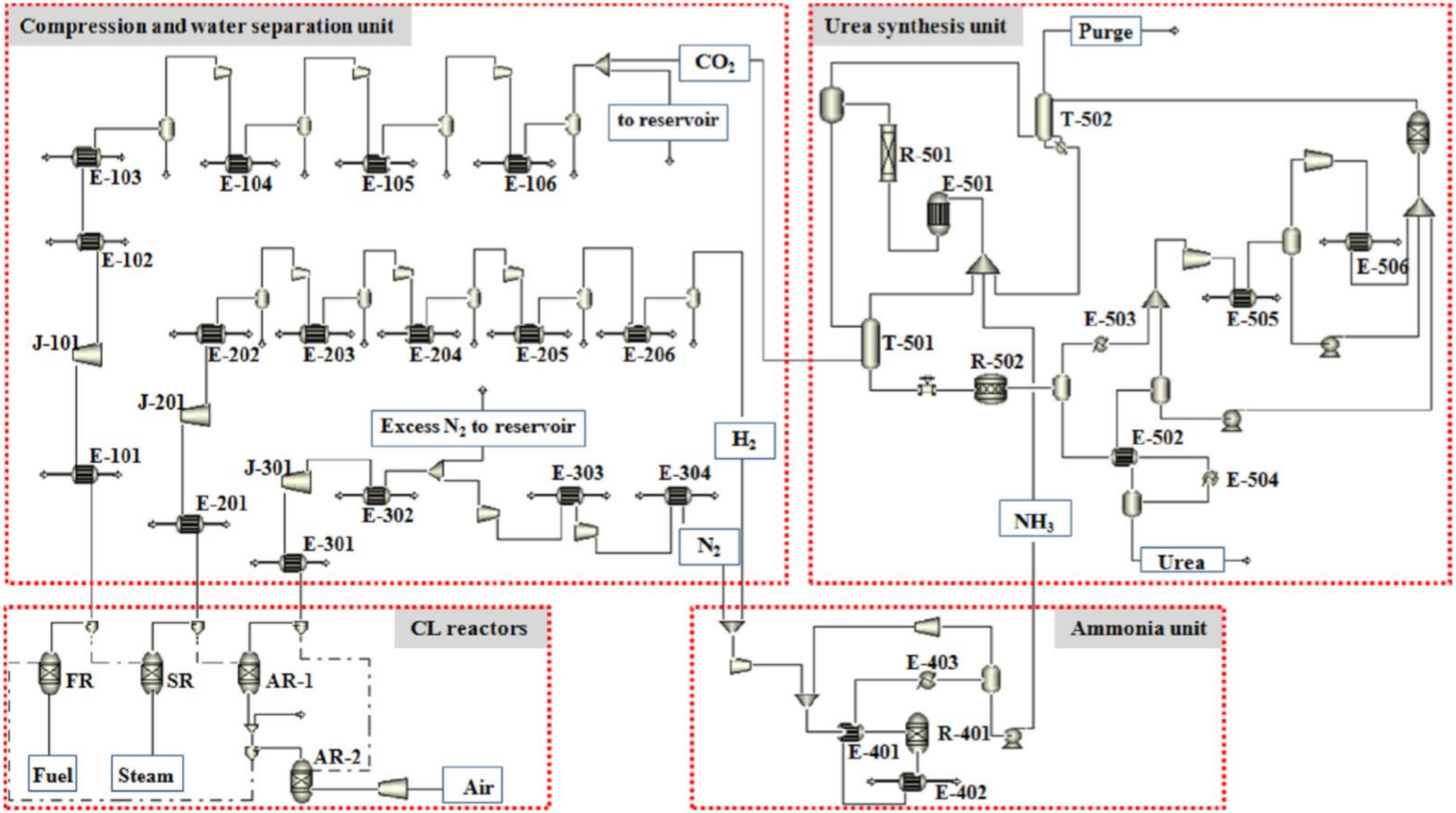


Figure 2.15 Proposed plant for urea production using chemical looping process (before heat and power integration) (Edrisi, 2016).

2.8 Techno-Economic Analysis (TEA)

Techno-Economic model is an integration of technological research and commercial development involves engineering process design with economic feasibility. Also, it is a key of financial evaluation to provide investment and marketing. In this work is focused on 2 main parts. First part is simulation since production route until material and process validation. Second part is economic analysis which mainly represents the capital expenditure, the operating expenditure, net present value, and payback period. The overall hierarchical approach that used as a base-case model to design and to develops the final production is shown in figure 2.16.

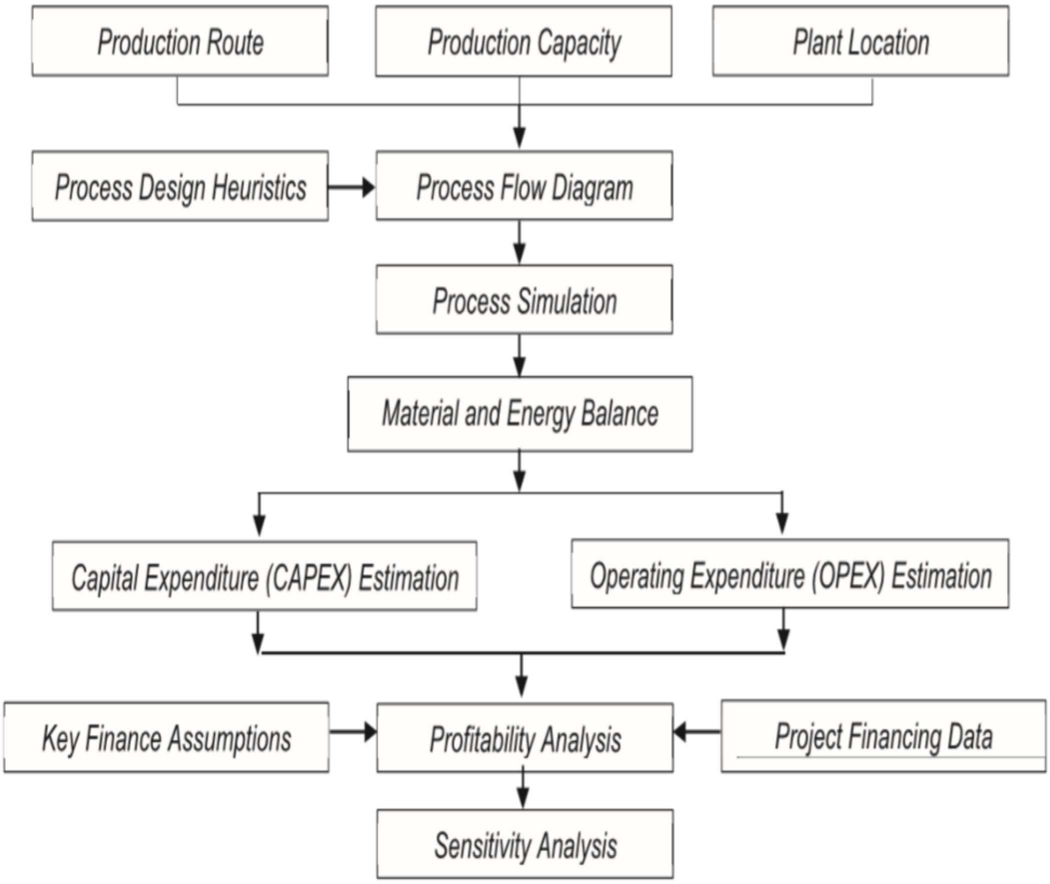


Figure 2.16 Overall methodology approach for techno-economic analysis (Cheah, 2017).

2.8.1 Capital Expenditure (CAPEX) Estimation

Capital expenditure represents a property, plant, equipment, and services that will be used for more than one year. This cost includes mainly purchasing process equipment, hardware purchases, vehicles and associates with constructing the plant includes investing activities.

2.8.2 Operating Expenditure (OPEX) Estimation

Operating expenditure represents a necessary expense of a business which incurs through its normal operations to keep the business running on a daily basis. This cost includes rent, utilities, salaries, equipment, inventory costs, marketing, general, & administrative expenses, property taxes, payroll, insurance, research expenses, and development.

2.8.3 Profitability Analysis

Profitability analysis is used to determine the amount of profit earned due to the efficiency of any operation. This technique helps in a financial decision, marketing and product management for a company.

2.8.4 Sensitivity Analysis

In this work, a definition of sensitivity analysis is a technique used to identify a differently independent variables which impacts to the main dependent variables. For example; production rate, stream/methane ratio, feed temperature/pressure of each reactors, synthesis loop pressure, and conversion percentage. For ammonia and urea processes, these variables are used to consider on the plant feasibility.

For cost index is used the most common one which is from IHS CERA index. The equipment costs were estimated using a guide to chemical engineering process design and economics book as shown below

Present cost = (capital cost index in 2019/capital cost index in 2000) x previous cost

2.8.5 Equipment Design and Cost Estimation

Calculation of equipment cost is based on material and energy balance, operation condition, material handling. Estimating equipment costs are represented as the following equations.

2.8.5.1 Reactor

In this simulation work, Reactor is based on residence time of 60 s. The purchased cost formulation is shown as the following equations (Seider, 2004)

$$V_R = 1.25T_R \times Q \tag{15}$$

$$C_{reactor} = 14000 + 15400V_R^{0.7} \tag{16}$$

Where V_R is the reactor volume in m^3, Q is the volumetric flow rate in m^3/s and T_R is residence time in s.

2.8.5.2 Flash Drum

The purchased cost of flash drum is formulated as the following equations (Seider, 2004)

$$V_F = QT_F \tag{17}$$

$$C_F = 12685V_F^{0.3641} \tag{18}$$

Where V_F is the flash drum volume in m^3, Q is the volumetric flow rate in m^3/s and T_F is the fixed residence time in s.

2.8.5.3 Distillation Column

The purchased cost of distillation column is calculated as the following equations (Seider, 2004)

$$A_n = 0.5V_m(\rho_v)^{0.5} \tag{19}$$

$$D_c = (4A_n)^{0.5}\,(0.88\pi)^{-0.5} \tag{20}$$

$$H_c = 1.2(N\text{-}1)Ts \tag{21}$$

$$C_{DC} = 4555\ H_c^{0.81} – D_c^{1.05} \tag{22}$$

Where H_c is height of the column in m, D_c is diameter of the column in m, N is the number of trays, Ts is the tray spacing in m (assume 1 m), A_n is the net activate area, ρ_v is the vapor mass density, and V_m is the vapor mass flow rate.

2.8.5.4 Centrifugal Pump

The purchased cost of Centrifugal Pump is calculated as the following equations (Seider, 2004)

$$S = Q(H)^{0.5} \tag{23}$$

$$C_p^0 = 5.4\ \exp(9.7171\text{-}0.6019[\mathrm{Ln}\ (S)]+ 0.0519[\mathrm{Ln}\ (S)]^2) \tag{24}$$

Where Q is the volumetric flow rate in the range of 0.2-500 L/s, H is the pump head in feet of fluid flowing.

2.8.5.5 Compressor

The purchased cost of carbon-steel centrifugal compressors are calculated by using following equation (Seider, 2004)

$$C_{com}^0 = 8400 + 3100\ P^{0.6} \tag{25}$$

Where P in driver power ranges from 132 to 29,000 kW.

2.8.5.6 Fired Heater

The purchased cost of stainless-steel fired heater with maximum heat pressure of 5000 KPa can be calculated by using following equation (Seider, 2004)

$$C_{FH}^{0} = 184967\ HD^{0.7636} \qquad (26)$$

Where HD is the heat duty in MW

2.9 Stochastic Model

Stochastic analysis is a basic tool in much of modern probability theory and is used in many applied areas from biology to physics, especially statistical mechanics. It has become particularly well known via the Black-Scholes formula as a way of modelling financial markets and strategies. Stochastic programming model also be used in logistics network design under uncertainty. One of the most important and strategic issues in supply chain management is the configuration of the logistics network that has a significant effect on the total performance of the supply chain.

Mir Saman Pishvaee at el. (2009). They developed a stochastic and optimization model for integrated forward and reverse logistics network design under uncertainty. This study proposes a scenario-based stochastic optimization model. The model used hybrid distribution, collection facilities that offer cost savings and pollution reduction because of sharing material handling equipment and infrastructure. The uncertainty in the quality of returned products is modeled by considering the share of recoverable and scrapped products in the returns as a stochastic parameter. Computational results showed that the stochastic model could handle data uncertainty with a reasonable increase in total costs compared with the deterministic model.

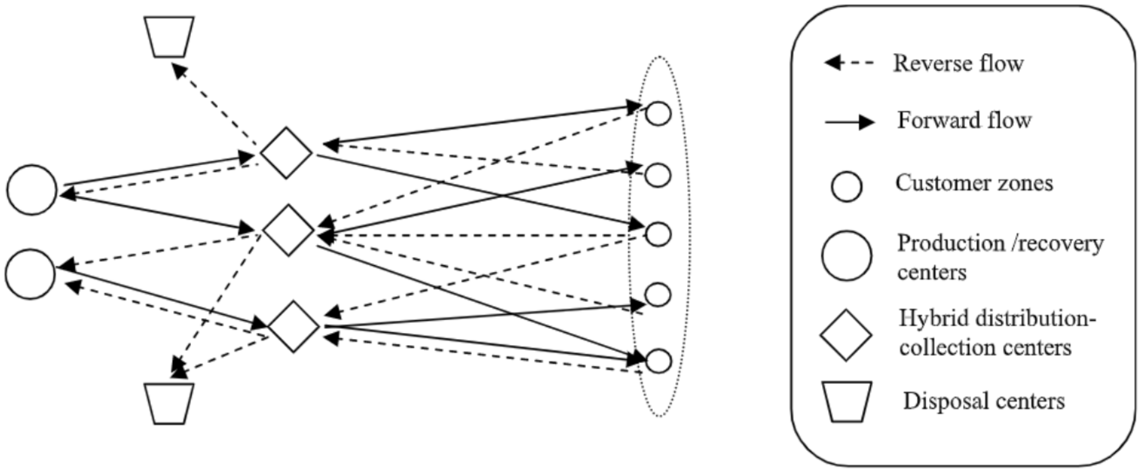


Figure 2.17 Structure of integrated forward/reverse logistics network (Pishvaee, 2009).

Figure 2.17 demonstrates the structure of integrated logistics network. With this strategy, excessive transportation of returned products (especially scrapped products) is prevented and the returned products can be shipped directly to the appropriate facilities (Pishvaee, 2009).

CHAPTER 3

EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Equipment

a. Computer Desktop model : ASUSTek Computer Inc. Intel® Core™ i7 6700K CPU @4.0GHz, 32 GB of RAM, Windows 10 ©2018 Microsoft Corporation. (64-bit Operating system)

b. Computer laptop model : ASUS TUF fx505GE Intel® Core™ i7-8750H CPU @2.2GHz, 8GB of RAM, Windows 10 ©2018 Microsoft Corporation. (64-bit Operating system)

3.1.2 Softwares

a. Simsci Pro II Version 10.0

b. GAMS

c. Microsoft office excel

3.2 Objectives and Scope of Research Work

3.2.1 Objectives

a. To design conceptual process of ammonia and urea plant with maximum capacity from 1,930 TPD of natural gas feed.

b. To analyze energy consumption of the process and economic feasibility for industrial case.

c. To estimate capital expenditure (CAPEX) and operating expenditure (OPEX) of ammonia and urea plants.

d. To optimize supply chain of ammonia and urea from uncertainty data of markets' demand with stochastic model analysis.

3.2.2 Scope of Research Work

a. This research is focused on assessment of the energy consumption and economic feasibility to achieve the optimum condition with the capacity of 3,000 TPD of ammonia plant and 5,000 TPD of urea plant.

b. The feedstock of the ammonia plant is considered only methane from natural gas.

c. The simulation software Pro II was determined the results in this experiment.

d. The stochastic optimization for supply chain of ammonia and urea will be done.

3.3 Methodology

3.3.1 Simulation for Ammonia and Urea Manufacturing Processes

a. Input flow rate, temperature, pressure, reactions of all streams into process by using Pro II software.

b. Apply more utility units design by Pro II software.

c. Analysis of total energy consumption and economic feasibility for industrial case.

3.3.2 Investment Expenditures of Ammonia and Urea Plants Assessment

a. Calculate capital expenditure (CAPEX) and operating expenditure (OPEX).

b. Calculate net present value and payback period.

c. Profitability analysis.

d. Sensitivity analysis.

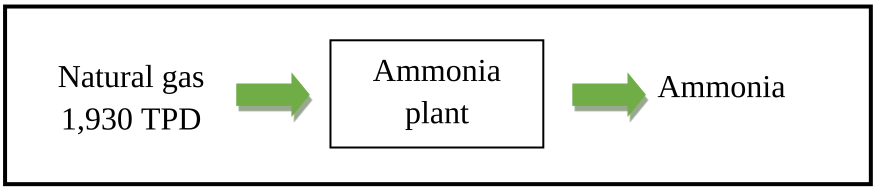
3.3.3 Case Studies

a. Simulation and energy assessment part, there are two cases: 1. Ammonia plant and 2. Urea plant.

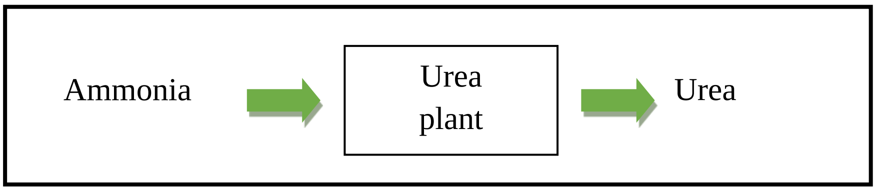
b. Economic feasibility part, there are three cases: 1. ammonia plant, 2. urea plant, and 3. Combination case (ammonia and urea plants).

c. Optimization for transportation part, there are two cases: c1. The stochastic analysis for the supply chain with fixed production rate of ammonia and urea. c2. The stochastic analysis for the supply chain with varied production rate of Ammonia and Urea.

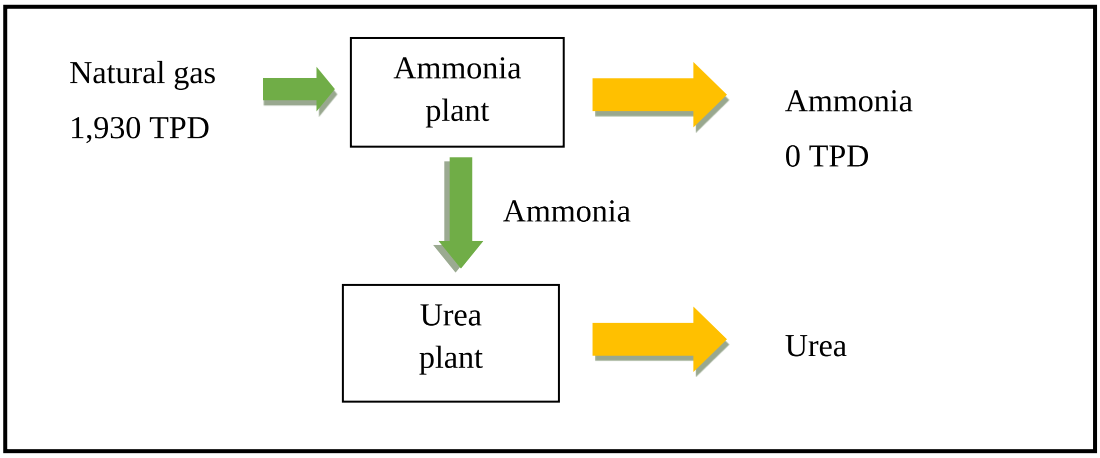
Case 1: Ammonia plant. (Maximum production capacity of ammonia from 1,930 TPD natural gas feed).



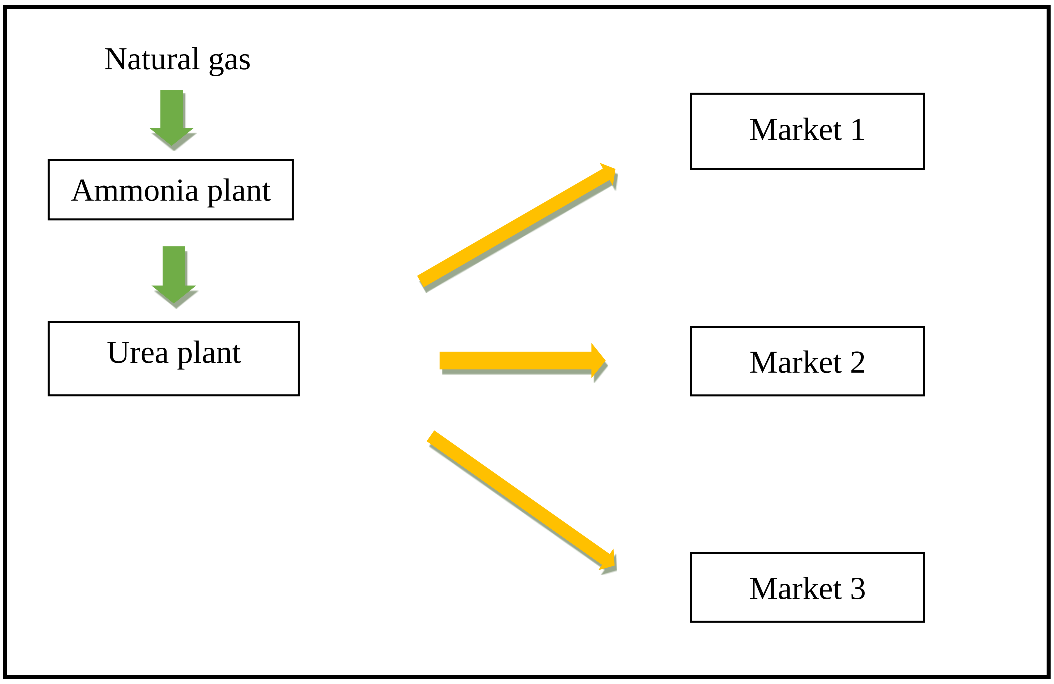
Case 2: Urea plant. (Maximum production capacity of urea from feed of ammonia product in case1)



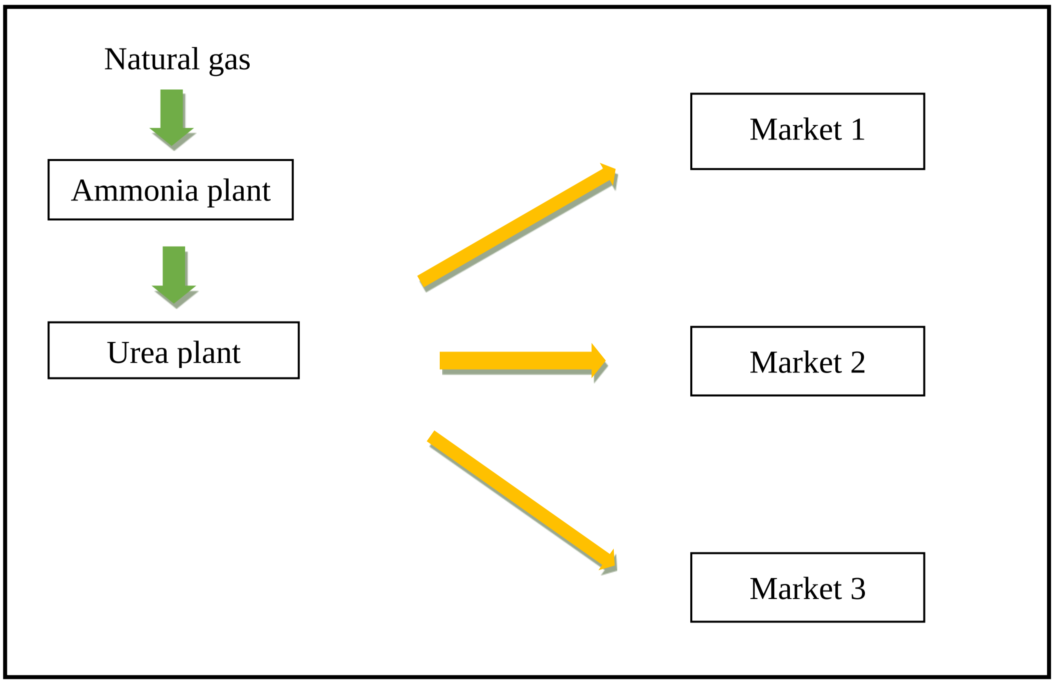
Case 3: Combination case (Maximum production capacity of urea from 1,930 TPD of natural gas feed).



Case c1: Ammonia and Urea plant with improved deterministic and stochastic supply chain optimization under fixed production rate of ammonia and urea.



Case c2: Ammonia and Urea plant with improved deterministic and stochastic supply chain optimization varied production rate of ammonia and urea.



CHAPTER 4

RESULTS AND DISCUSSION

4.1 Properties and Specification for Simulation Processes – Ammonia Plant

This research proposes the ammonia and urea synthesis process by the PROII software to simulate workflow and estimate the energy consumption. The main feedstock of the process is 1,930 ton per day of natural gas. The ammonia production of the conceptual process is 3,870 ton per day. The carbon dioxide eliminated from gas sweetening process is about 5,202 ton per day and consumed in the urea synthesis process about 4,986 ton per day. The properties and specification of natural gas feedstock, steam feed, air feed, and water make up are shown in the table 6.1, 6.2, 6.3, and 6.4, respectively. The ammonia product specifications are shown in the table 6.5. The input data of the conceptual ammonia manufacturing are shown in the table 6.6.

Table 4.1 Compositions of natural gas feed

Condition: Temperature 15.556^{o}C, Pressure 340 psia and Flow rate of 1,930 TPD

Natural gas feed	
Component	% mole
Carbon dioxide	0.028496
Nitrogen	2.105208
Methane	97.471142
Ethane	0.394549
Propane	0.000605
Flow rate (ton/day)	1,930

Table 4.2 Properties of steam feed

Condition: Temperature 510°C, Pressure 334 psia and Flow rate of 3,224 TPD

Steam feed	
Component	% mole
H_2O	100
Flow rate (ton/day)	3,224

Table 4.3 Properties of air feed

Condition: Temperature 25°C, Pressure 180 psia and Flow rate of 7,517 TPD

Air feed	
Component	% mole
Oxygen	21
Nitrogen	78.1
Argon	1
Flow rate (ton/day)	7,517

Table 4.4 Properties of water make up

Condition: Temperature 25°C, Pressure 15 psia and Flow rate of 2,852 TPD

Water make up	
Component	% mole
H_2O	100
Flow rate (ton/day)	3,224

Table 4.5 Ammonia production specification

Ammonia product	
Ammonia purity (% mole)	99.3%
Flow rate (ton/day)	3,870
Temperature (°C)	-27.04
Pressure (psia)	4,450

Table 4.6 Input data of ammonia process

Reaction Name	Desulfurization	
Reaction type	Isothermal	
Reaction	$ZnO + H_2S \rightarrow ZnS + H_2O$; $\Delta H = -206.30$ kJ/mol	
Basis	Flash drum	DESULFER
Temperature = 393.33 °C	Reaction phases	Vapor
Pressure = 334 psia	Pressure drop	2 psi

Reaction Name	Primary Reforming	
Reaction type	Gibbs Reactor	
Reaction	$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$; $\Delta H = -165.0$ kJ/mol	
Basis Reactor No.RX1	Base component	Methane
Temperature = 880 °C	Reaction phases	Vapor phase
Pressure = 334 psia		

Reaction Name	Primary Reforming	
Reaction type	Gibbs Reactor	
Reaction	$CH_4 + H_2O \leftrightharpoons 3H_2 + CO$; $\Delta H = +206.30$ kJ/mol	
Basis Reactor NO.RX1	Base component	Methane
Temperature = 880 °C	Reaction phases	Vapor phase
Pressure = 334 psia		

Reaction Name	Secondary Reforming	
Reaction type	Gibbs Reactor	
Reaction	$CO + H_2O \leftrightharpoons CO_2 + H_2$; $\Delta H = -41.15$ kJ/mol	
Basis Reactor No.RX2	Base component	Methane
Temperature = 1,340 °C	Reaction phases	Vapor phase
Pressure = 180 psia		

Reaction Name	Secondary Reforming	
Reaction type	Gibbs Reactor	
Reaction	$O_2 + 2CH_4 \rightarrow 2CO + 4H_2$; $\Delta H = -35.98$ kJ/mol	
Basis Reactor No.RX2	Base component	Methane
Temperature = 1,340 ^{o}C	Reaction phases	Vapor phase
Pressure = 180 psia		

Reaction Name	High Temperature Shift Conversion	
Reaction type	Equilibrium Reactor	
Reaction	$CO + H_2O \leftrightharpoons CO_2 + H_2$; $\Delta H = -41.33$ kJ/mol	
Basis Reactor No. HTSR	Base component	Carbon monoxide
Temperature = 140 ^{o}C	Reaction phases	Vapor phase
Pressure = 176 psia		

Reaction Name	Low Temperature Shift Conversion	
Reaction type	Equilibrium Reactor	
Reaction	$CO + H_2O \leftrightharpoons CO_2 + H_2$; $\Delta H = -41.33$ kJ/mol	
Basis Reactor No. LTSR	Base component	Carbon monoxide
Temperature = 80 ^{o}C	Reaction phases	Vapor phase
Pressure = 176 psia		

Reaction Name	Ammonia Conversion	
Reaction type	Equilibrium Reactor	
Reaction	$N_2 + 3H_2 \leftrightharpoons 2NH_3$; $\Delta H = -92$ kJ/mol	
Basis Reactor No. RX3	Base component	Hydrogen
Temperature = 336 ^{o}C	Reaction phases	Vapor phase
Pressure = 4,470 psia	Equilibrium data	A = -32.975
		B = 22930.4
		(Pro II data base)

4.2 Process Flow Diagram – Case 1 Ammonia Manufacturing Process

Natural gas, temperature 15^{o}C pressure 340 psia and flow rate of 1,930 ton per day, was fed into the process simulation. The ammonia manufacturing process from the software has 3,870 ton per day productivity of Ammonia. The process is divided into 4 stage: 1. Catalytic reforming stage, 2. Shift conversion and sweetening stage, 3. Compression stage, and 4. Conversion stage. The product specifications are temperature -27 ^{o}C, pressure 4,470 psia and purity of 99.90 %. This simulation had been developed by Commercial software Pro II program version 10.0 which was used in ammonia manufacturing process. SRK thermodynamic model was used to achieve the ammonia specification product more accurately.

4.2.1 A Conceptual Design of Ammonia Production – Stage 1 Catalytic Reforming

Catalytic reforming is a chemical synthesis for product syngas (hydrogen and carbon monoxide) from natural gas and steam. The purpose of catalytic reforming is to produce hydrogen. The catalytic reforming in the simulation has consist of 2 main reaction; primary reforming and secondary reforming. The primary reformer, methane is combined with steam to be reformed to hydrogen and carbon monoxide including carbon dioxide is occurred. In the secondary stream reformer, hot air is added. The catalytic reforming stage is illustrated in Figure 4.1.

4.2.2 A Conceptual Design of Ammonia Production – Stage 2 Shift Conversion and Gas Sweetening

Shift conversion or water gas shift reaction is a reaction of carbon monoxide and water vapor to from hydrogen and carbon dioxide. Shift conversion has 2 section; High temperature shift reaction (HTSR) and Low temperature shift reaction (LTSR). Afterward, these gases are sent to sweetening section to remove carbon dioxide from the stream. In the sweetening section, AMINE01 thermodynamic model from the software was used to achieve the specification product more accurately. The specification of this section is to control operating condition to reach 0.2-0.5mol% CO and 0.005-0.2% CO_2. The removal carbon dioxide then be sent to the Urea manufacturing process. The shift conversion and gas sweetening stage is shown in Figure 4.2.

4.2.3 A Conceptual Design of Ammonia Production – Stage 3 Compression

The purified synthesis gas is compressed in a three stages unit to achieve the proper pressure to produce ammonia in the next stage. Very high pressure, about 4,400 psia, is required to produce ammonia. The aftercooler is installed to control raising temperature from compression stage. The compression stage is represented in Figure 4.3.

4.2.4 A Conceptual Design of Ammonia Production – Stage 4 Conversion

The conversion stage is a reaction of hydrogen and nitrogen with high pressure to from ammonia. From stoichiometry, 3 mole of hydrogen and 1 mole of nitrogen are mixed to from 2 mole of ammonia. The specifications of the product from simulation are 3,870 ton per day of flow rate with 99.90 % purity, -27 ^{o}C of temperature, and 4,450 psia of pressure. The ammonia conversion stage is represented in Figure 4.4.

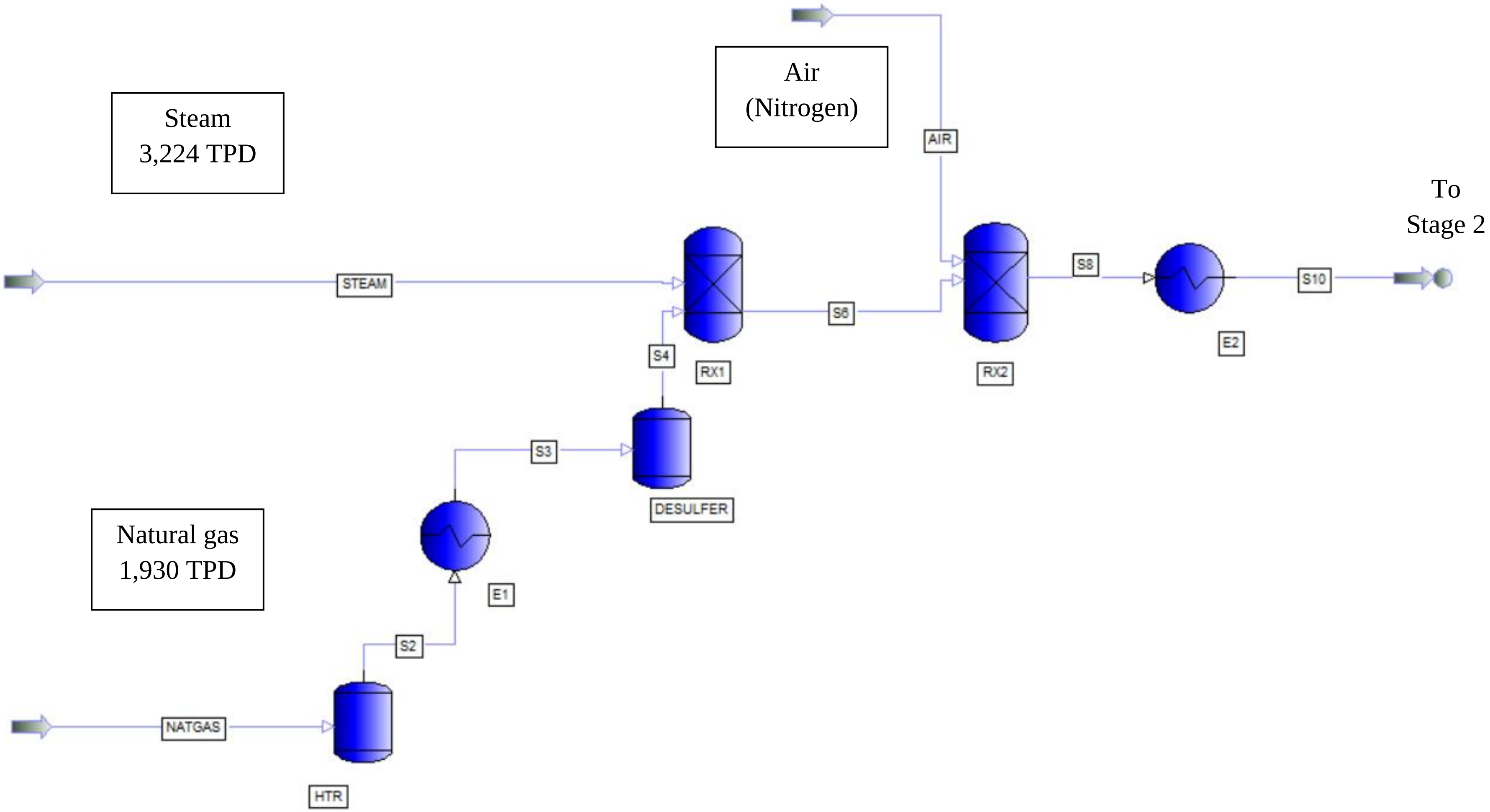


Figure 4.1 The simulation of ammonia production – stage 1 Catalytic reforming.

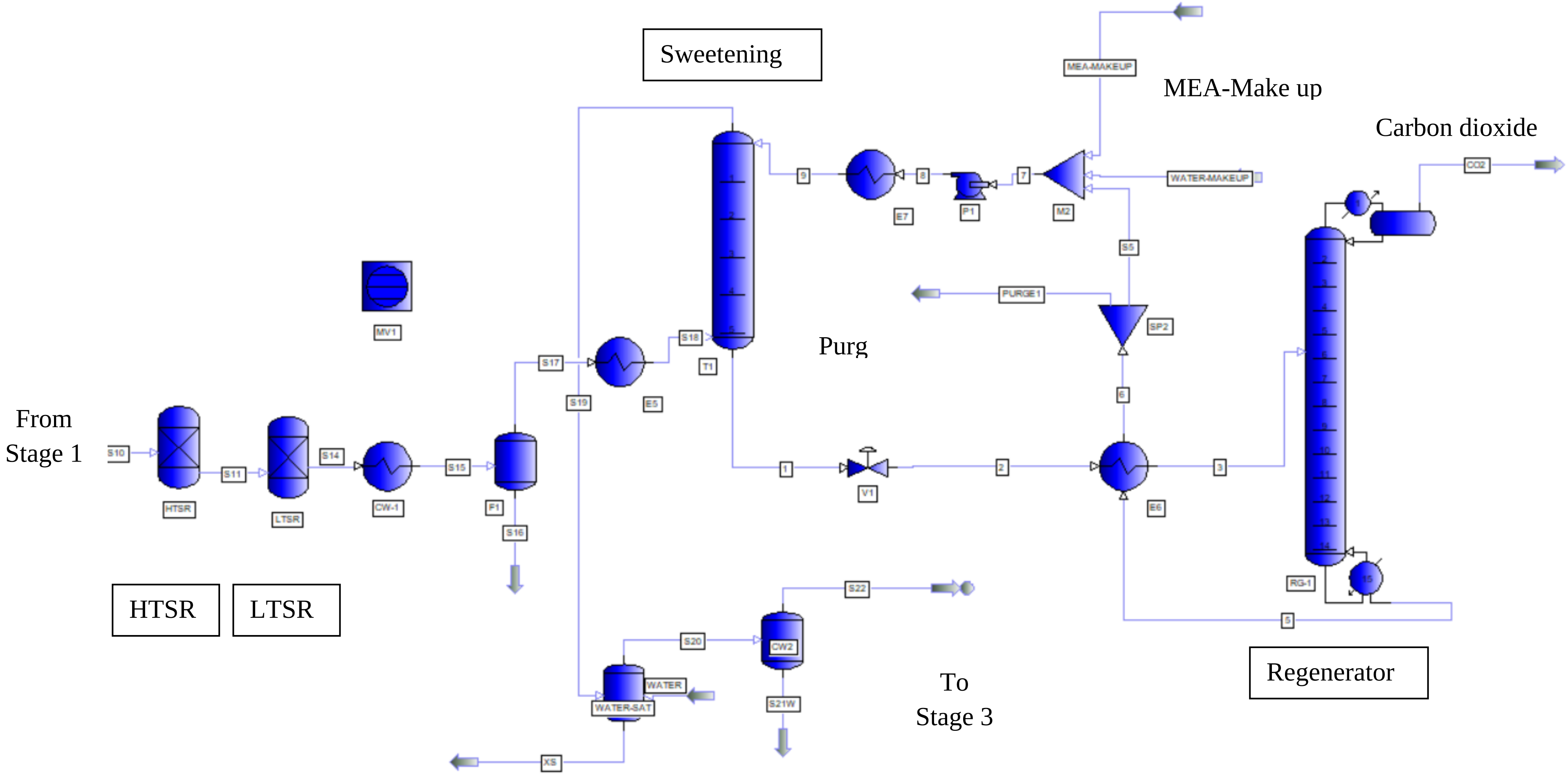


Figure 4.2 The simulation of ammonia production – stage 2 shift conversion and gas sweetening.

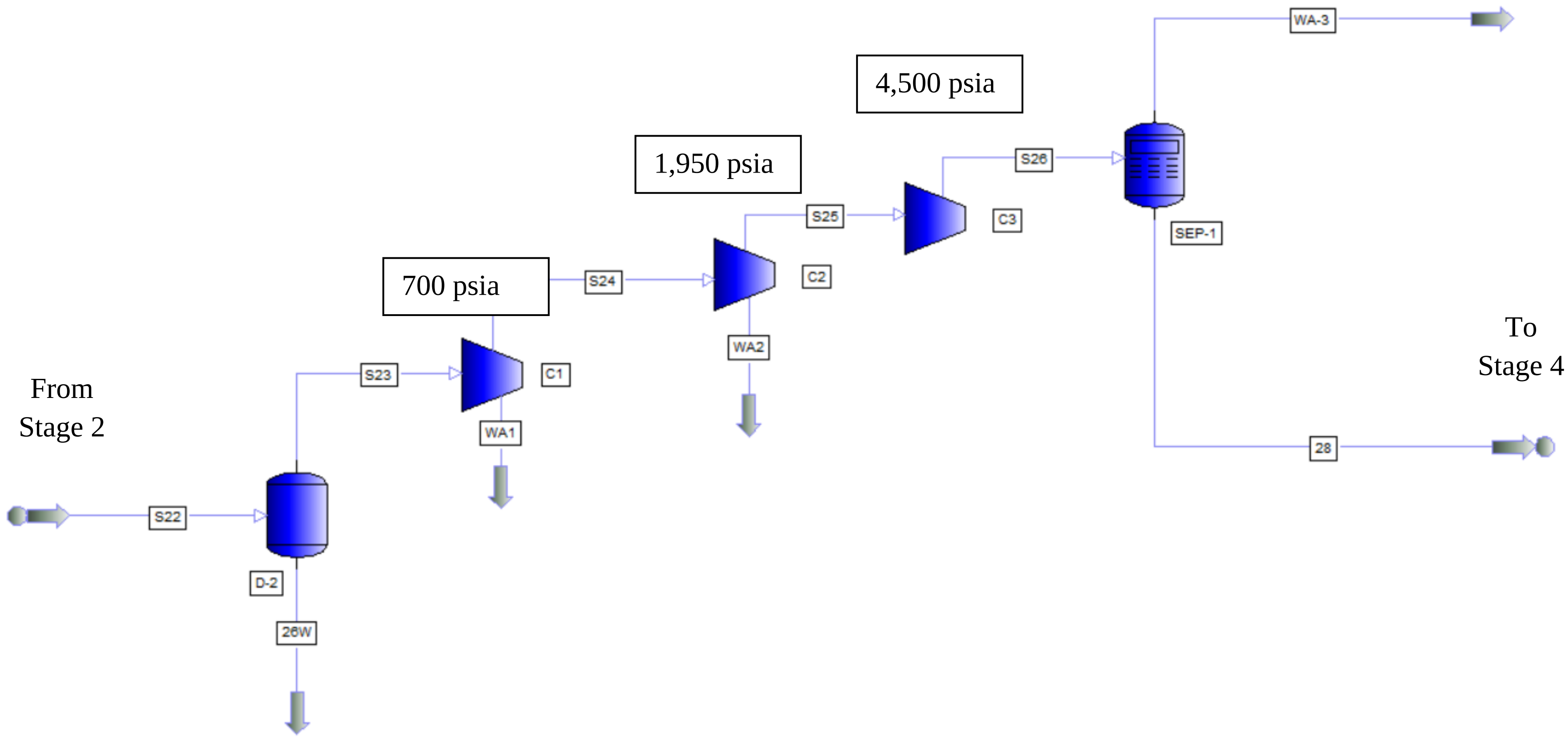


Figure 4.3 The simulation of ammonia production – stage 3 compression.

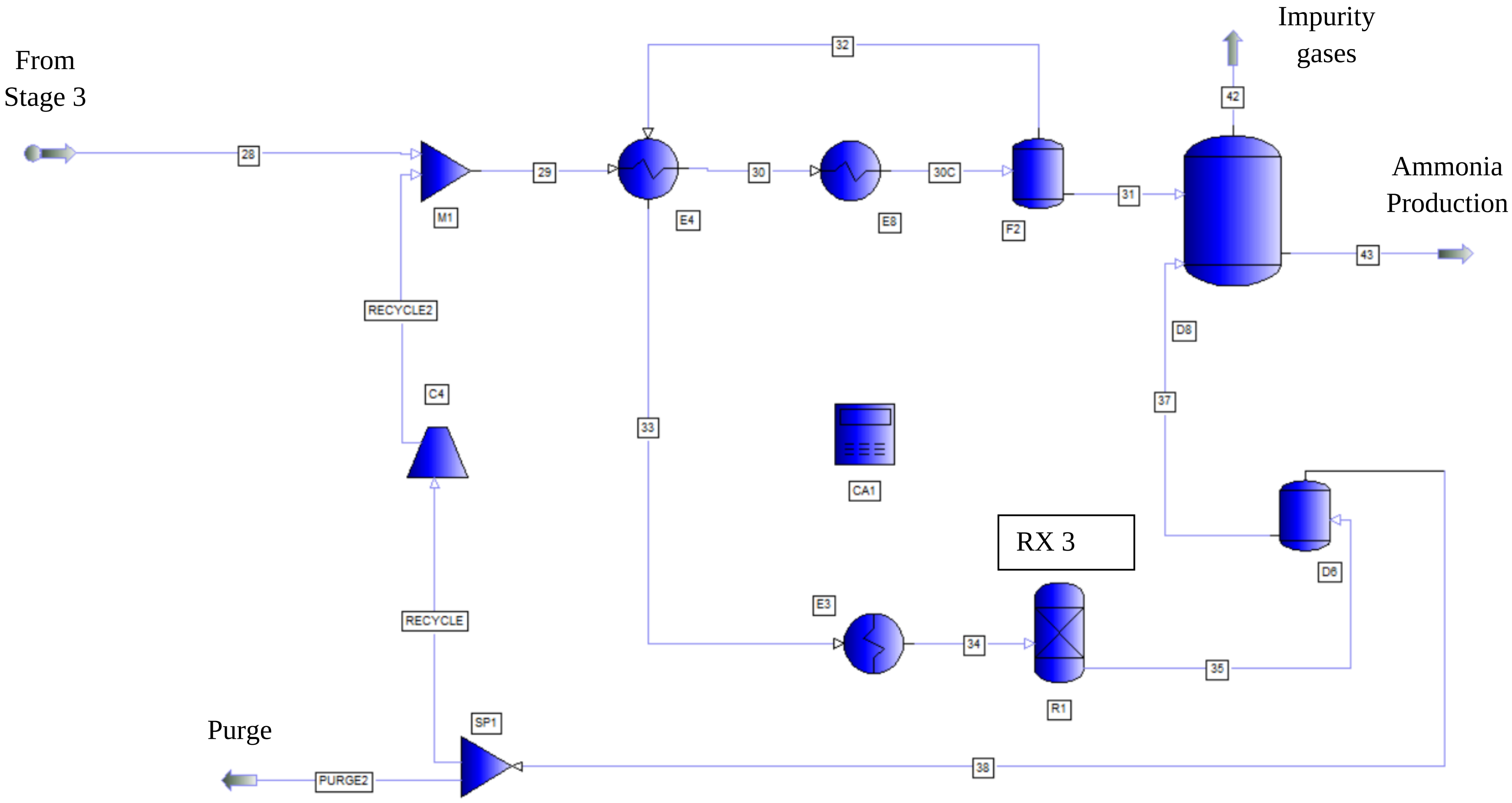


Figure 4.4 The simulation of ammonia production – stage 4 ammonia conversion.

4.3 Energy Consumption Analysis – Ammonia Manufacturing Process

The ammonia manufacturing process, stage 1 is Catalytic reforming. This stage consists of 5 units. The hot utility consumes energy about 8.7184 x 10^7 kJ/hr. The cold utilities consume energy of 1.0504 x 10^9 kJ/hr. Stage 2 is Catalytic shift and gas sweetening. This stage consists of 15 units. The hot utilities consume energy about 1.9088 x 10^9 kJ/hr. The cold utilities consume energy about 2.1646 x 10^9 kJ/hr. Stage 3 is Compression. This stage consists of 5 units and there is no energy consumption of hot utilities. The cold utilities consume energy about 3.4445 x 10^8 kJ/hr. The shaft work from compressor is about 9.49 x 10^4 kW. Stage 4 is Ammonia conversion. This stage consists of 10 units. The hot utilities consume energy about 2.4292 x 10^8 kJ/hr. The refrigerant utilities consume energy about 9.2539 x 10^8 kJ/hr. The Urea synthesis process consists of 21 units. The hot utilities consume energy of 3.6204 x 10^8 kJ/hr. The cold utilities consume energy about 4.6607 x 10^8 kJ/hr. The shaft work is about 8.49 x 10^4 kW. For ammonia manufacturing process, total energy consumption in stage 1 catalytic reforming, stage 2 shift conversion and gas sweetening, stage 3 compression, and stage 4 ammonia conversion are shown in the figure 29, 30, 31, and 32 respectively.

Table 4.7 Overall energy consumption for ammonia manufacturing process

Stage	Energy Consumption (MMKJ/HR)
Stage-1 Catalytic Reforming	1137.647
Stage-2 Shift conversion and gas sweetening	934.57
Stage-3 Compression	344.45
Stage-4 Ammonia Conversion	1168.31
Summary	3584.977

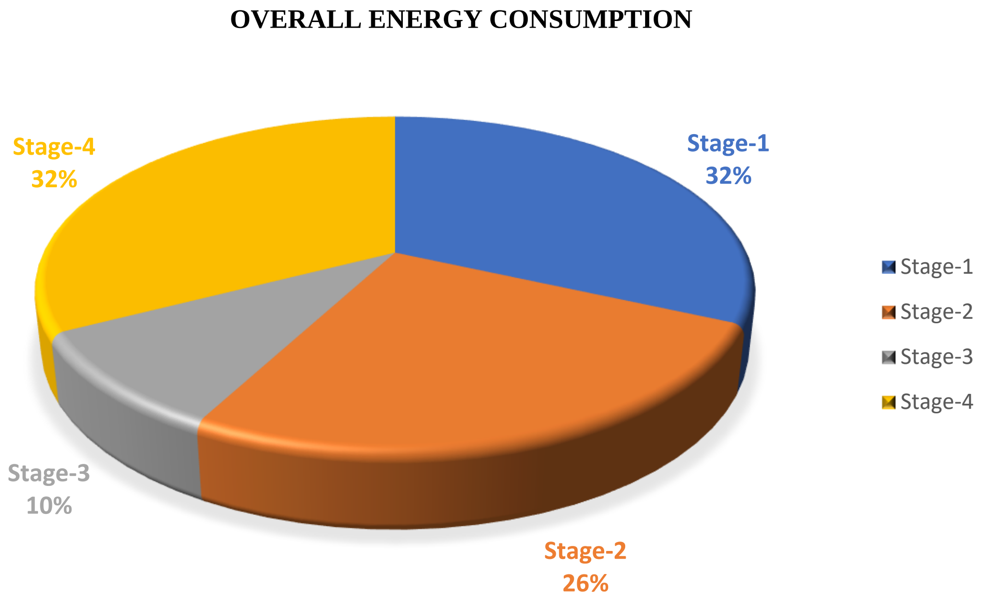


Figure 4.5 Overall energy consumption of ammonia manufacturing process.

Table 4.8 Energy consumption of ammonia production in stage 1

Unit	Hot (MMKJ/HR)	Cold (MMKJ/HR)
Flash Drum 'HTR'	1.6881	
UNIT 8, 'E1'	85.496	
Flash Drum 'DESULFER'		1.53926
UNIT 1, 'RX1', 'Primary Reformer'		
UNIT 11, 'RX2', 'Sec Reformer'	9.21E-09	
UNIT 12, 'E2', 'Cool Reformed Gas'		1048.924
Summery	87.1841	1050.463

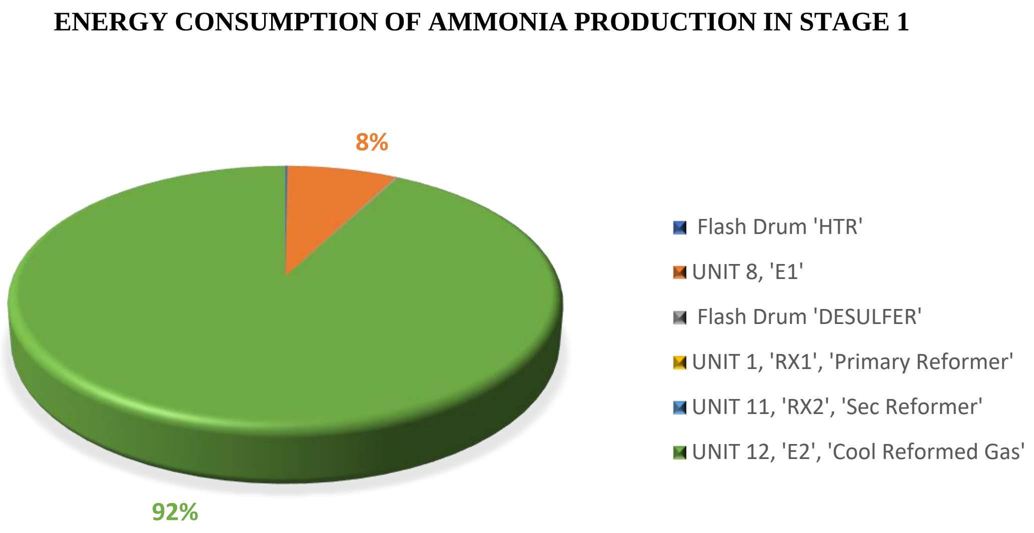


Figure 4.6 Energy consumption of ammonia process in stage 1.

Table 4.9 Energy consumption of ammonia production in stage 2

Unit	Hot (MMKJ/HR)	Cold (MMKJ/HR)
UNIT 2, 'Hight Temp Shift RX'		369.3353
UNIT 5, 'Low Temp Shift RX'		108.838
UNIT 10, 'CW-1'		100.286
UNIT 6, 'E5'	7.359	
UNIT 31, 'E6'	247.78	
Rigorous Column 'RG-1', 'Regenerator'	165.37	104.47
Pump 'P1'	Shaft work	Shaft work
UNIT 36, 'E7'		541.423
Summery	420.509	1224.352

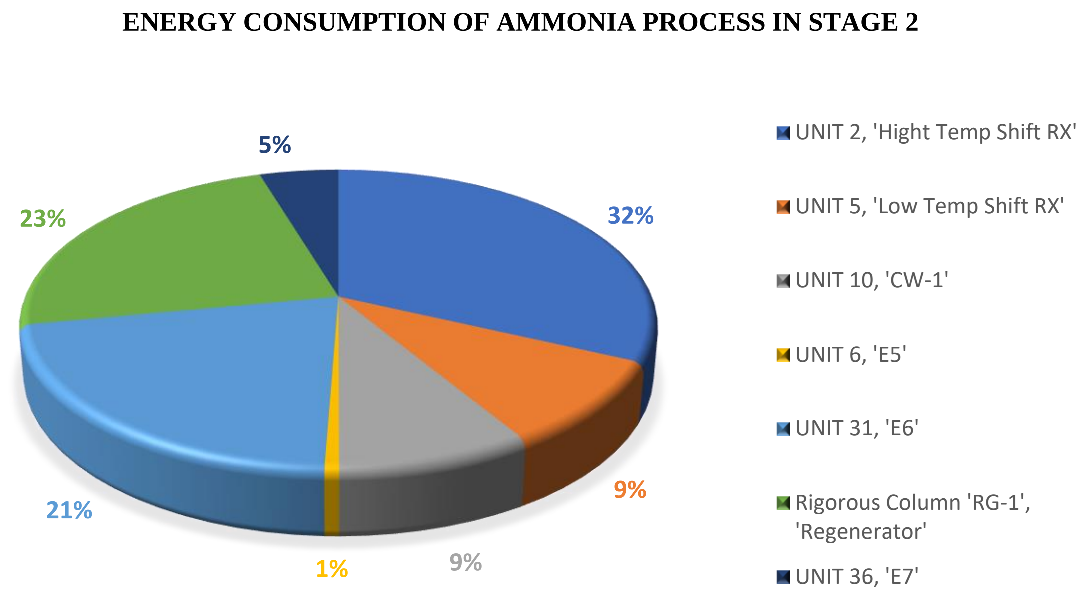


Figure 4.7 Energy consumption of ammonia process in stage 2.

Table 4.10 Energy consumption of ammonia production in stage 3

Unit	Cold (MMKJ/HR)	Shaft work (HP)
UNIT 16, 'C1'	198.29	73049.46
UNIT 19, 'C2'	80.57	29426.79
UNIT 20, 'C3'	65.59	24837.57
Summary	344.45	127313.8

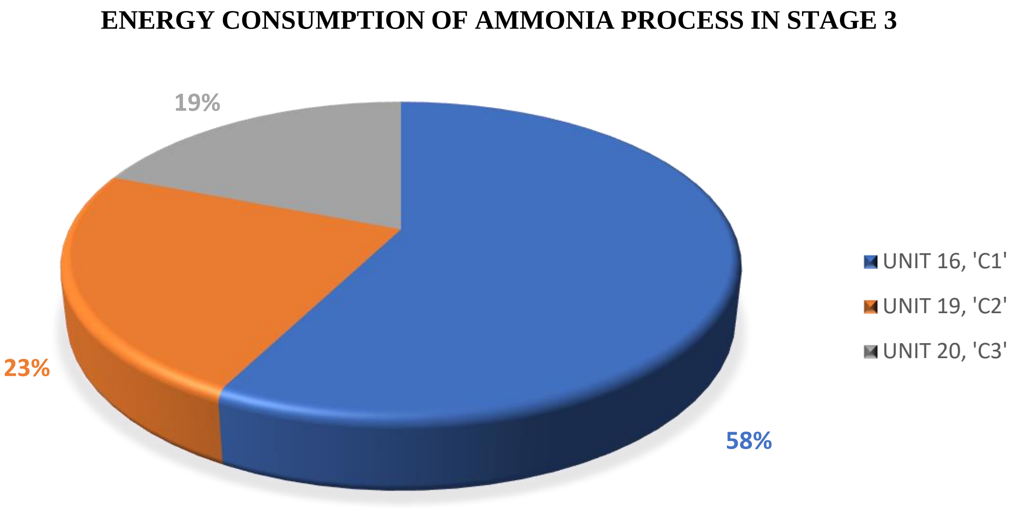


Figure 4.8 Energy consumption of ammonia process in stage 3.

Table 4.11 Energy consumption of ammonia production in stage 4

Unit	Hot (MMKJ/HR)	Cold Refrigerant (MMKJ/HR)
UNIT 22, 'E4'	13.31	
UNIT 38, 'E8		2.416
UNIT 26, 'E3'	229.601	
UNIT 29, 'RX3'	4.35E-03	
Flash Drum 'D6', 'Pri Sep'		922.9744
UNIT 27, 'C4'	Shaft work	Shaft work
Summery	242.9154	925.3904

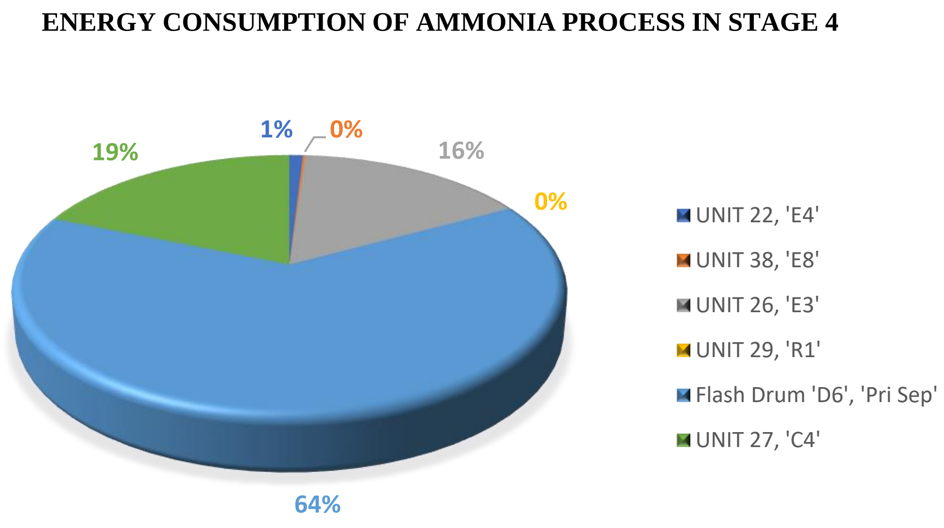


Figure 4.9 Energy consumption of ammonia process in stage 4.

4.4 Properties and Specification for Simulation Processes – Urea Plant

For case 2 – Urea manufacturing process, the urea production of the conceptual process is 3,870 ton per day. The carbon dioxide that be eliminated from gas sweetening process is 5,202 ton per day and will be consumed in this process about 5,046 ton per day. The properties and specification of ammonia and carbon dioxide feedstock are shown in the table 1 and 2. The urea product specifications are shown in the table 5. The input data of the conceptual urea manufacturing are shown in the table 6.

Table 4.12 Ammonia feed for urea manufacturing process

Ammonia feed stock specification	
Ammonia purity (% mole)	99.90%
Flow rate (ton/day)	3,870
Temperature (°C)	-33.33
Pressure (psia)	320

Table 4.13 Carbon dioxide feed for urea manufacturing process

Carbon dioxide feed stock specification	
Carbon dioxide purity (% mole)	100%
Flow rate (ton/day)	5,046
Temperature (°C)	37.78
Pressure (psia)	300

Table 4.14 Urea product specification

Urea product specification	
Urea purity (% mole)	99.90%
Flow rate (ton/day)	5,472
Temperature (^oC)	93.33
Pressure (psia)	-

Table 4.15 Input data of urea process

Reaction Name	Urea synthesis 1	
Reaction type	Conversion	
Reaction	$8NH_3 + 4CO_2 \leftrightharpoons 3\ CH4N2O2 + 3H_2O + NH_2COONH_4$	
Basis Reactor No. RX4	Base component	Carbon dioxide
Temperature = 180 ^oC	Reaction phases	Vapor phase
Pressure = 15 psia		

Reaction Name	High pressure decomposer	
Reaction type	Conversion	
Reaction	$NH_2COONH_4 \leftrightharpoons 2NH_3 + CO_2$	
Basis Reactor No. RX5	Base component	Ammonium Carbamate
Temperature = 180 ^oC	Reaction phases	Vapor phase
Pressure = 600 psia		

Reaction Name	Low pressure decomposer	
Reaction type	Conversion	
Reaction	$NH_2COONH_4 \leftrightharpoons 2NH_3 + CO_2$	
Basis Reactor No. RX6	Base component	Ammonium Carbamate
Temperature = 120 ^oC	Reaction phases	Vapor phase
Pressure = 300 psia		

4.5 Process Flow Diagram – Case 2 Urea Manufacturing Process

Ammonia, temperature -33^{o}C pressure 320 psia and flow rate of 3,870 ton per day, was fed into the process simulation to mix with Carbon dioxide, temperature 37^{o}C pressure 300 psia and flow rate of 5,046 ton per day. The urea manufacturing process from the software has 5,472 ton per day productivity of urea. The product specifications are temperature 93^{o}C, Solid state and purity of 99.90%. This simulation had been developed by Commercial software Pro II program version 10.0 which was used in urea manufacturing process. NRTL01 thermodynamic model was used to achieve the urea specification product more accurately.

The urea plants are capable of processing 5,472 ton per day. There have 3 main reactors in the process simulation: Urea synthesis reactor, high-pressure decomposer, and low-pressure decomposer. This process is to convert carbon dioxide and synthetic ammonia with high pressure reacted to form into urea which is shown in Figure 4.10.

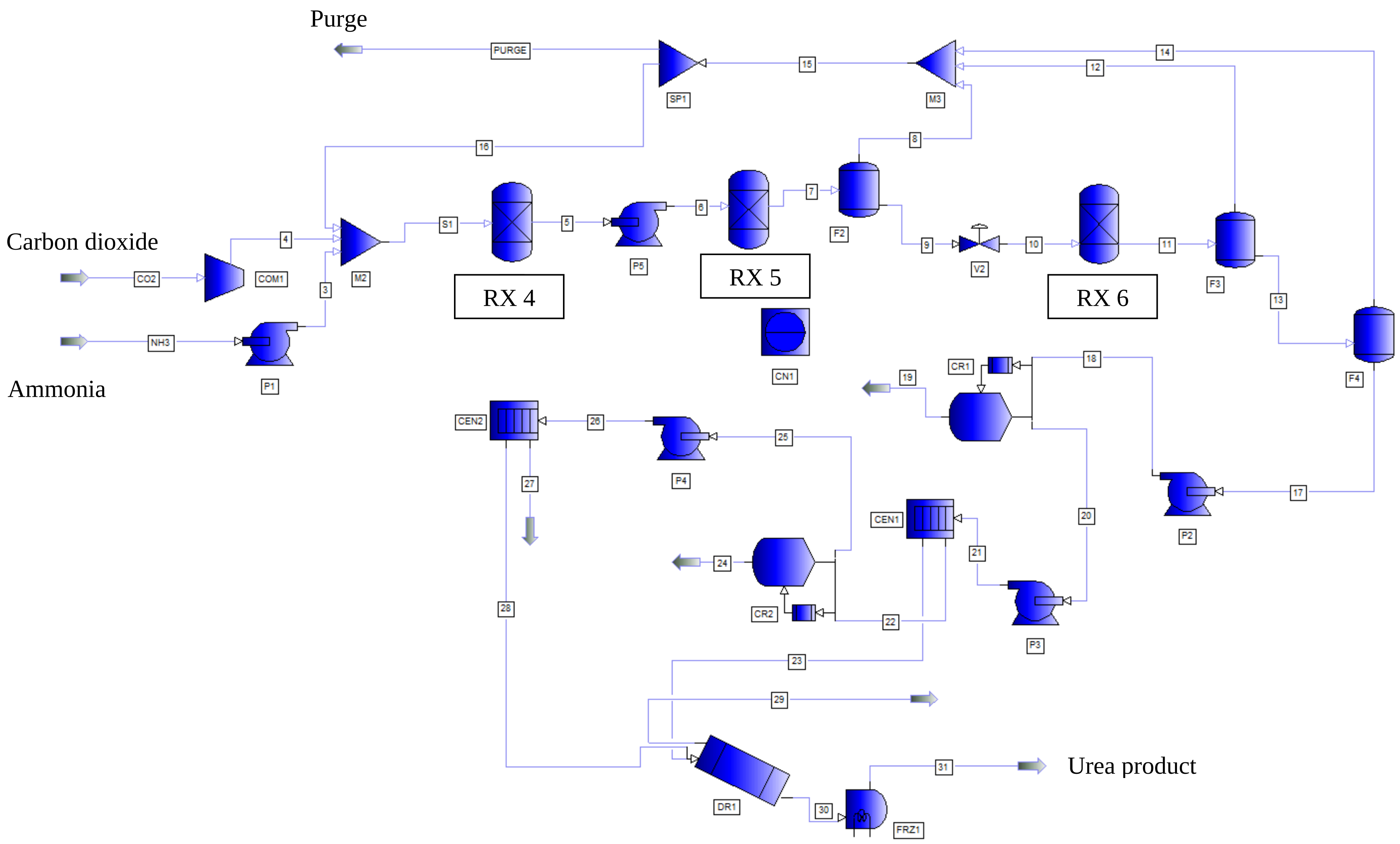


Figure 4.10 The simulation of urea production.

4.6 Energy Consumption Analysis – Urea Manufacturing Process

The Urea synthesis process consists of 21 units. The hot utilities consume energy about 4.28 x 10^8 kJ/hr. The cold utilities consume energy about 4.93 x 10^8 kJ/hr. The shaft work is about 8.49 x 10^4 kW.

Table 4.16 Energy consumption of urea production

Unit	Hot (MMKJ/HR)	Cold (MMKJ/HR)	Shaft work (HP)
UNIT 1, 'COM1'		113.07	4,2120.6
Pump 'P1'			2,238.42
UNIT 3, 'RX4'		295.3946	
Pump 'P5'			8,3334.51
UNIT 6, 'RX4', 'HP_Decomposer'	288.4287		
UNIT 8, 'RX5', 'LP_Decomposer'		41.1598	
Pump 'P2', 'PUMP2'			4.11
Crystalizer 'CR1', 'CSTAGE1'	55.9019		
Pump 'P3', 'PUMP3'			3.2
Crystalizer 'CR2', 'CSTAGE2'	18.2524		
Pump 'P4', 'PUMP4'			1.29
Solids Dryer 'DR1', 'DRYER'	65.16		
UNIT 19, 'FRZ1', 'FREEZER'		43.3824	
Summery	427.743	493.0068	127702

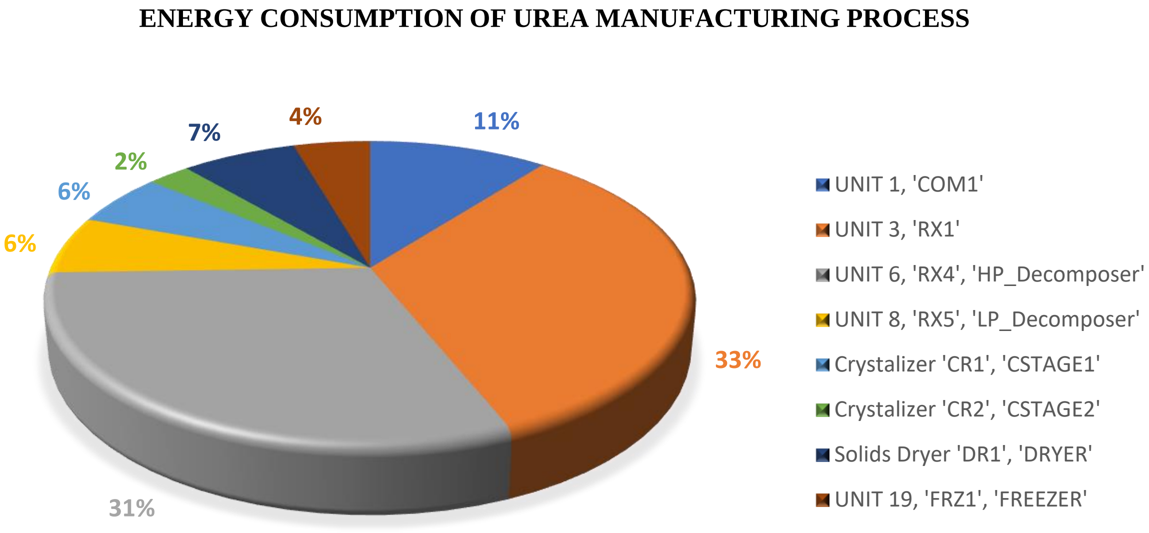


Figure 4.11 Energy consumption of urea process.

4.7 Techno Economic Analysis of the Manufacturing Process

Techno Economic Analysis is to estimate cost of investment and the profitability of project. This cost assessment technique represents the capital expenditure, the operating expenditure, net present value, pay-back period, and return of investment. There are 3 main parts to estimate total investment cost of the project which are

4.7.1 Fixed Capital Cost

This cost includes mainly purchasing process equipment. This cost associates with constructing the plant and includes the raw material costs.

4.7.1.1 Direct Manufacturing Expenditure

Manufacturing fixed capital investment consisted of site preparation, piping, instrument, process equipment, raw material cost, auxiliary facilities, admin office, warehouses, lab, transportation, shipping, utilities, waste disposal facilities.

4.7.1.2 Indirect Manufacturing Expenditure

Expenses which are not directly involved with material and labour e.g. engineering, supervision, legal expenses, maintenance and repair, local taxes, and insurance.

4.7.2 Working Capital Investment

This cost includes mainly raw materials and supplies, finished product in stock, operating expenses, and taxes. It can be calculated by 15% of fixed capital cost.

4.7.3 Depreciable Investment

Generally, this cost includes all property (Physical facilities, including design and engineering, shipping, and field erection except land) with a limited useful life of more than 1 year. It can be calculated by 10% of fixed capital cost.

Typical process utilities including process steam, electricity, refrigerants, compression air, cooling water, hot oil, process water. For preliminary cost estimation can be treated like utility expense. The two-factor utility cost equation are needed such as the following: and the utilities cost coefficients are represented in table 4.17

$$C_{s,u} = a\ (\ CEPCI\ ) + b\ (C_{s,f}) \qquad (6.1)$$

Where $C_{s,u}$ is the price of the utility, a and b are utility cost coefficients $C_{s,f}$ is the price of fuel in \$/GJ, and CEPCI is an inflation parameter for projects in the U.S.*

* Evaluated monthly by the staff of Chemical Engineering

Table 4.17 Utility cost coefficient with 470 of CEPCI and 7.2 of $C_{s,f}$

Utility type	Cost coefficient	
	a	b
Onsite power charged to grass-roots plant	1.1×10^{-4}	0.010
Hot water for process steam (Qh is total heat capacity in kJ/s, T is absolute temperature)	$6.0 \times 10^{-7}Qh^{-0.9}(T)^{0.5}$	$6.0 \times 10^{-8}T^{0.5}$
Cooling Water (q is water capacity in m^3/s)	$0.00007 + 2.5 \times 10^{-5}q^{-1}$	0.003
Refrigerant (Qc is total cooling capacity in kJ/s, T is absolute temperature)	$0.5Qc^{-0.9}(T^{-3})$	$1.1 \times 10^{6}T^{-5}$

4.7.4 Expenditure Assessment for Ammonia and Urea Processes

The ammonia manufacturing process or detail on total expenditure are consist of 3 main of utilities cost: 1. Hot water for heat transfer media in the process, 2. Cooling water for cooling temperature of each equipment, and 3. Refrigerant for liquefy ammonia in the process. The details are represented in Table 4.18

Table 4.18 Expenditure assessment for ammonia manufacturing process

Unit	Energy Consumption type				Cost ($/year)
	Hot (MM kJ/hr)	Cool (MM kj/hr)	Shaft work (HP)	Refrigerant (MM kJ/hr)	
Stage-1 Catalytic Reforming					
Flash Drum 'HTR'	1.6881	-	-	-	157,105
UNIT 8, 'E1'	85.496	-	-	-	7,956,763
Flash Drum 'DESULFER'	-	1.53926	-	-	7,043
UNIT 11, 'RX2', 'Sec Reformer'	9.21E-09	-	-	-	8.57E-04
UNIT 12, 'E2', 'Cool Reformed Gas'	-	1048.924	-	-	4,799,657
Stage-2 Shift Conversion					
UNIT 2, 'Hight Temp Shift RX'	-	369.3353	-	-	1,690,001
UNIT 5, 'Low Temp Shift RX'	-	108.838	-	-	498,020
UNIT 10, 'CW-1'	-	100.286	-	-	458,888
UNIT 6, 'E5'	7.359	-	-	-	684,872
UNIT 31, 'E6'	24.78	-	-	-	2,330,446
Rigorous Column 'RG-1',	165.37	104.47	-	-	16,031,241
Pump 'P1'			37.722	-	30,481
UNIT 36, 'E7'	-	54.142	-	-	247,744

Table 4.18 Expenditure assessment for Ammonia manufacturing process (Continue)

Unit	Energy Consumption type				Cost ($/year)
	Hot (MM kJ/hr)	Cool (MM kj/hr)	Shaft work (HP)	Refrigerant (MM kJ/hr)	
Stage-3 Compression					
UNIT 16, 'C1'	-	198.29	73049.46	-	59,027,567
UNIT 19, 'C2'	-	80.57	29426.79	-	23,778,298
UNIT 20, 'C3'	-	65.59	24837.57	-	20,069,982
Stage-4 Ammonia Conversion					
UNIT 22, 'E4'	13.31	-	-	-	1,238,707
UNIT 38, 'E8'	-	-	-	2.416	186,064
UNIT 26, 'E3'	229.601	-	-	-	21,368,025
UNIT 29, 'R1'	4.35E-03	-	-	-	405
Flash Drum 'D6', 'Pri Sep'	-	-	-	922.9744	71,081,132
UNIT 27, 'C4'	-	-	269.4	-	217,688
Summarizes					231,860,129

Table 4.19 Expenditure assessment for urea manufacturing process from 3,870 TPD ammonia feed

Unit	Energy Consumption type				Cost ($/year)
	Hot (MM kJ/hr)	Cool (MM kj/hr)	Shaft work (HP)	Refrigerant (MM kJ/hr)	
Urea conversion					
UNIT 1, 'COM1'	-	113.07	42120.6	-	34,552,907
Pump 'P1'	-	-	2283.42	-	1,845,116
UNIT 3, 'RX1'	-	295.3946	-	-	1,351,664
Pump 'P5'	-	-	83334.51	-	67,338,395
UNIT 6, 'RX4', 'HP_Decomposer'	288.4287	-	-	-	26,842,879
UNIT 8, 'RX3', 'LP_Decomposer'	-	41.1598	-	-	188,339
Pump 'P2', 'PUMP2'	-	-	4.11	-	3,321
Crystalizer 'CR1', 'CSTAGE1'	65.4908	-	-	-	6,094,961
Pump 'P3', 'PUMP3'	-	-	3.2	-	2,586
Crystallizer 'CR2', 'CSTAGE2'	18.2524	-	-	-	1,698,676
Pump 'P4', 'PUMP4'	-	-	1.29	-	1,042
Solids Dryer 'DR1', 'DRYER'	65.16	-	-	-	6,064,174
UNIT 19, 'FRZ1', 'FREEZER'	-	43.3824	-	-	198,509
Summarizes					146,182,569

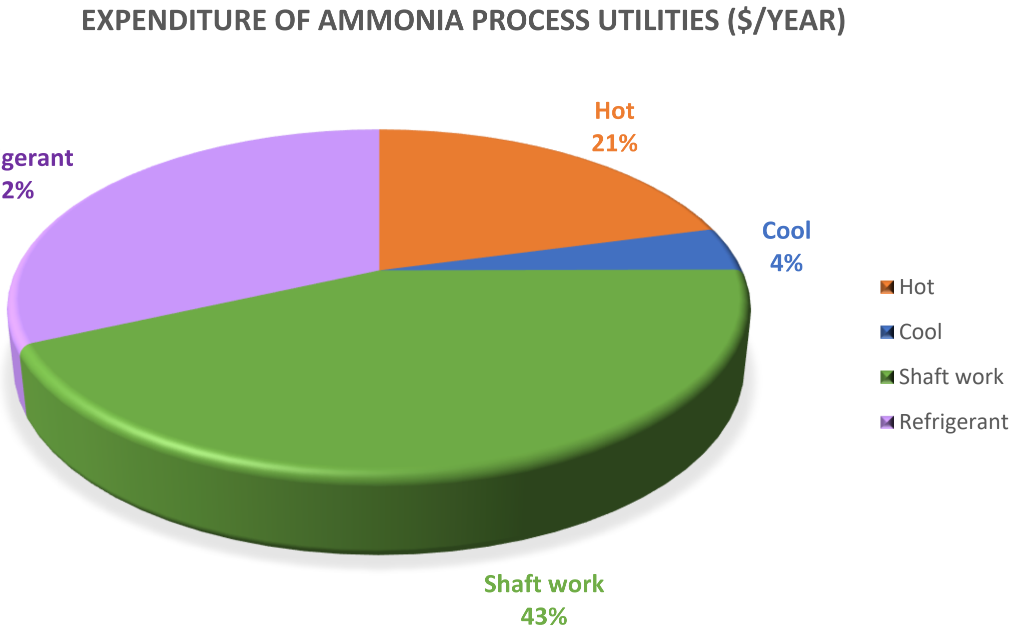


Figure 4.12 Expenditure of ammonia process divided by utility type.

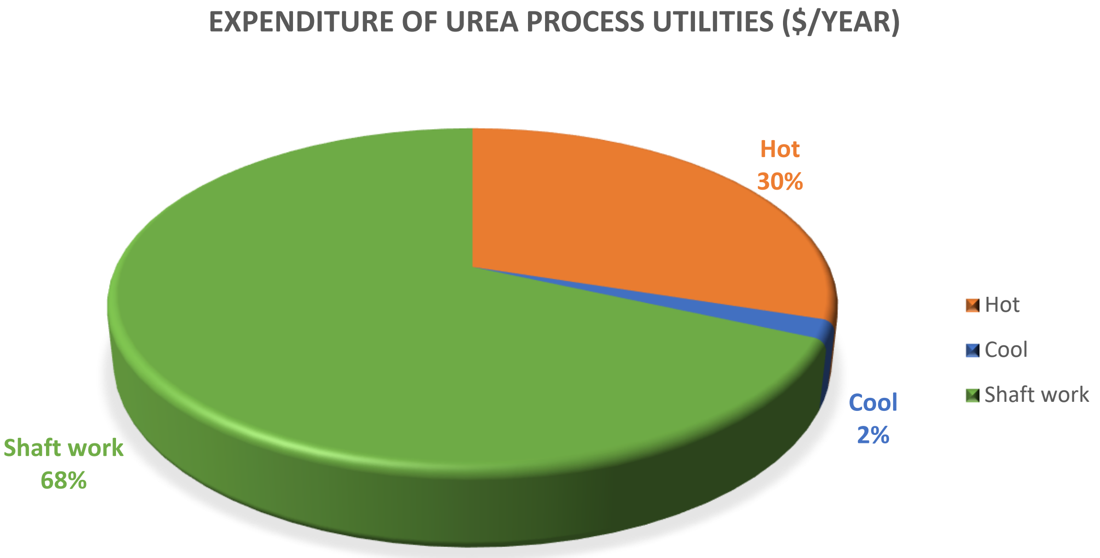


Figure 4. 13 Expenditure of urea process divided by utility type.

Table 4.20 Detail Purchased Equipment Cost

Unit	Purchased Cost ($)
Reactors (10)	15,991,253
Flash drum (11)	1,432,874
Distillation column (2)	38,854
Centrifugal Pump (6)	79,536
Centrifugal Compressor (5)	6,180,612
Fired Heated	19,013,389.14
Summarizes	42,736,518.3

Table 4.21 Detail total expenditure for ammonia and urea manufacturing

Components	%	Cost ($)
Direct cost		
Purchased equipment installation	47	20,086,164
Instrumentation (installed)	12	5,128,382
Piping (installed)	66	28,206,102
Electrical (installed)	11	4,701,017
Building (including Service)	18	7,692,573
Yard improvement	10	4,273,652
Service facilities	70	29,915,563
Land	6	2,564,191
Total direct cost		145,304,162
Indirect cost		
Engineering and supervision	33	14,103,051
Construction Expenses	41	17,521,973
Total Indirect Cost		31,625,024
Total Direct & Indirect Cost		176,929,186
Contractor’s fee	5	8,846,459
Contingency	10	17,692,919
Fixed Capital Investment		203,468,564
Working Capital investment	15	30,520,285
Total Capital Investment (CAPEX)		233,988,848

Table 4.22 Key assumptions used to develop the techno-economic model

Base year	2019
Plant lifetime	10 years
Operating hour per year (h)	8760
Annual Ammonia Capacity (ton)	1,412,550
Ammonia price ($/ton)	206
Annual Urea Capacity (ton)	1,997,280
Urea price ($/ton)	288
CAPEX ($)	233,988,848
Interest rate (%)	10
Payback period (y)	5.4
Net present value ($)	197,175,232

Ammonia product from the case-1 can be as the substrate for the urea process by mixing with carbon dioxide and react at high temperature. The expenditure of urea process be varied with the energy consumption that be changed with the amount of feedstock. For being economical, correlation between ammonia and urea manufacturing process will be considered. The maximum capacity of ammonia manufacturing is 3,870 TPD which feed for substrate in urea process. It can be distributed into 11 operating scenarios by 10 % reducing amount of ammonia feed to urea process as shown in table 4.23.

Table 4.23 Correlation between ammonia feed to urea product

Scenario No.	Ammonia Feed to urea process (Ton/day)	Urea Production (Ton/day)	Ammonia Production (Ton/day)	Urea Expenditure ($/day)
1	3,870	5,472	0	400,500
2	3,483	4,925	387	360,435
3	3,096	4,378	774	320,390
4	2,707	3,831	1,161	280,339
5	2,322	3,283	1,548	240,293
6	1,935	2,736	1,935	200,243
7	1,548	2,189	2,322	160,193
8	1,161	1,642	2,707	120,145
9	774	1,094	3,096	80,097
10	387	547	3,483	40,048
11	0	0	3,870	0

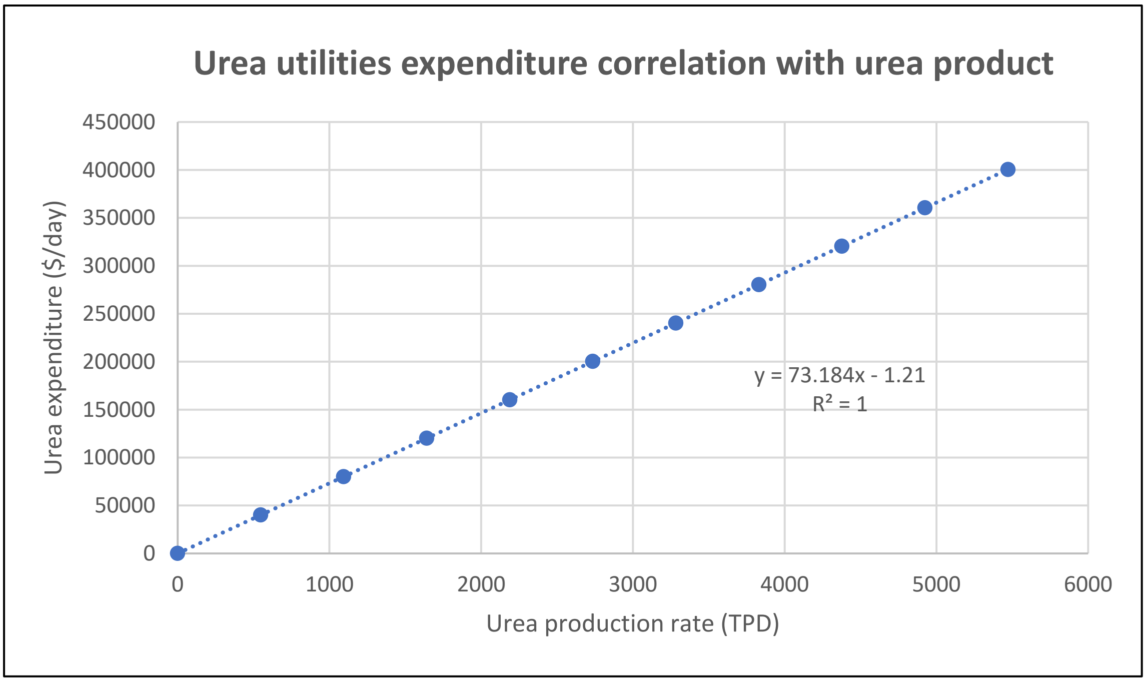


Figure 4.15 Urea utilities expenditure correlation with urea product.

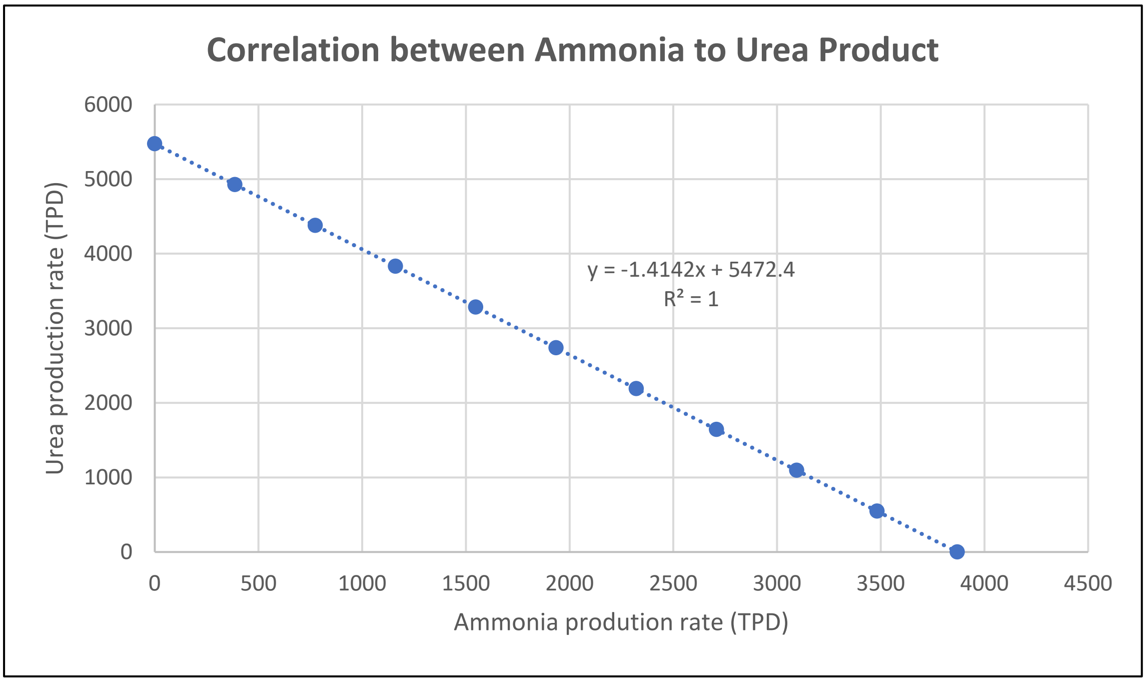


Figure 4.14 Correlation between ammonia to urea product.

4.8 Investigation on Optimization of Market Demand (with Fixed Production Capacity of Ammonia and Urea)

The supply chain can be defined as the flow of materials or information from basic commodities or raw materials to final products for end-customer through many processes that are linked together to chain. In this first case study, the network has with 2 echelons; Plant (i) with 2 products (ammonia and urea), and Market (j) with 2 products (ammonia and urea). The mathematical model for designing the network is expressed as show below.

$$\text{Max } Z = \text{Price}_{\text{Amm}} * \Sigma_i \Sigma_j X_{ij} + \text{Price}_{\text{Urea}} \Sigma_i \Sigma_j Y_{ij} - [\text{Cost1} + \text{Cost2} + \text{Cost3}] \quad (6.1)$$

Subject to constraints,

$$\Sigma_j X_{ij} = \text{LimCapAmm}_i \quad (6.2)$$

$$\Sigma_j Y_{ij} = \text{LimCapUrea}_i \quad (6.3)$$

$$\Sigma_i X_j + \Sigma_i \text{PenaltyAmm}_{ij} - \text{PPAmm}_j = \text{LimAmm}_j \text{ (Demand)} \quad (6.4)$$

$$\Sigma_i Y_{ij} + \Sigma_i \text{PenaltyUrea}_{ij} - \text{PPUrea}_j = \text{LimUrea}_j \text{ (Demand)} \quad (6.5)$$

$$\text{Cost1} = 795470 \quad (6.6)$$

$$\text{Cost2} = (\Sigma_i \Sigma_j X_{ij} + \Sigma_i \Sigma_j Y_{ij}) * \text{transportcost} \quad (6.7)$$

$$\begin{aligned}\text{Cost3} = {} & \Sigma_i \Sigma_j \text{ PenaltyAmm}_{ij} * \text{PAmmCost} + \Sigma_i \Sigma_j \text{ PPAmm}_j * \text{PPAmmCost} + \\ & \Sigma_i \Sigma_j \text{ PenaltyUrea}_{ij} * \text{PUreaCost} + \Sigma_i \Sigma_j \text{ PPUrea}_j * \text{PPUreaCost}\end{aligned} \quad (6.8)$$

Where

X_{ij} = Ammonia transportation amount (TPD)
Y_{ij} = Urea transportation amount (TPD)
LimCapAmm_i = Ammonia production capacity of plant i in cases (TPD)
LimCapUrea_i = Urea production capacity of plant i in cases (TPD)
PenaltyAmm_{ij} = Ammonia amount which less than demand of market (TPD)
PenaltyUrea_{ij} = Urea amount which less than demand of market (TPD)
PPAmm_j = Ammonia amount which greater than demand of market (TPD)
PPUrea_j = Urea amount which greater than demand of market (TPD)

$LimAmm_j$ (Demand) = Ammonia demand of market j in cases (TPD)

$LimUrea_j$ (Demand) = Urea demand of market j in cases (TPD)

Opportunity loss cost = $\Sigma_i\Sigma_j$ $PenaltyAmm_{ij}$ * PAmmCost (\$/day)

Surplus Production cost = $\Sigma_i\Sigma_j$ $PPAmm_j$ * PPAmmCost (\$/day)

Cost1 = Ammonia and urea production cost at urea production rate 2,322 TPD (\$/day)

Cost2 = transportation cost (\$/day)

Cost3 = Penalty cost (\$/day)

The main objective of this model is to maximize profit from sale products. The objective function is expressed into 3 parts; revenue, transportation cost, and penalty cost as shown in equation 6.1. The penalty cost is opportunity loss that the products are lower than demand of the market and cannot be sold. Equation 6.2 and 6.3 are deal with maximum capacity of plant in ammonia product and urea product, respectively. Equation 6.4 and 6.5 are deal with minimum demand of the market in ammonia product and urea product, respectively. The market's demand data was assumed as a historical for optimized programming by using normal distribution of mean and standard derivation as shown in figure 4.18.

The case study for deterministic and stochastic models use historical demand data of 30 days. The simple supply chain network with 2 echelons; Plant (i) and Market (j) with 2 products (ammonia and urea) is shown in figure 4.16.

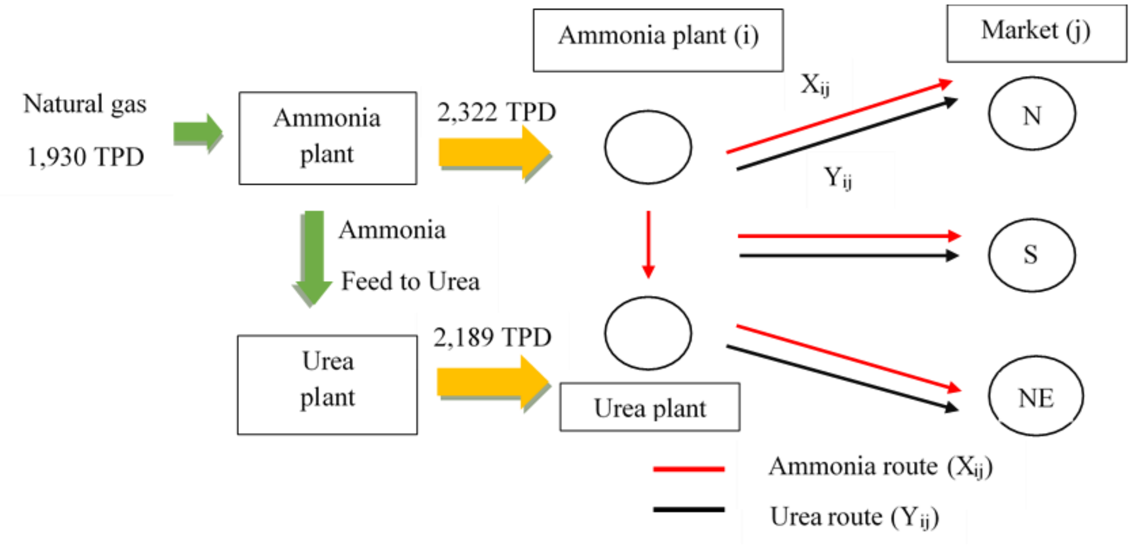
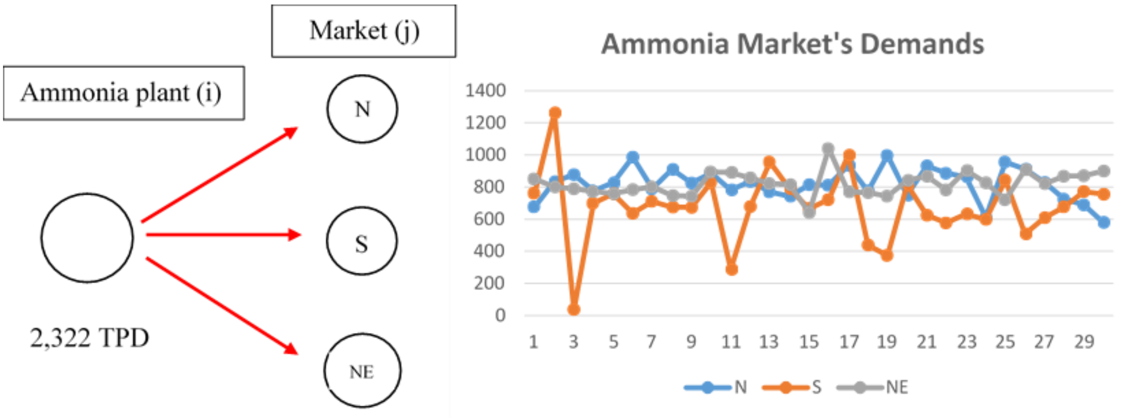


Figure 4.16 The simple supply chain network diagram.

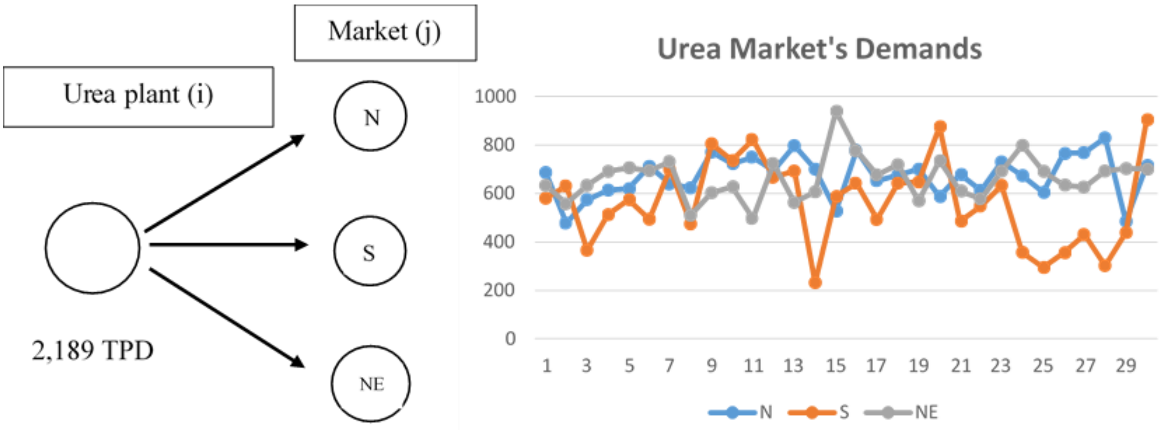
Table 4.24 The data related to the network

Market	Distance (miles)
N	531
S	684
NE	208
Product sale price*	($/ton)
Ammonia	206 (Yuzhny)
Urea	288 (granular Indonesia/Malaysia)
Transportation cost ($/ton/miles)	0.05
Opportunity loss ($/unit)	50% of product selling price
Surplus Production Cost ($/unit)	25% of product selling price

*Source; AfricaFertilizer.org FOB International Fertilizer Prices – updated at December 2019 (price data from Jul-19)



	N	S	NE
Mean	800	700	800
SD	100	300	100



	N	S	NE
Mean	650	500	650
SD	100	200	100

Ammonia and urea capacity are from correlation function: $y = -1.4142x + 5472.4$

Figure 4. 17 Ammonia and urea demands of each market.

Table 4.25 The result of supply chains model network – fixed production capacity of ammonia and urea

Supply chain No.X using product demand of	Market (j) (TPD)			Penalty cost ($)	Transportation cost ($)	Profit Z cost ($)
	N (j1)	S (j2)	NE (j3)			
No.1 using demand of day 1				22,312	100,906	190,076
Ammonia Demand	677	762	851			
Ammonia shipping amount (x)	677	762	801	1,648	53,218	
Urea Demand	687	581	634			
Urea shipping amount (y)	687	581	921	20,664	47,688	
No.2 using demand of day 2				96,737	99,495	117,062
Ammonia Demand	834	1,262	801			
Ammonia shipping amount (x)	834	687	801	59,225	53,969	
Urea Demand	478	632	558			
Urea shipping amount (y)	478	632	1,079	37,512	45,527	
No.3 using demand of day 3				75,932	79,996	157,366
Ammonia Demand	878	38	790			
Ammonia shipping amount (x)	878	38	1,406	31,724	39,233	
Urea Demand	575	366	634			
Urea shipping amount (y)	575	366	1,248	44,208	40,763	
No.4 using demand of day 4				30,348	98,248	184,698
Ammonia Demand	777	700	773			
Ammonia shipping amount (x)	777	700	845	3,708	53,357	
Urea Demand	614	513	692			
Urea shipping amount (y)	614	513	1,062	26,640	44,891	
No.5 using demand of day 5				23,033	101,494	188,767
Ammonia Demand	828	758	759			
Ammonia shipping amount (x)	828	735	759	2,369	55,014	
Urea Demand	621	575	706			
Urea shipping amount (y)	621	575	993	20,664	46,480	

Table 4.25 The result of supply chains model network – fixed production capacity of ammonia and urea (Continue)

Supply chain No.X using product demand of	Market (j) (TPD) N (j1)	S (j2)	NE (j3)	Penalty cost ($)	Transportation cost ($)	Profit Z ($)
No.6 using demand of day 6				29,594	99,224	184,476
Ammonia Demand	987	637	784			
Ammonia shipping amount (x)	987	551	784	8,858	53,203	
Urea Demand	712	494	695			
Urea shipping amount (y)	712	494	983	20,736	46,022	
No.7 using demand of day 7				9,382	103,638	200,274
Ammonia Demand	790	711	801			
Ammonia shipping amount (x)	790	711	821	1,030	53,829	
Urea Demand	640	702	731			
Urea shipping amount (y)	640	702	847	8,352	49,809	
No.8 using demand of day 8				42,996	98,773	171,525
Ammonia Demand	911	675	748			
Ammonia shipping amount (x)	911	663	748	1,236	54,641	
Urea Demand	623	475	511			
Urea shipping amount (y)	623	475	1,091	41,760	44,132	
No.9 using demand of day 9				4,768	107,890	200,636
Ammonia Demand	825	674	743			
Ammonia shipping amount (x)	825	674	823	4,120	53,514	
Urea Demand	771	805	604			
Urea shipping amount (y)	771	805	613	648	54,376	
No.10 using demand of day 10				37,142	103,301	172,851
Ammonia Demand	888	829	895			
Ammonia shipping amount (x)	888	539	895	29,870	51,318	
Urea Demand	723	737	628			
Urea shipping amount (y)	723	737	729	7,272	51,983	

Table 4.25 The result of supply chains model network – fixed production capacity of ammonia and urea (Continue)

Supply chain No.X using product demand of	Market (j) (TPD)			Penalty cost ($)	Transportation cost ($)	Profit Z ($)
	N (j1)	S (j2)	NE (j3)			
No.11 using demand of day 11				27,160	98,098	188,037
Ammonia Demand	782	288	891			
Ammonia shipping amount (x)	782	288	1,252	18,592	43,633	
Urea Demand	750	823	497			
Urea shipping amount (y)	750	823	616	8,568	54,466	
No.12 using demand of day 12				12,741	102,469	198,084
Ammonia Demand	836	680	857			
Ammonia shipping amount (x)	836	680	857	5,253	52,620	
Urea Demand	694	667	724			
Urea shipping amount (y)	694	667	828	7,488	49,848	
No.13 using demand of day 13				32,926	106,105	174,263
Ammonia Demand	770	956	822			
Ammonia shipping amount (x)	770	730	822	23,278	53,958	
Urea Demand	798	693	564			
Urea shipping amount (y)	798	693	698	9,648	52,147	
No.14 using demand of day 14				49,612	93,916	169,766
Ammonia Demand	743	791	816			
Ammonia shipping amount (x)	743	763	816	2,884	54,308	
Urea Demand	701	232	607			
Urea shipping amount (y)	701	232	1,256	46,728	39,608	
No.15 using demand of day 15				19,773	98,473	195,048
Ammonia Demand	815	667	642			
Ammonia shipping amount (x)	815	667	840	10,197	53,186	
Urea Demand	528	588	940			
Urea shipping amount (y)	528	588	1,073	9,576	45,287	

Table 4.25 The result of supply chains model network – fixed production capacity of ammonia and urea (Continue)

Supply chain No.X using product demand of	Market (j) (TPD)			Penalty cost ($)	Transportation cost ($)	Profit Z ($)
	N (j1)	S (j2)	NE (j3)			
No.16 using demand of day 16				27,396	98,860	187,038
Ammonia Demand	812	722	1,040			
Ammonia shipping amount (x)	812	470	1,040	25,956	48,449	
Urea Demand	779	643	777			
Urea shipping amount (y)	779	633	777	1,440	50,412	
No.17 using demand of day 17				65,729	98,955	148,610
Ammonia Demand	935	999	771			
Ammonia shipping amount (x)	935	616	771	39,449	53,910	
Urea Demand	653	493	678			
Urea shipping amount (y)	653	493	1,043	26,280	45,045	
No.18 using demand of day 18				28,362	96,140	188,793
Ammonia Demand	776	439	766			
Ammonia shipping amount (x)	776	439	1,107	17,562	47,129	
Urea Demand	676	644	719			
Urea shipping amount (y)	676	644	869	10,800	49,010	
No.19 using demand of day 19				30,101	98,685	184,509
Ammonia Demand	997	375	743			
Ammonia shipping amount (x)	997	375	950	10,661	49,175	
Urea Demand	701	648	570			
Urea shipping amount (y)	701	648	840	19,440	49,509	
No.20 using demand of day 20				10,442	106,476	196,376
Ammonia Demand	751	815	842			
Ammonia shipping amount (x)	751	729	842	8,858	53,628	
Urea Demand	588	876	736			
Urea shipping amount (y)	588	865	736	1,584	52,849	

Table 4.25 The result of supply chains model network – fixed production capacity of ammonia and urea (Continue)

Supply chain No.X using product demand of	Market (j) (TPD) N (j1)	S (j2)	NE (j3)	Penalty cost ($)	Transportation cost ($)	Profit Z ($)
No.21 using demand of day 21				40,417	96,922	175,955
Ammonia Demand	932	625	868			
Ammonia shipping amount (x)	932	578	868	10,609	51,624	
Urea Demand	679	486	610			
Urea shipping amount (y)	679	486	1,024	29,808	45,298	
No.22 using demand of day 22				36,211	97,938	179,145
Ammonia Demand	887	578	783			
Ammonia shipping amount (x)	887	578	857	3,811	52,230	
Urea Demand	613	548	578			
Urea shipping amount (y)	613	548	1,028	32,400	45,708	
No.23 using demand of day 23				17,713	100,924	194,657
Ammonia Demand	864	633	904			
Ammonia shipping amount (x)	864	554	904	8,137	51,288	
Urea Demand	731	633	692			
Urea shipping amount (y)	731	633	825	9,576	49,637	
No.24 using demand of day 24				40,474	90,436	182,384
Ammonia Demand	612	599	827			
Ammonia shipping amount (x)	612	599	1,111	14,626	48,289	
Urea Demand	674	357	799			
Urea shipping amount (y)	674	357	1,158	25,848	42,147	
No.25 using demand of day 25				63,378	94,504	155,412
Ammonia Demand	955	844	721			
Ammonia shipping amount (x)	955	646	721	20,394	54,947	
Urea Demand	605	295	692			
Urea shipping amount (y)	605	295	1,289	42,984	39,557	

Table 4.25 The result of supply chains model network – fixed production capacity of ammonia and urea (Continue)

Supply chain No.X	Market (j)			Penalty	Transportation	Profit Z
using product demand of	N (j1)	S (j2)	NE (j3)	cost ($)	cost ($)	($)
No.26 using demand of day 26				32,072	94,403	186,819
Ammonia Demand	913	509	908			
Ammonia shipping amount (x)	913	501	908	824	50,818	
Urea Demand	766	355	634			
Urea shipping amount (y)	766	355	1068	31,248	43,586	
No.27 using demand of day 27				39,609	94,236	179,450
Ammonia Demand	627	610	822			
Ammonia shipping amount (x)	627	610	1,085	13,545	48,793	
Urea Demand	769	431	627			
Urea shipping amount (y)	769	431	989	26,064	45,443	
No.28 using demand of day 28				38,136	95,368	179,791
Ammonia Demand	726	677	686			
Ammonia shipping amount (x)	726	677	919	12,000	51,986	
Urea Demand	830	303	693			
Urea shipping amount (y)	830	303	1,056	26,136	43,382	
No.29 using demand of day 29				41,669	94,427	177,198
Ammonia Demand	690	772	871			
Ammonia shipping amount (x)	690	761	871	1,133	53,404	
Urea Demand	485	438	703			
Urea shipping amount (y)	485	438	1,266	40,536	41,023	
No.30 using demand of day 30				23,386	104,211	185,697
Ammonia Demand	580	756	901			
Ammonia shipping amount (x)	580	756	986	4,378	51,509	
Urea Demand	716	904	701			
Urea shipping amount (y)	716	772	701	19,008	52,703	

Table 4.25 The result of supply chains model network – fixed production capacity of ammonia and urea (Continue)

Supply chain No.X using product demand of	Market (j)			Penalty cost ($)	Transportation cost ($)	Profit Z ($)
	N (j1)	S (j2)	NE (j3)			
Deterministic using average demand				21,488	100,521	191,286
Ammonia Demand	813	679	814			
Ammonia shipping amount (x)	813	679	830	824	53,439	
Urea Demand	673	565	664			
Urea shipping amount (y)	673	565	951	20,664	47,082	

* The amounts of transportation are assumed to be sold all of product in day (not accumulate)

From Table 4.25, The optimal ammonia shipping amount (x) and urea shipping amount (y) are represented for 30 days. There are 30 supply chains both ammonia and urea. The products shipping amount both ammonia and urea (x and y) that are transported greater than demand of the market (j) or oversupply product will be sold with cheaper selling price about 25% of product selling price. The products which are transported lower than demand of the market (j) or lacked product will have penalty cost about 50% of product selling price. The transportation cost is from the distance between plant and market and amount of product which transported to the market. The distance between plant and markets N(j1), S(j2), and NE(j3) are assumed as 531, 684, 208 miles, respectively. The transportation cost is 0.05 $/tons/miles as shown in the table 4.24. These conditions are made for programming optimization. In this part, 6.8 Investigation on Optimization of Market Demand (with Fixed Production Capacity of Ammonia and Urea), The capacity of ammonia and urea are fixed with 2,322 and 2,189 TPD, respectively. These productions capacities are from amount of natural gas feed stock of 1,930 TPD and the correlation between ammonia and urea production capacity.

For deterministic optimization method, the average demand of the market in 30 days are considered for optimal ammonia and urea transportation for maximizing profit. The average of ammonia demands in 3 markets N(j1), S(j2), and NE(j3) are 813, 679, and 814 TPD, respectively. The average of urea demands in 3 markets N(j1), S(j2), and NE(j3) are 673, 565, and 664 TPD, respectively. The optimization programming for deterministic method were carried out to determine the appropriate amount of ammonia and urea transported to each market that make the highest profit for 30 days. The average demands are representative for the data set to program assessment. The optimal value of ammonia and urea transportation are used for products transportation further all 30 days. The summation of profit in 30 days for the deterministic method is $ 4,417,229 as shown in table 4.26. From deterministic method, profit and transported products amount were limited to deterministic values of all economic parameters represents only current average demand of the markets, its do not represent the range of profit. However, stochastic analysis method as a probabilistic approach can provide more accurate and dependable result considering effect of uncertainty demand of market according to randomness in input variable.

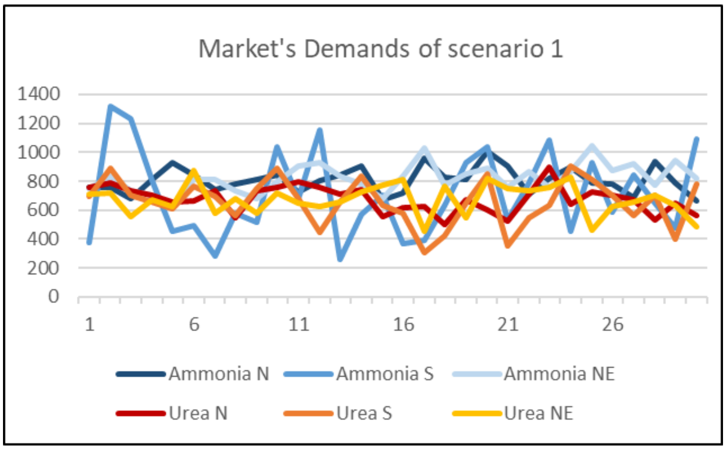
For stochastic optimization method, the demands of market in 30 days are considered for optimal the ammonia and urea transportation amount for maximizing profit as the previous part. To deal with uncertainties occurred due to randomness, stochastic optimization method was conducted. The demands of produces each day were considered for programming optimization. In stochastic method, there are 30 supply chains with 30 optimal values of ammonia and urea transporting amount for each day in 30 days. These values of each supply chains are used for products transportation all 30 days and assessment summation profit of each supply chains. The ammonia and urea transportation amount and summation profit of each supply chains are represented in table 4.26. The difference of profit in 30 days of each supply chains are from differential amount of products transportation and the transported products which not satisfy market's demand of each day. From supply chain No.12 and No.13 give the optimal value for all 30 days which higher profit compare with other supply chains.

Table 4.26 The optimal value of ammonia and urea transportation for 30 days (historical)

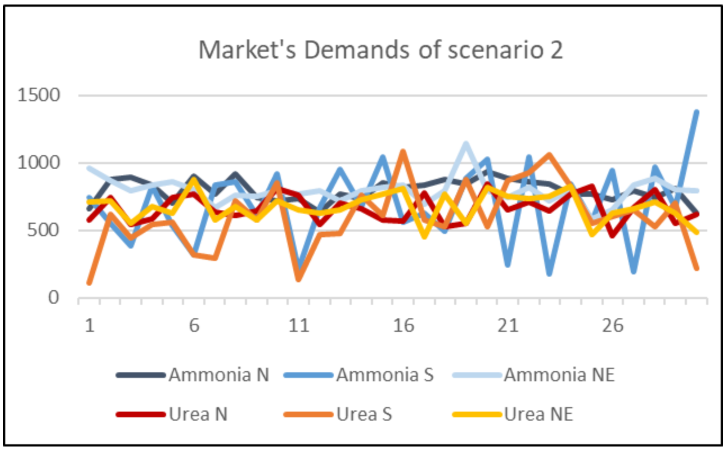
Supply chain No.	Ammonia (TPD)			Urea (TPD)			
	N(j1)	S(j2)	NE(j3)	N(j1)	S(j2)	NE(j3)	ΣProfit in 30 days ($)
1	677	762	883	687	581	921	4,261,121
2	834	687	801	478	632	1,079	3,612,559
3	878	38	1,406	575	366	1,248	1,272,161
4	777	700	845	614	513	1,062	4,024,657
5	828	735	759	621	575	993	4,163,854
6	987	551	784	712	494	983	3,967,235
7	790	711	821	640	702	847	4,482,196
8	911	663	748	623	475	1,091	3,803,846
9	825	674	823	771	805	613	4,396,103
10	888	539	895	723	737	729	4,491,968
11	782	288	1,252	750	823	616	3,194,335
12	836	629	857	694	667	828	4,619,053
13	770	730	822	798	693	698	4,622,681
14	743	763	816	701	232	1,256	2,920,295
15	815	667	840	528	588	1,073	3,811,853
16	812	470	1,040	779	633	777	4,194,749
17	935	616	771	653	493	1,043	3,961,130
18	776	439	1,107	676	644	869	3,905,657
19	997	375	950	701	648	840	3,924,620
20	751	729	842	588	865	736	4,168,108
21	932	522	868	679	486	1,024	3,939,965
22	887	578	857	613	548	1,028	4,032,835
23	864	554	904	731	633	825	4,497,610
24	612	599	1,111	674	357	1,158	2,901,301
25	955	646	721	605	295	1,289	2,750,758
26	913	501	908	766	355	1,068	3,470,858
27	627	610	1,085	769	431	989	3,476,222
28	726	677	919	830	303	1,056	3,349,787
29	690	761	871	485	438	1,266	2,884,286
30	580	756	986	716	772	701	4,064,320
Deterministic	813	679	830	673	565	951	4,417,229

The uncertainty demands of ammonia and urea for 30 days evaluated in previous part are assumed as historical data for the optimal programming. After optimal value of ammonia and urea transported for each market are estimated, the validation part is essential for reach more precise of optimal programming.

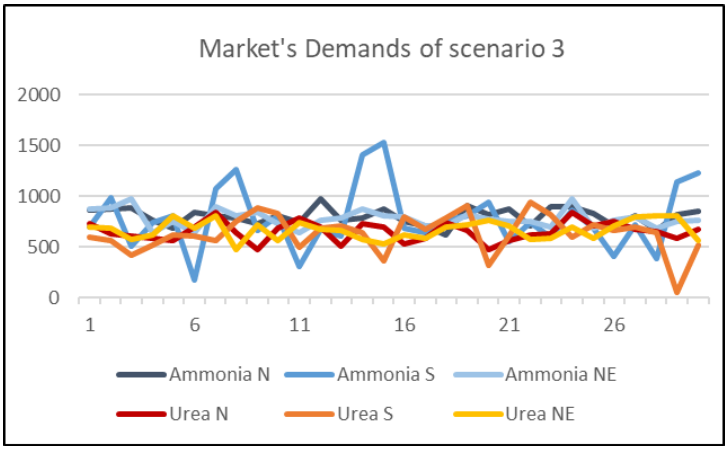
The validation part is created from new set of uncertainty demands of ammonia and urea by using the same statistic values of mean and standard deviation as the historical data as shown in figure 4.19. The mean of ammonia demand of 3 markets N(j1), S(j2), and NE(j3) are 800, 700, and 800 TPD and the standard deviation are 100, 300, and 100, respectively. The mean of urea demand of 3 markets N(j1), S(j2), and NE(j3) are 650, 500, and 650 TPD and the standard deviation are 100, 200, and 100, respectively. In validation part, the new set of market's demands are divided into 12 scenarios, 30 days per scenarios (all 360 days of various data).



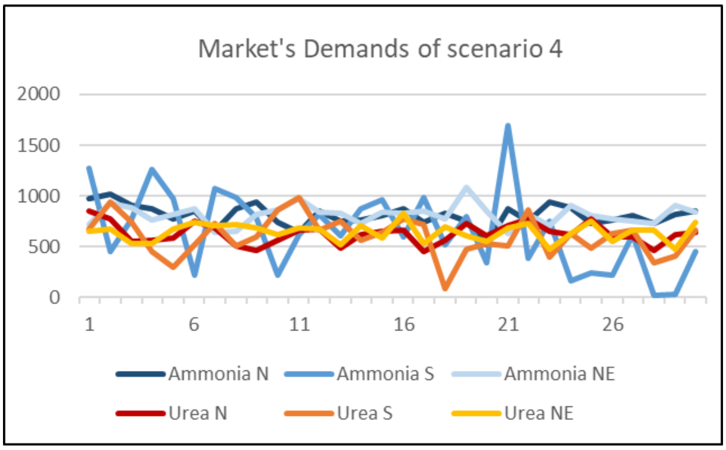
Supply chain	ΣProfit in 30 days ($)
No.12	4,434,405
No.13	4,374,110
Deterministic	4,029,897



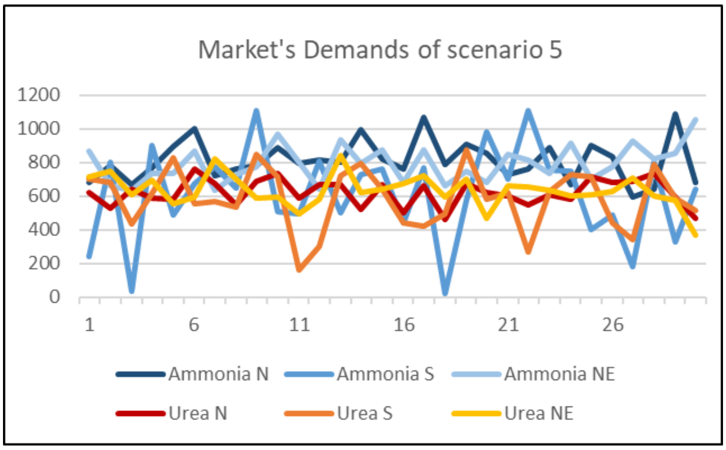
Supply chain	ΣProfit in 30 days ($)
No.12	4,159,928
No.13	4,258,861
Deterministic	3,953,018



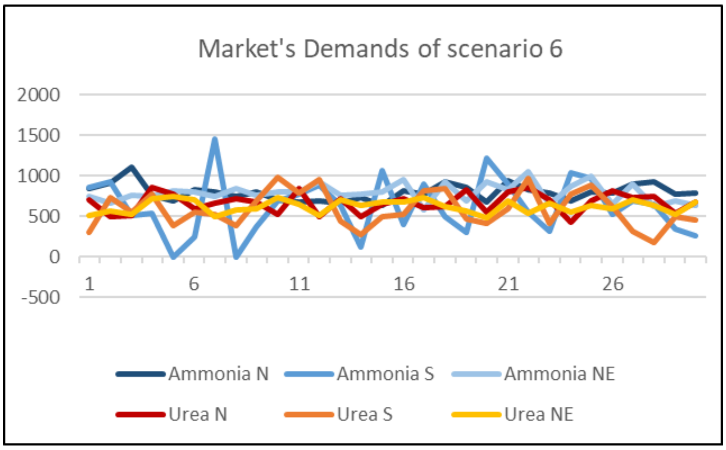
Supply chain	ΣProfit in 30 days ($)
No.12	4,349,241
No.13	4,358,452
Deterministic	4,065,812



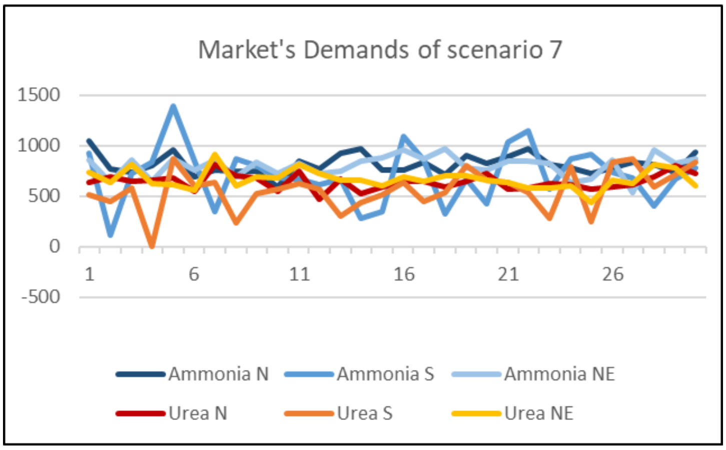
Supply chain	ΣProfit in 30 days ($)
No.12	4,156,064
No.13	4,116,949
Deterministic	3,861,718



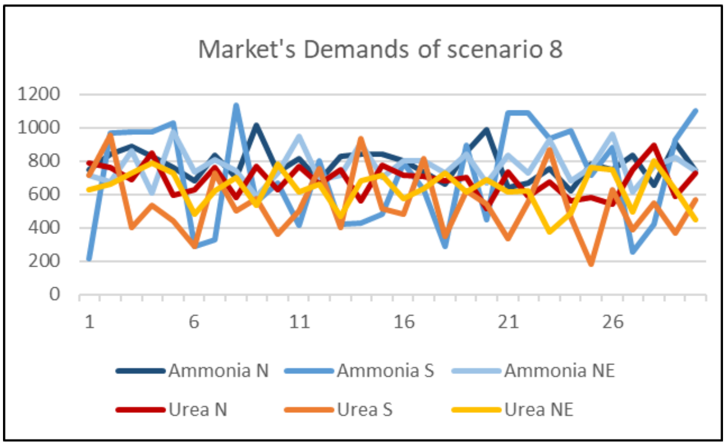
Supply chain	ΣProfit in 30 days ($)
No.12	4,412,096
No.13	4,344,521
Deterministic	4,176,433



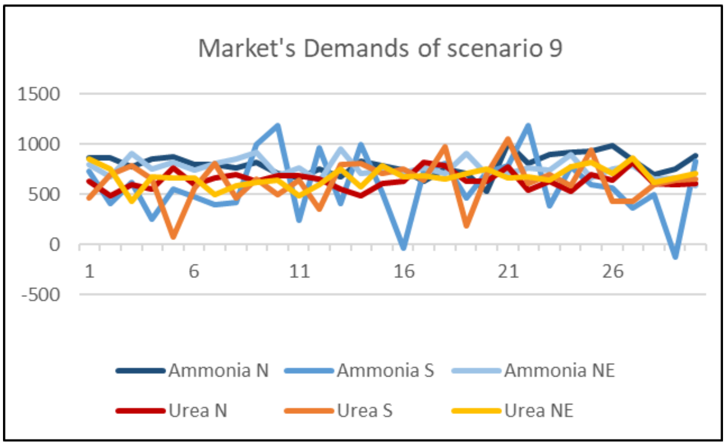
Supply chain	ΣProfit in 30 days ($)
No.12	3,956,282
No.13	4,078,928
Deterministic	3,723,418



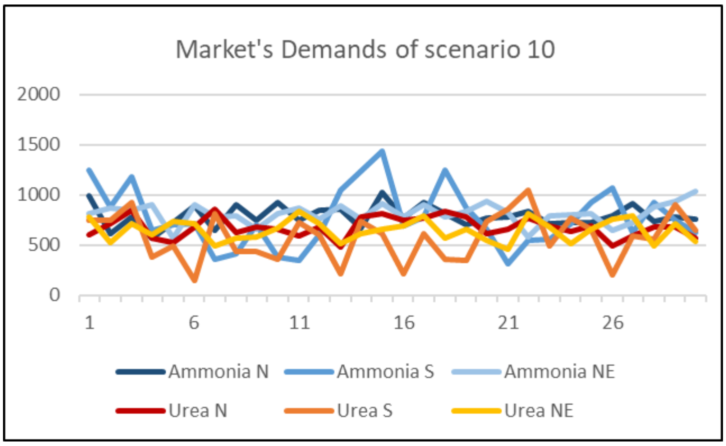
Supply chain	ΣProfit in 30 days ($)
No.12	4,401,392
No.13	4,326,011
Deterministic	4,247,703



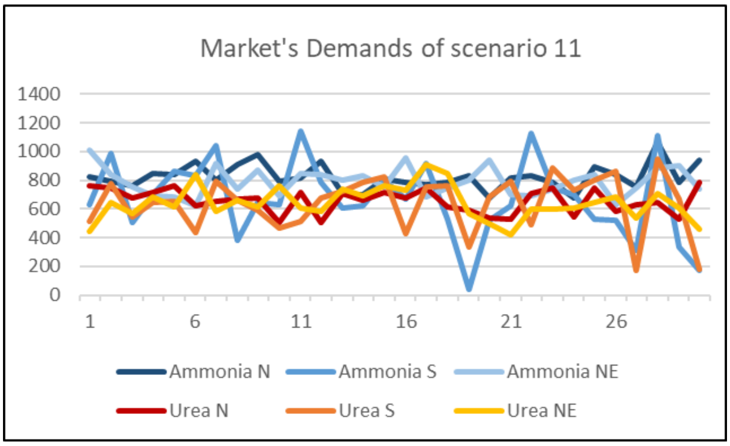
Supply chain	ΣProfit in 30 days ($)
No.12	4,096,421
No.13	4,191,370
Deterministic	3,958,085



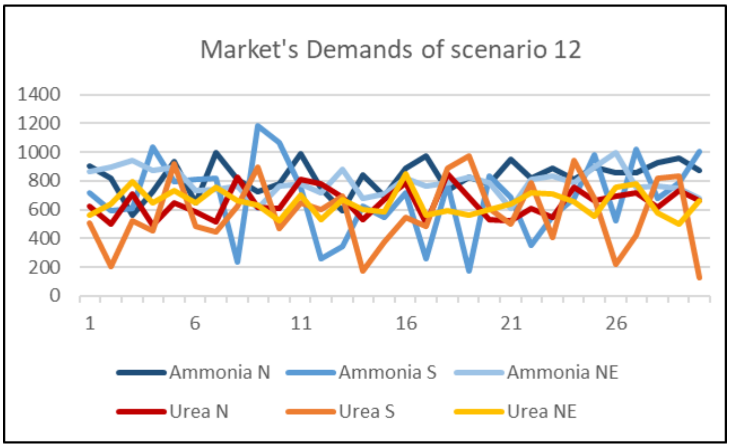
Supply chain	ΣProfit in 30 days ($)
No.12	4,388,921
No.13	4,287,785
Deterministic	4,057,015



Supply chain	ΣProfit in 30 days ($)
No.12	4,104,520
No.13	4,169,793
Deterministic	3,852,227

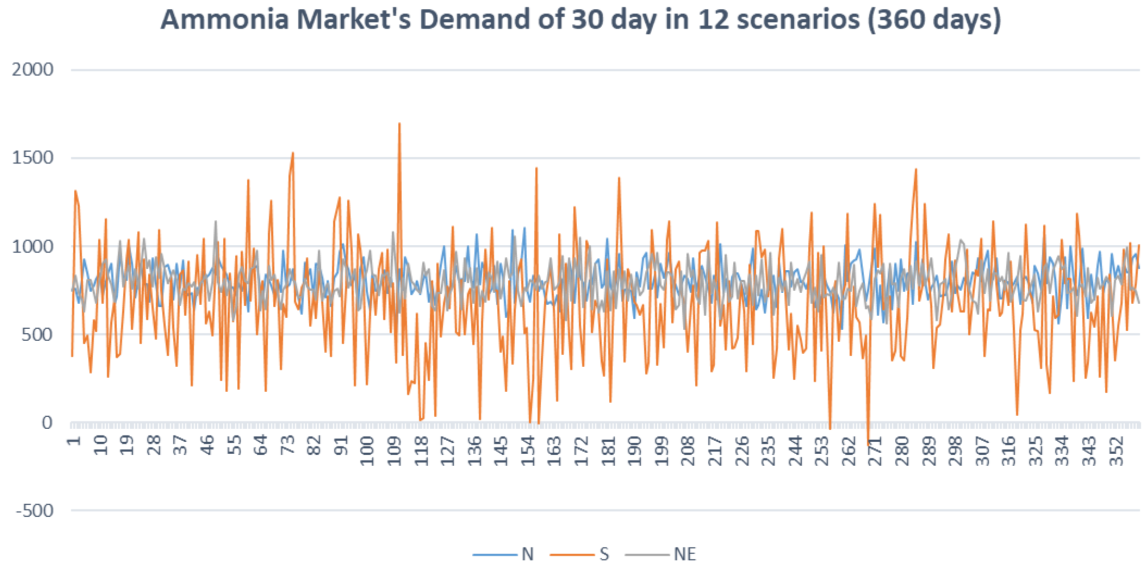


Supply chain	ΣProfit in 30 days ($)
No.12	4,412,883
No.13	4,350,937
Deterministic	4,055,404

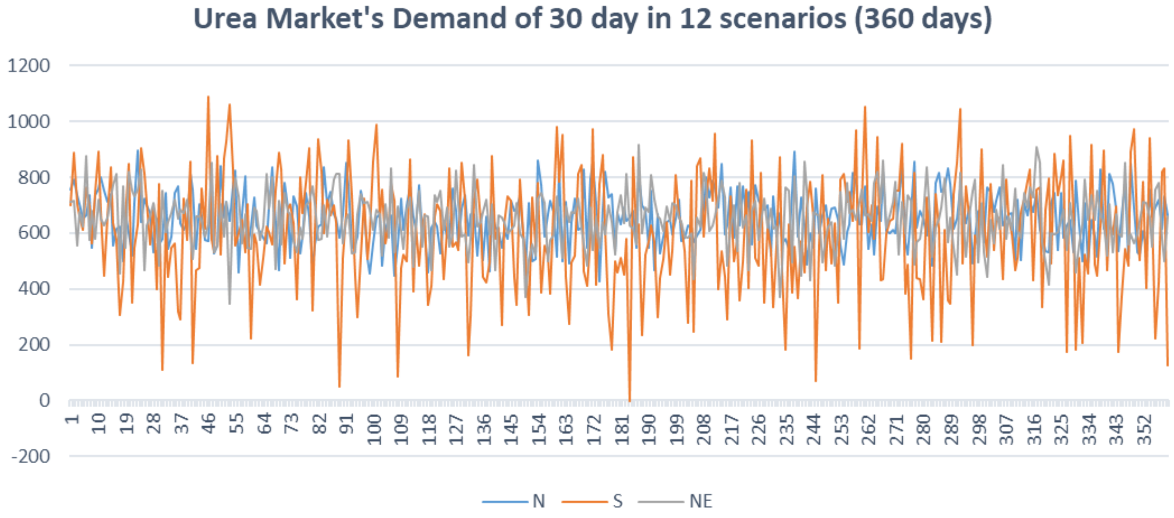


Supply chain	ΣProfit in 30 days ($)
No.12	4,193,688
No.13	4,184,211
Deterministic	3,987,759

Figure 4.18 The results from validation part of 12 scenarios – fixed production rate.



	N	S	NE
Mean	800	700	800
SD	100	300	100



	N	S	NE
Mean	650	500	650
SD	100	200	100

Figure 4.19 The new set of uncertainty market's demands of ammonia and urea in 12 scenarios, 30 days per scenarios (360 days) for validation part.

The optimized value of both ammonia and urea transportation of supply chain No.12 and No.13 in previous part are validated with new set of market's demands in 12 scenarios, 30 days per scenario. The summation of profit in 30 days of each scenarios were converted to profit cumulative frequency curve for evaluated the probability and upper limit profit of each supply chains as shown in figure 4.20

According to the profit cumulative frequency curve in figure 4.20a, at the targeted profit of $ 4,000,000, the stochastic supply chain No.12 has 8.33 % risk giving profit less than targeted profit and its upper limit of profit is $ 4,435,000. For figure 4.20b, the stochastic supply chain No.13 has 0 % risk giving profit less than targeted profit and its upper limit of profit is $ 4,375,000 while the deterministic supply chain has higher risk of 50 % giving profit less than targeted profit and its upper limit of profit is $ 4,250,000 lower than stochastic supply chains.

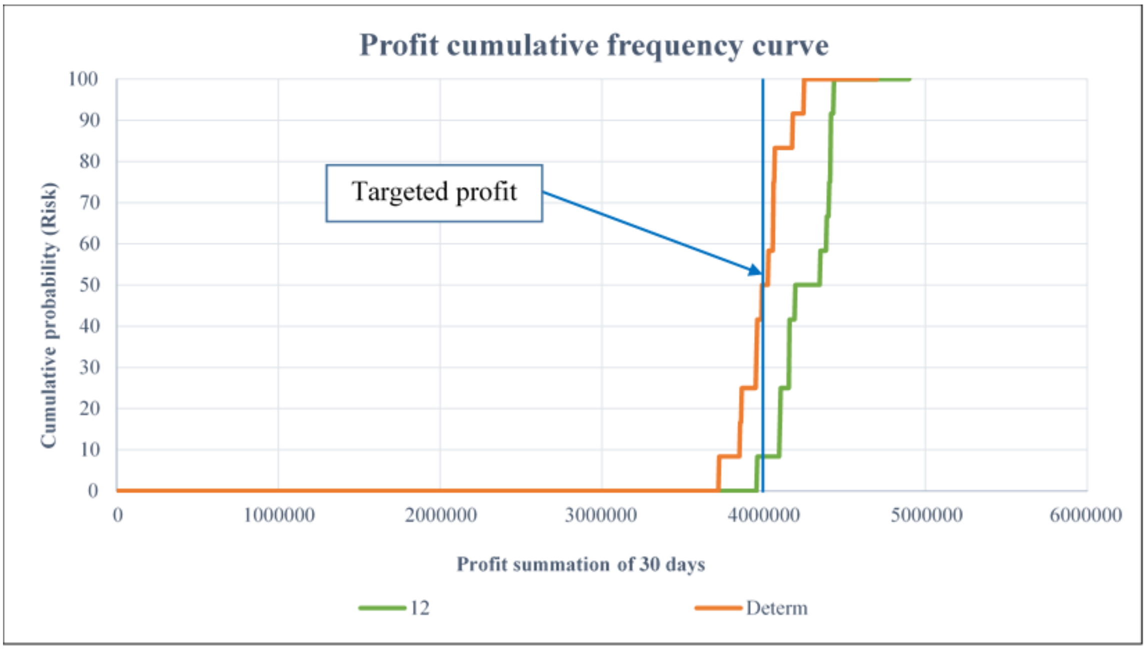


Figure 4.20a profit cumulative frequency curve for supply chain No.12 and deterministic one.

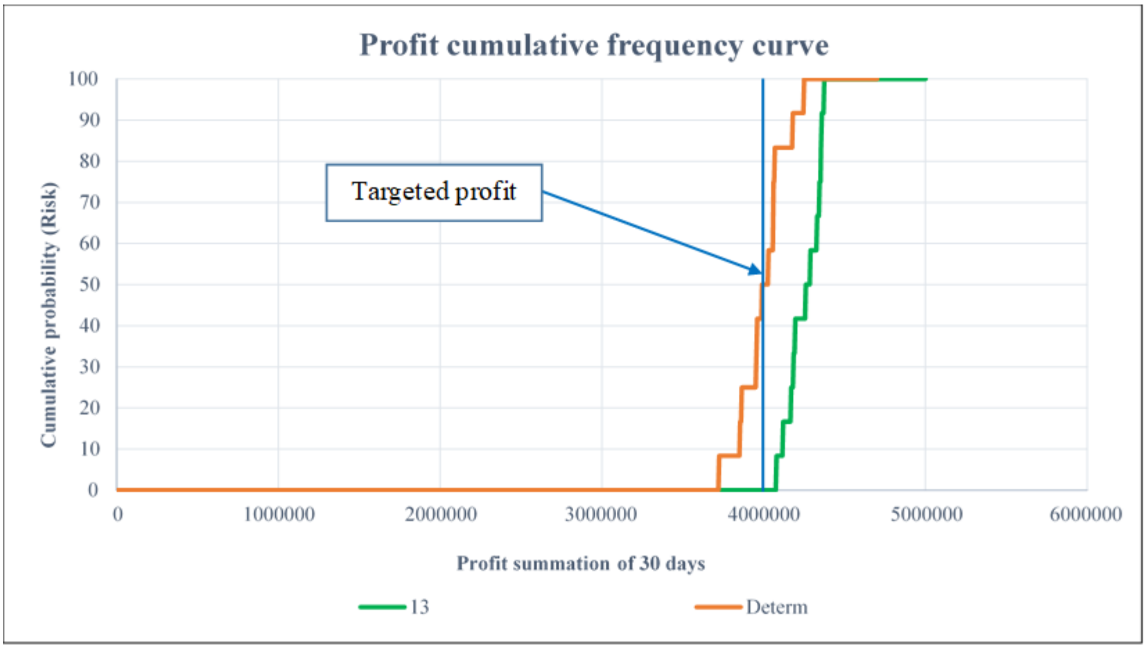


Figure 4.20b profit cumulative frequency curve for supply chain No.13 and deterministic one.

4.9 Investigation on Optimization of Market Demand (with Varied Production Capacity of Ammonia and Urea)

The optimization programming from part 4.8 is assumed to be fixed production capacity of ammonia and urea at 2,322 and 2,189 TPD, respectively. The penalty cost from opportunity loss and surplus production cost are presented from amount of products transportation that satisfy demanding of the markets. To improve the optimization programing, the ammonia/urea production capacity and urea production cost are adjusted to appropriate demand of markets. The mathematical model for designing the network is expressed as show below.

$$\text{Max } Z = \text{Price}_{\text{Amm}}*\Sigma_i\Sigma_jX_{ij} + \text{Price}_{\text{Urea}}\Sigma_i\Sigma_jY_{ij} - [\text{Cost1} + \text{Cost2} + \text{Cost3}] \tag{6.1}$$

Subject to constraints,

$$\text{LimCapAmm}_i = \text{AmmIn}_i - \text{AmmFeed}_i \tag{6.8}$$

$$\text{LimCapUrea}_i = 1.4142*\text{AmmFeed}_i - 0.014 \tag{6.9}$$

$$\Sigma_jX_{ij} = \text{LimCapAmm}_i \tag{6.10}$$

$$\Sigma_jY_{ij} = \text{LimCapUrea}_i \tag{6.11}$$

$$\Sigma_iX_j + \Sigma_i\text{PenaltyAmm}_{ij} - \text{PPAmm}_j = \text{LimAmm}_j\ \text{(Demand)} \tag{6.12}$$

$$\Sigma_iY_{ij} + \Sigma_i\text{PenaltyUrea}_{ij} - \text{PPUrea}_j = \text{LimUrea}_j\ \text{(Demand)} \tag{6.13}$$

$$\text{Cost1} = 635233 + \Sigma_i\ \text{LimCapUrea}_i *73.184 - 1.21 \tag{6.14}$$

$$\text{Cost2} = (\ \Sigma_i\Sigma_jX_{ij} + \Sigma_i\Sigma_jY_{ij}\ )*\ \text{transportcost} \tag{6.15}$$

$$\begin{aligned}\text{Cost3} = {} & \Sigma_i\Sigma_j\ \text{PenaltyAmm}_{ij} * \text{PAmmCost} + \Sigma_i\Sigma_j\ \text{PPAmm}_j * \text{PPAmmCost} + \\ & \Sigma_i\Sigma_j\ \text{PenaltyUrea}_{ij} * \text{PUreaCost} + \Sigma_i\Sigma_j\ \text{PPUrea}_j * \text{PPUreaCost}\end{aligned} \tag{6.16}$$

Where

X_{ij} = Ammonia transportation amount (TPD)

Y_{ij} = Urea transportation amount (TPD)

$LimCapAmm_i$ = Ammonia production capacity of plant i in cases (TPD)

$LimCapUrea_i$ = Urea production capacity of plant i in cases (TPD)

$AmmIn_i$ = Maximum ammonia production capacity of plant i in cases (TPD)

$AmmFeed_i$ = Ammonia amount which feed to produce urea (TPD)

$PenaltyAmm_{ij}$ = Ammonia amount which less than demand of market (TPD)

$PenaltyUrea_{ij}$ = Urea amount which less than demand of market (TPD)

$PPAmm_j$ = Ammonia amount which greater than demand of market (TPD)

$PPUrea_j$ = Urea amount which greater than demand of market (TPD)

$LimAmm_j$ (Demand) = Ammonia demand of market j in cases (TPD)

$LimUrea_j$ (Demand) = Urea demand of market j in cases (TPD)

Opportunity loss cost = $\Sigma_i\Sigma_j$ $PenaltyAmm_{ij}$ * PAmmCost ($/day)

Surplus Production cost = $\Sigma_i\Sigma_j$ $PPAmm_j$ * PPAmmCost ($/day)

Cost1 = Ammonia and urea production cost ($/day)

Cost2= Transportation cost ($/day)

Cost3 = Penalty cost ($/day)

The main objective of this model is to maximize profit from sale products. The objective function is expressed into 3 parts; revenue, transportation cost, and penalty cost as shown in equation 6.1. Equation 6.8 and 6.9 are deal with maximum capacity of plant in ammonia product and urea product, respectively. The urea capacity is from correlation between ammonia to urea product. Cost1, Production cost, is from ammonia which produced form natural gas feed 1,930 ton per day and urea production cost from urea utilities expenditure correlation with urea production function. The case study for deterministic and stochastic model for varied urea production can be divided into 30 days. The simple network with 2 echelons; Plant (i) and Market (j) with 2 products (ammonia and urea) is shown in figure 4.22 for varied production capacity.

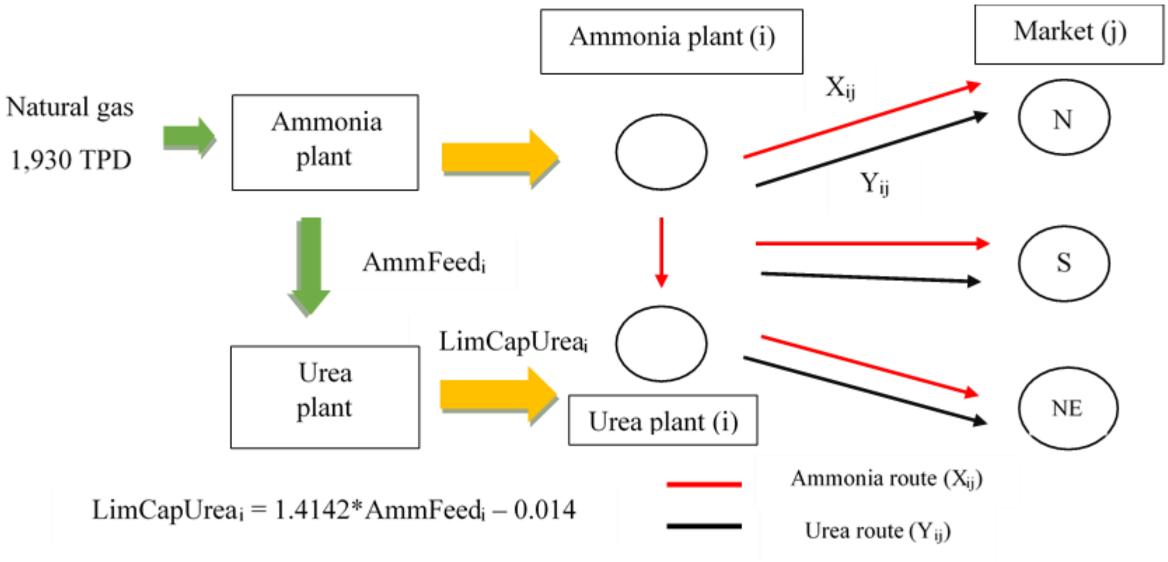


Figure 4.21 The simple network diagram for varied production capacity of ammonia and urea.

Table 4.27 The result of supply chains model network – varied production capacity of ammonia and urea

Supply chain No.X	Market (j) (TPD)			Penalty	Transportation	Profit Z
using product demand of	N (j1)	S (j2)	NE (j3)	cost ($)	cost ($)	($)
No.1 using demand of day 1				27,600	101,575	198,259
Ammonia Demand	677	762	851			
Ammonia shipping amount (x)	677	762	851	0	52,885	
Urea Demand	687	581	634			
Urea shipping amount (y)	687	581	1,017	27,600	48,690	
No.2 using demand of day 2				17,559	107,912	159,275
Ammonia Demand	834	1,262	801			
Ammonia shipping amount (x)	834	1,092	801	17,559	67,803	
Urea Demand	478	632	558			
Urea shipping amount (y)	478	632	558	0	40,109	
No.3 using demand of day 3				110,608	83,180	190,757
Ammonia Demand	878	38	790			
Ammonia shipping amount (x)	878	38	790	0	32,827	
Urea Demand	575	366	634			
Urea shipping amount (y)	575	366	2,170	110,608	50,354	
No.4 using demand of day 4				37,649	99,090	194,607
Ammonia Demand	777	700	773			
Ammonia shipping amount (x)	777	700	773	0	52,609	
Urea Demand	614	513	692			
Urea shipping amount (y)	614	513	1,215	37,649	46,481	
No.5 using demand of day 5				22,000	46,673	197,583
Ammonia Demand	828	758	759			
Ammonia shipping amount (x)	828	758	759	0	55,801	
Urea Demand	621	575	706			
Urea shipping amount (y)	621	575	1,012	22,000	46,673	

Table 4.27 The result of supply chains model network – varied production capacity of ammonia and urea (continue)

Supply chain No.X using product demand of	Market (j) (TPD)			Penalty cost ($)	Transportation cost ($)	Profit Z ($)
	N (j1)	S (j2)	NE (j3)			
No.6 using demand of day 6				15,657	101,432	198,806
Ammonia Demand	987	637	784			
Ammonia shipping amount (x)	987	637	784	0	56,144	
Urea Demand	712	494	695			
Urea shipping amount (y)	712	494	912	15,657	45,288	
No.7 using demand of day 7				14,066	104,256	207,939
Ammonia Demand	790	711	801			
Ammonia shipping amount (x)	790	711	801	0	53,621	
Urea Demand	640	702	731			
Urea shipping amount (y)	640	702	926	14,066	50,635	
No.8 using demand of day 8				44,216	99,538	179,378
Ammonia Demand	911	675	748			
Ammonia shipping amount (x)	911	675	748	0	55,051	
Urea Demand	623	475	511			
Urea shipping amount (y)	623	475	1,125	44,216	44,487	
No.9 using demand of day 9				12,471	108,766	210,891
Ammonia Demand	825	674	743			
Ammonia shipping amount (x)	825	674	743	0	52,682	
Urea Demand	771	805	604			
Urea shipping amount (y)	771	805	777	12,471	56,084	
No.10 using demand of day 10				18,794	105,928	189,067
Ammonia Demand	888	829	895			
Ammonia shipping amount (x)	888	647	895	18,794	54,996	
Urea Demand	723	737	628			
Urea shipping amount (y)	723	737	628	0	50,932	

Table 4.27 The result of the supply chains model network – varied production capacity of ammonia and urea (continue)

Supply chain No.X	Market (j) (TPD)			Penalty	Transportation	Profit Z
using product demand of	N (j1)	S (j2)	NE (j3)	cost ($)	cost ($)	($)
No.11 using demand of day 11				49,004	100,184	210,420
Ammonia Demand	782	288	891			
Ammonia shipping amount (x)	782	288	891	0	39,878	
Urea Demand	750	823	497			
Urea shipping amount (y)	750	823	1,178	49,004	60,306	
No.12 using demand of day 12				5,973	103,994	209,351
Ammonia Demand	836	680	857			
Ammonia shipping amount (x)	836	680	857	0	54,365	
Urea Demand	694	667	724			
Urea shipping amount (y)	694	667	807	5,973	49,629	
No.13 using demand of day 13				9,798	109,187	192,521
Ammonia Demand	770	956	822			
Ammonia shipping amount (x)	770	861	822	9,798	58,434	
Urea Demand	798	693	564			
Urea shipping amount (y)	798	693	564	0	50,753	
No.14 using demand of day 14				47,555	94,993	179,019
Ammonia Demand	743	791	816			
Ammonia shipping amount (x)	743	791	816	0	55,265	
Urea Demand	701	232	607			
Urea shipping amount (y)	701	232	1,267	47,555	39,728	
No.15 using demand of day 15				33,414	99,857	210,396
Ammonia Demand	815	667	642			
Ammonia shipping amount (x)	815	667	642	0	51,126	
Urea Demand	528	588	940			
Urea shipping amount (y)	528	588	1,404	33,414	48,731	

Table 4.27 The result of the supply chains model network – varied production capacity of ammonia and urea (continue)

Supply chain No.X using product demand of	Market (j) (TPD)			Penalty cost ($)	Transportation cost ($)	Profit Z ($)
	N (j1)	S (j2)	NE (j3)			
No.16 using demand of day 16				22,964	100,196	198,304
Ammonia Demand	812	722	1040			
Ammonia shipping amount (x)	812	499	1040	22,964	49,442	
Urea Demand	779	643	777			
Urea shipping amount (y)	779	643	777	0	50,754	
No.17 using demand of day 17				9,145	105,221	181,167
Ammonia Demand	935	999	771			
Ammonia shipping amount (x)	935	910	771	9,145	63,972	
Urea Demand	653	493	678			
Urea shipping amount (y)	653	493	678	0	41,249	
No.18 using demand of day 18				49,199	98,140	210,313
Ammonia Demand	776	439	766			
Ammonia shipping amount (x)	776	439	766	0	43,583	
Urea Demand	676	644	719			
Urea shipping amount (y)	676	644	1,402	49,199	54,557	
No.19 using demand of day 19				44,195	100,107	200,246
Ammonia Demand	997	375	743			
Ammonia shipping amount (x)	997	375	743	0	47,023	
Urea Demand	701	648	570			
Urea shipping amount (y)	701	648	1,184	44,195	53,085	
No.20 using demand of day 20				5,939	107,822	207,773
Ammonia Demand	751	815	842			
Ammonia shipping amount (x)	751	757	842	5,939	54,597	
Urea Demand	588	876	736			
Urea shipping amount (y)	588	876	736	0	53,225	

Table 4.27 The result of the supply chains model network – varied production capacity of ammonia and urea (continue)

Supply chain No.X using product demand of	Market (j) (TPD)			Penalty cost ($)	Transportation cost ($)	Profit Z ($)
	N (j1)	S (j2)	NE (j3)			
No.21 using demand of day 21				22,998	99,461	191,773
Ammonia Demand	932	625	868			
Ammonia shipping amount (x)	932	625	868	0	55,147	
Urea Demand	679	486	610			
Urea shipping amount (y)	679	486	929	22,998	44,315	
No.22 using demand of day 22				43,613	98,788	189,141
Ammonia Demand	887	578	783			
Ammonia shipping amount (x)	887	578	783	0	51,461	
Urea Demand	613	548	578			
Urea shipping amount (y)	613	548	1,184	43,613	47,328	
No.23 using demand of day 23				5,210	102,995	208,374
Ammonia Demand	864	633	904			
Ammonia shipping amount (x)	864	633	904	0	53,989	
Urea Demand	731	633	692			
Urea shipping amount (y)	731	633	764	5,210	49,006	
No.24 using demand of day 24				58,443	92,191	201,444
Ammonia Demand	612	599	827			
Ammonia shipping amount (x)	612	599	827	0	45,335	
Urea Demand	674	357	799			
Urea shipping amount (y)	674	357	1,611	58,443	46,856	
No.25 using demand of day 25				26,501	98,895	179,546
Ammonia Demand	955	844	721			
Ammonia shipping amount (x)	955	844	721	0	61,718	
Urea Demand	605	295	692			
Urea shipping amount (y)	605	295	1,060	26,501	37,176	

Table 4.27 The result of the supply chains model network – varied production capacity of ammonia and urea (continue)

Supply chain No.X using product demand of	Market (j) (TPD)			Penalty cost ($)	Transportation cost ($)	Profit Z ($)
	N (j1)	S (j2)	NE (j3)			
No.26 using demand of day 26				34,111	95,090	194,321
Ammonia Demand	913	509	908			
Ammonia shipping amount (x)	913	509	908	0	51,091	
Urea Demand	766	355	634			
Urea shipping amount (y)	766	355	1,108	34,111	43,999	
No.27 using demand of day 27				56,521	95,900	197,604
Ammonia Demand	627	610	822			
Ammonia shipping amount (x)	627	610	822	0	46,058	
Urea Demand	769	431	627			
Urea shipping amount (y)	769	431	1,412	56,521	49,842	
No.28 using demand of day 28				53,538	96,903	196,650
Ammonia Demand	726	677	686			
Ammonia shipping amount (x)	726	677	686	0	49,563	
Urea Demand	830	303	693			
Urea shipping amount (y)	830	303	1,437	53,538	47,340	
No.29 using demand of day 29				43,094	95,172	184,963
Ammonia Demand	690	772	871			
Ammonia shipping amount (x)	690	772	871	0	53,780	
Urea Demand	485	438	703			
Urea shipping amount (y)	485	438	1,302	43,094	41,392	
No.30 using demand of day 30				2,829	108,250	221,539
Ammonia Demand	580	756	901			
Ammonia shipping amount (x)	580	756	901	0	50,625	
Urea Demand	716	904	701			
Urea shipping amount (y)	716	904	740	2,829	57,626	

Table 4.27 The result of the supply chains model network – varied production capacity of ammonia and urea (continue)

Supply chain No.X	Market (j) (TPD)			Penalty	Transportation	Profit Z
using product demand of	N (j1)	S (j2)	NE (j3)	cost ($)	cost ($)	($)
Deterministic using average demand				25,971	101,121	188,795
Ammonia Demand	813	679	814			
Ammonia shipping amount (x)	813	679	814	0	53,273	
Urea Demand	673	565	664			
Urea shipping amount (y)	673	565	1,025	25,971	47,848	

From Table 4.27, The optimal ammonia shipping amount (x) and urea shipping amount (y) are represented for 30 days. There are 30 supply chains both ammonia and urea. The products shipping amount both ammonia and urea (x and y) which are transported greater than demand of the market (j) or oversupply will be sold with cheaper selling price about 25% of product selling price. The products which are transported lower than demand of the market (j) or lacked product will have penalty cost about 50% of product selling price. The transportation cost is from the distance between plant and market and amount of product which transported to the market. The distance between plant and markets N(j1), S(j2), and NE(j3) are assumed as 531, 684, 208 miles, respectively. The transportation cost is 0.05$/tons/miles as shown in table 4.24. These conditions are made for programming optimization. In this part, 6.9 Investigation on Optimization of Market Demand (with Varied Production Capacity of Ammonia and Urea), The capacity of ammonia has maximum with 3,870 TPD from natural gas feedstock of 1,930 TPD. The correlation between ammonia feed to urea production capacity is $LimCapUrea_i = 1.4142*AmmFeed_i - 0.014$ as shown in equation (6.9). The adjustable of product capacity both ammonia and urea can increase optimal values in terms of products transportation meet the specification of market’s demand and can increasing profit of plant.

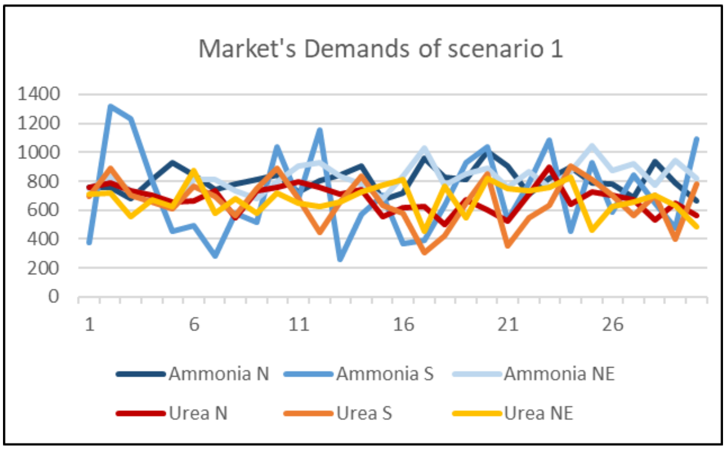
For deterministic optimization method, the average demand of market in 30 days are considered for optimal ammonia and urea transportation for maximizing profit. The average of ammonia demands in 3 markets N(j1), S(j2), NE(j3) are 813, 679, and 814 TPD, respectively. The average of urea demands in 3 markets N(j1), S(j2) and NE(j3) are 673, 565, and 664 TPD, respectively. The demands and average of each market are represented in Table 4.27. The summation of profit in 30 days for deterministic optimization method is $ 4,610,028 as shown in table 4.28.

Table 4.28 The optimal value of Ammonia and Urea for 30 days – varied ammonia and urea production rate (historical)

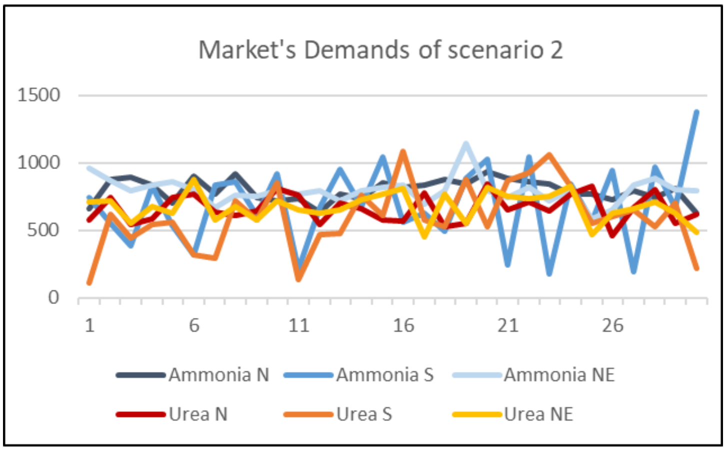
Supply chain	Ammonia			Urea			
No.	N(j1)	S(j2)	NE(j3)	N(j1)	S(j2)	NE(j3)	ΣProfit in 30 days
1	677	762	851	687	581	1,017	4,474,415
2	834	1,092	801	478	632	558	2,582,525
3	878	38	790	575	366	2,170	2,075,029
4	777	700	773	614	513	1,215	4,155,399
5	828	758	759	621	575	1,012	4,398,067
6	987	637	784	712	494	912	4,303,131
7	790	711	801	640	702	926	4,683,721
8	911	675	748	623	475	1125	4,017,636
9	825	674	743	771	805	777	4,850,215
10	888	647	895	723	737	628	4,581,932
11	782	288	891	750	823	1,178	4,246,215
12	836	680	857	694	667	807	4,863,511
13	770	861	822	798	693	564	4,141,595
14	743	791	816	701	232	1,267	3,099,781
15	815	667	642	528	588	1,404	3,564,999
16	812	499	1040	779	643	777	4,473,759
17	935	910	771	653	493	678	3,843,946
18	776	439	766	676	644	1,402	4,293,763
19	997	375	743	701	648	1,184	4,074,405
20	751	757	842	588	876	736	4,360,092
21	932	625	868	679	486	929	4,319,067
22	887	578	783	613	548	1,184	4,179,456
23	864	633	904	731	633	764	4,806,255
24	612	599	827	674	357	1,611	3,360,171
25	955	844	721	605	295	1,060	2,880,120
26	913	509	908	766	355	1,108	3,690,985
27	627	610	822	769	431	1,412	3,898,627
28	726	677	686	830	303	1,437	3,273,245
29	690	772	871	485	438	1,302	3,080,003
30	580	756	901	716	904	740	4,388,508
Deterministic	813	679	814	673	565	1,025	4,610,028

For stochastic optimization method, the demands of the market in 30 days are considered for optimal ammonia and urea transportation amount for maximizing profit as the previous part. To deal with uncertainties occurred due to randomness, stochastic optimization method was conducted. The demands of produces each day were considered for programming optimization. In stochastic method, there are 30 supply chains with 30 optimal values of ammonia and urea transporting amount for each day in 30 days. These values of each supply chains are used for products transportation all 30 days and assessment summation profit of each supply chains. The ammonia and urea transportation amount and profit summation of each supply chains are represented in table 4.28. The difference of profit in 30 days of each supply chains are from differential amount of products transportation and the transported products which not satisfy market's demand of each day. From supply chain No.9, No 12, and No.23 give the optimal values for all 30 days which higher profit compare with other supply chains.

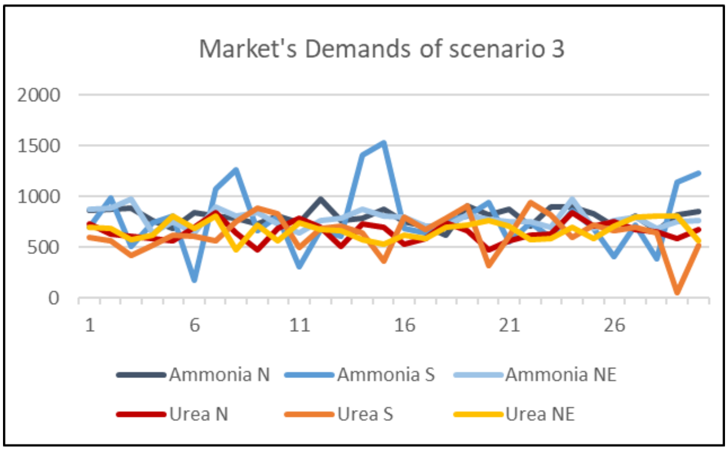
The validation part is created from new set of uncertainty demands of ammonia and urea by using the same statistic value of mean and standard deviation as the historical data as shown in the figure 4.19. The mean of ammonia demand of 3 markets N(j1), S(j2), and NE (j3) are 800, 700, and 800 TPD and the standard deviation are 100, 300, and 100, respectively. The mean of urea demand of 3 markets N(j1), S(j2), and NE(j3) are 650, 500, and 650 TPD and the standard deviation are 100, 200, and 100, respectively. In validation part, the new set of market's demands are divided into 12 scenarios, 30 days per scenarios (all 360 days of various data) as same as part 6.8.



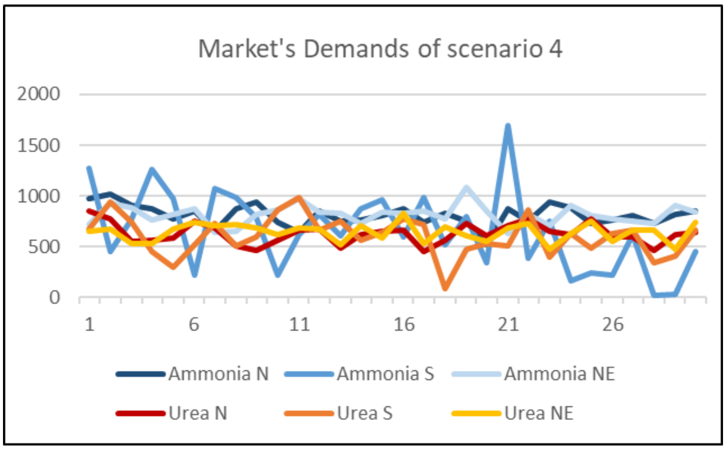
Supply chain	ΣProfit in 30 days ($)
No.9	4,752,336
No.12	4,636,669
No.23	4,544,178
Deterministic	4,217,781



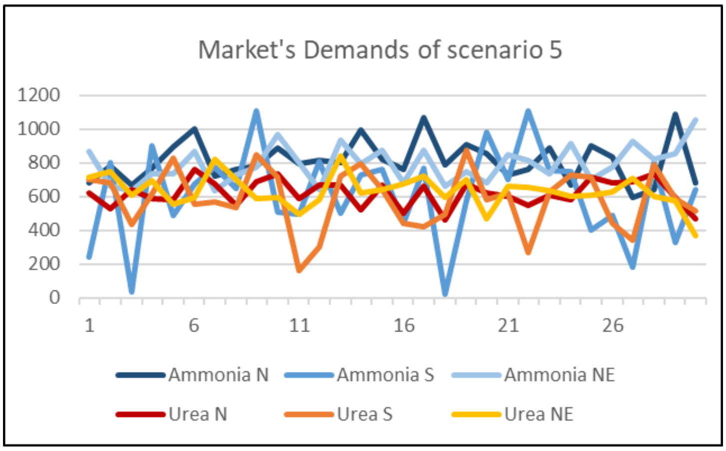
Supply chain	ΣProfit in 30 days ($)
No.9	4,542,493
No.12	4,385,549
No.23	4,309,481
Deterministic	4,155,869



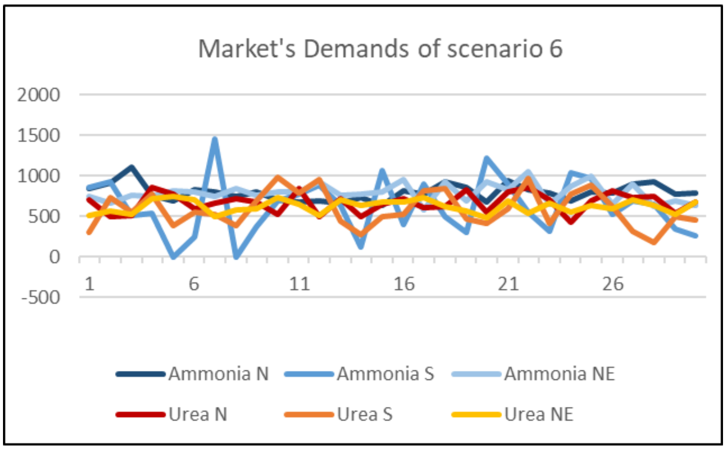
Supply chain	ΣProfit in 30 days ($)
No.9	4,739,650
No.12	4,610,258
No.23	4,432,352
Deterministic	4,271,919



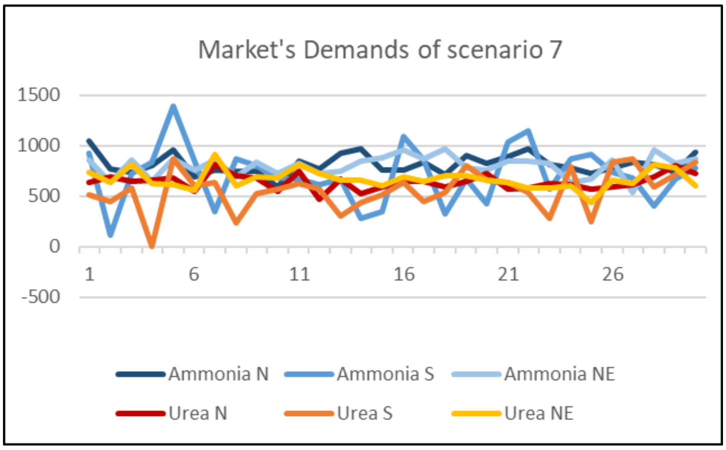
Supply chain	ΣProfit in 30 days ($)
No.9	4,349,496
No.12	4,362,289
No.23	4,289,086
Deterministic	4,046,277



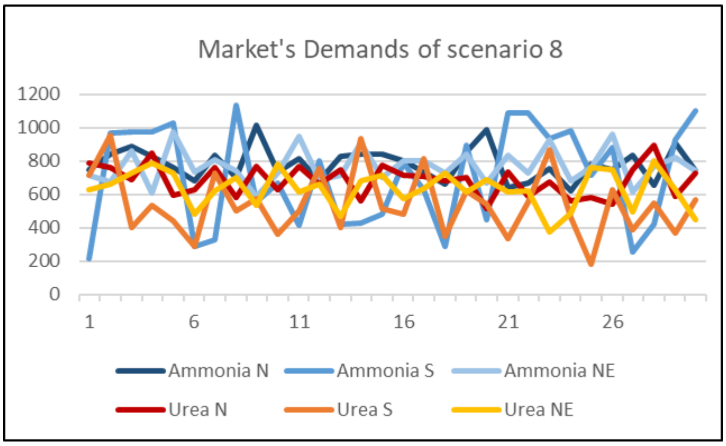
Supply chain	ΣProfit in 30 days ($)
No.9	4,622,828
No.12	4,628,223
No.23	4,519,803
Deterministic	4,371,670



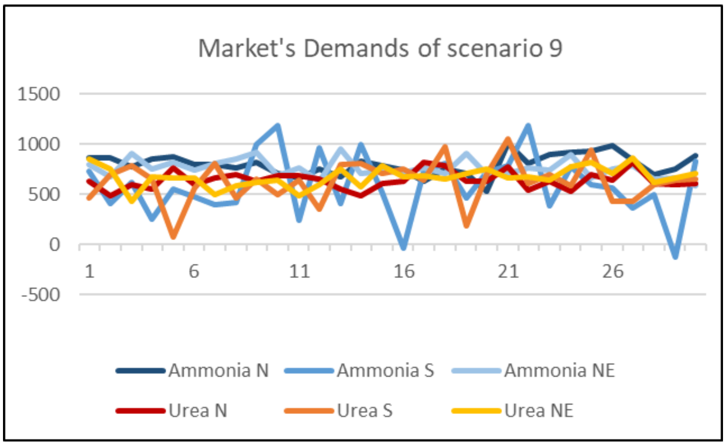
Supply chain	ΣProfit in 30 days ($)
No.9	4,373,627
No.12	4,162,503
No.23	4,148,803
Deterministic	3,923,030



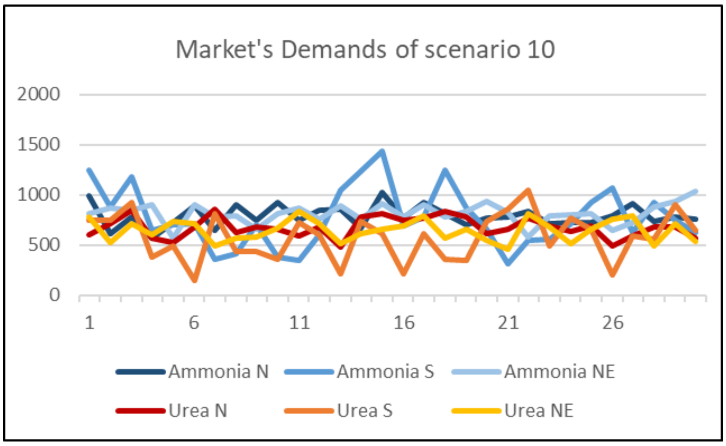
Supply chain	ΣProfit in 30 days ($)
No.9	4,572,972
No.12	4,652,777
No.23	4,503,266
Deterministic	4,429,242



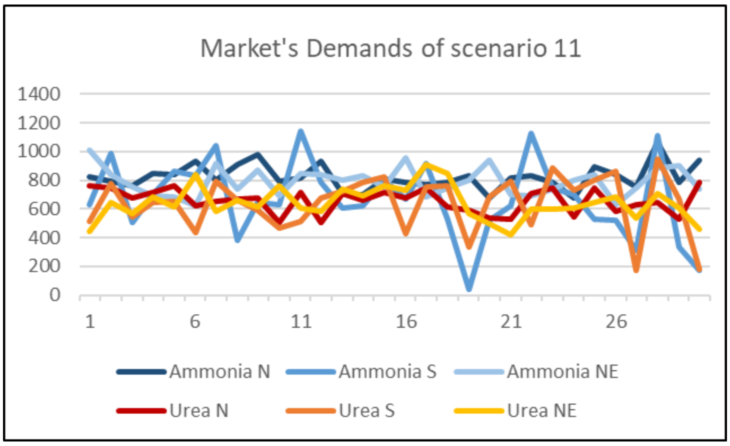
Supply chain	ΣProfit in 30 days ($)
No.9	4,487,103
No.12	4,328,850
No.23	4,292,671
Deterministic	4,160,601



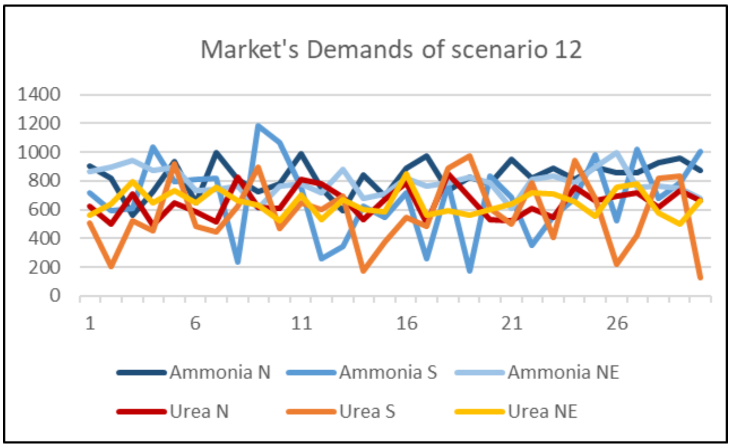
Supply chain	ΣProfit in 30 days ($)
No.9	4,738,893
No.12	4,571,620
No.23	4,451,390
Deterministic	4,265,565



Supply chain	ΣProfit in 30 days ($)
No.9	4,417,995
No.12	4,347,503
No.23	4,246,138
Deterministic	4,041,861



Supply chain	ΣProfit in 30 days ($)
No.9	4,816,588
No.12	4,612,233
No.23	4,494,434
Deterministic	4,249,583



Supply chain	ΣProfit in 30 days ($)
No.9	4,545,867
No.12	4,430,984
No.23	4,358,699
Deterministic	4,186,478

Figure 4.22 The results from validation part of 12 scenarios – varied production rate.

The optimized value of both ammonia and urea transportation of supply chain No.9, No.12, and No.23 in part 6.9 are validated with new set of market's demands in 12 scenarios, 30 days per scenarios. The summation of profit in 30 days of each scenarios were converted to profit cumulative frequency curve for evaluated the probability and upper limit profit of each supply chains as shown in figure 4.23.

According to the profit cumulative frequency curve in figure 4.23a, at targeted profit of \$ 4,400,000, the stochastic supply chain No.9 has 16.67 % risk giving profit less than targeted profit and its upper limit profit is \$ 4,820,000 . According to the profit cumulative frequency curve in figure 4.23b, the stochastic supply chain No.12 has 41.67 % risk giving profit less than targeted profit and its upper limit profit is \$ 4,655,000 . According to the profit cumulative frequency curve in figure 4.23c, the stochastic supply chain No.23 has 50 % risk giving profit less than targeted profit and its upper limit profit is \$ 4,545,000 while the deterministic supply chain has higher risk of 91.67 % giving profit less than targeted profit and its upper limit of profit is \$ 4,430,000 lower than stochastic supply chains.

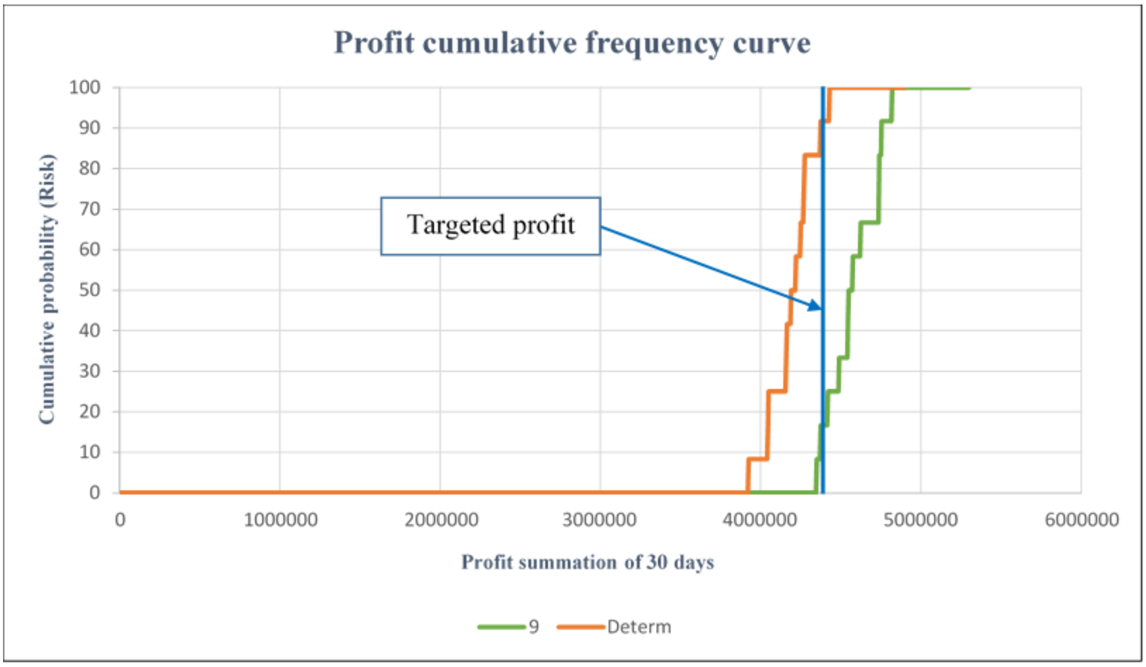


Figure 4.23 Profit cumulative frequency curve for stochastic supply chains No.9 and deterministic one – varied production capacity.

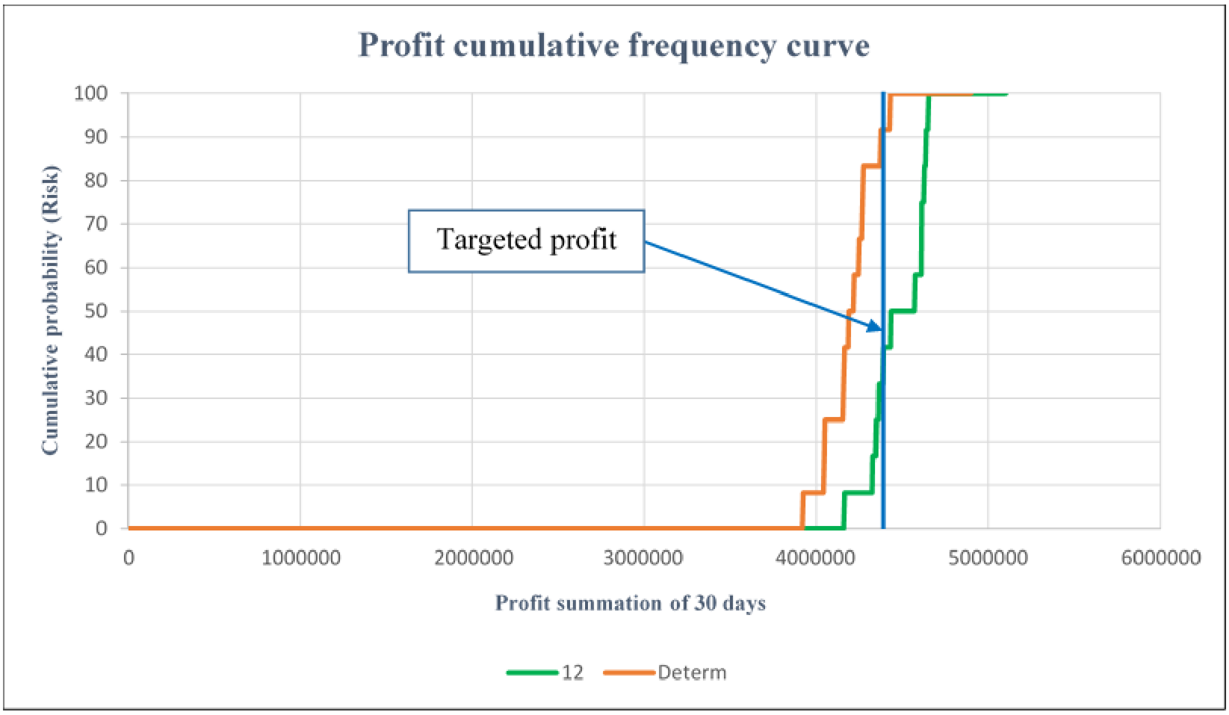


Figure 4.23b Profit cumulative frequency curve for stochastic supply chains No.12 and deterministic one – varied production capacity.

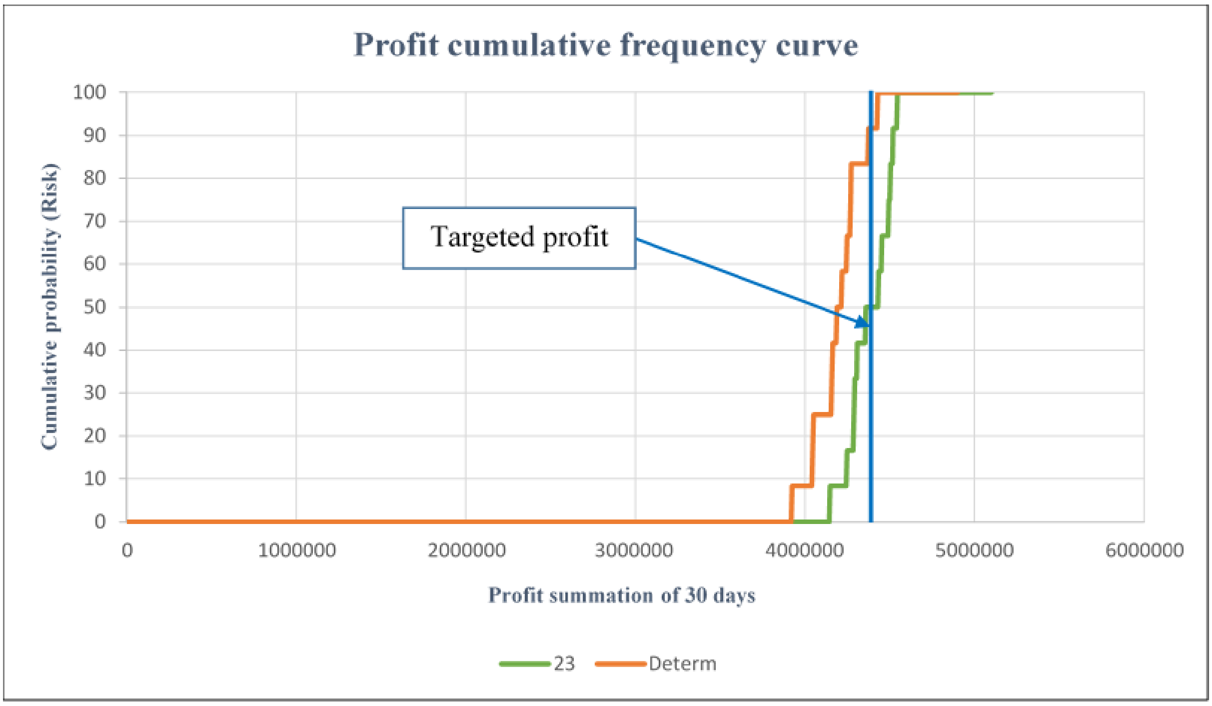


Figure 4.23c Profit cumulative frequency curve for stochastic supply chains No.23 and deterministic one – varied production capacity.

According to the result, the adjusting of ammonia and urea production rate can give higher profit in both of deterministic and stochastic method compared with fixed products production rate as a result of products satisfy market's demands and can decreasing excess costs from product transportation, lacked product penalty cost, and oversupply product sold with cheaper selling price. From the deterministic method, the optimization of ammonia and urea transportation are using single fixed value of average from markets demands in 30 days. To provide the upper and lower limit of profit, scenario analysis is performed with various demand from each market. Stochastic analysis method is dealing with uncertain market's demands, in this research assume to be the historical data. For all studied cases, it was also found that the optimization with stochastic analysis method give the optimal value or higher profit compared with deterministic analysis using the same data.

CHAPTER 5

CONCLUSION

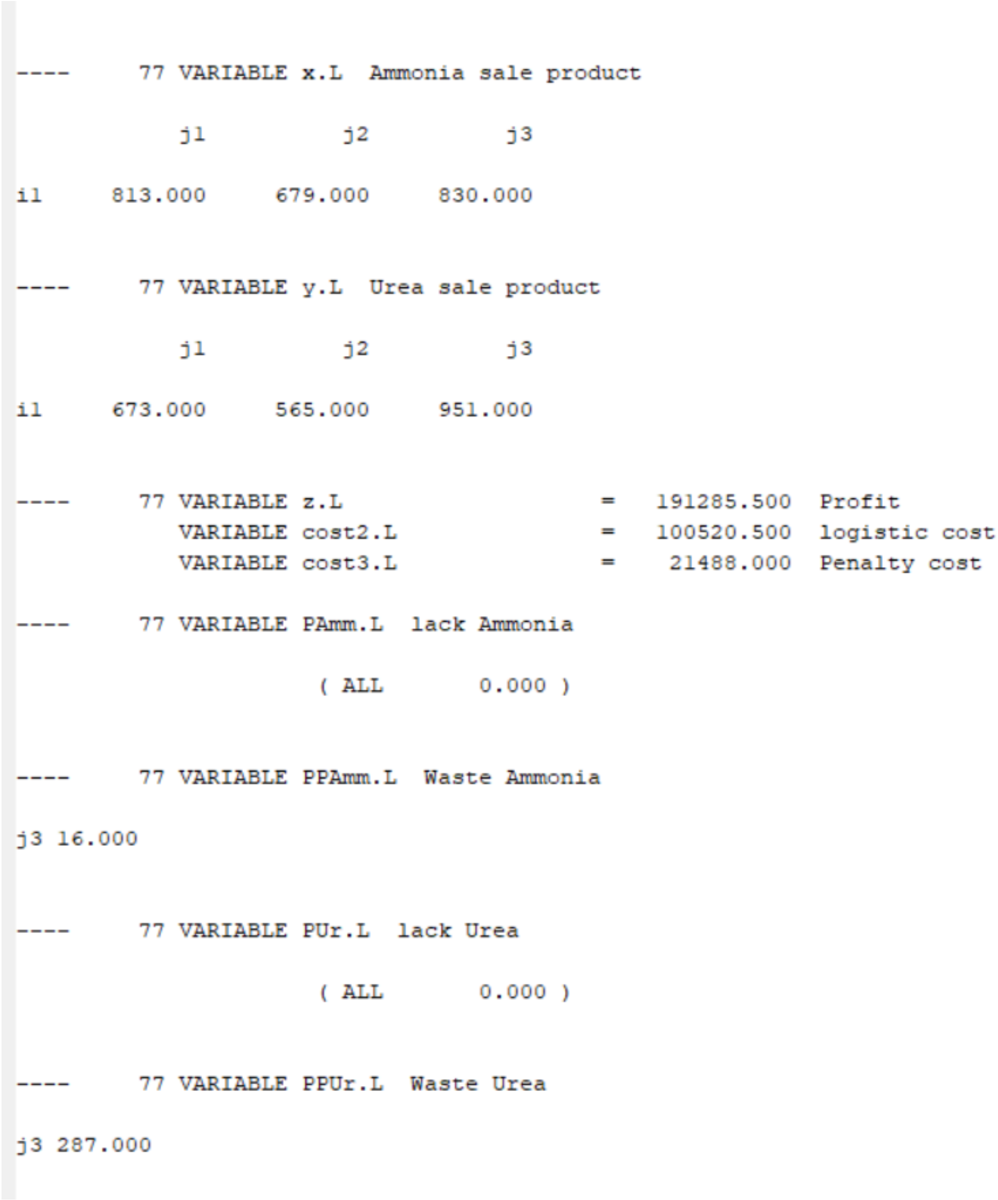
According to the results of this research, ammonia and urea manufacturing process are done by Pro II simulation programming. Ammonia production is a significant material used in a production of urea by reacting with CO_2. This conceptual plant applied ammonia and urea processes can be more efficient in the production of urea, where by-products of each process can be used to produce more urea and reduce CO_2 emission. From 1,930 t/d of natural gas feed, the production capacity of the ammonia process is 3,870 TPD and the production capacity of the urea process is 5,472 TPD. From energy consumption and economic assessment, the capital expenditure (CAPEX) of overall process is 233,988,848 $. The most operating expenditure of overall process is 45 % from electricity. Improving this section can highly effect on economic of the process. The operating expenditure of urea process can be varied with energy consumption changed due to amount of ammonia feed and urea production rate. Therefore, the correlation between urea production and ammonia feed is essentially considered. For case of varied ammonia and urea production rate, the maximum 30-days profit of $ 4,863,511 from stochastic supply chain No.12 and 30-days profit of $ 4,610,028 from deterministic supply chain are higher than the ones from case of fixed ammonia and urea production rate, where the maximum 30-days profit of $ 4,622,681 from stochastic supply chain No.13 and 30-days profit of $ 4,417,229 from deterministic supply chain. According to the results of supply chains optimization, the adjusting of ammonia and urea production rate give higher profit in both of stochastic and deterministic method compared with fixed production rate as a result of products satisfy market's demands. For stochastic analysis, the validation part approves that optimization with stochastic method provided optimal value compared with deterministic method using identical data. The profit cumulative curve show that stochastic method provides supply chain with a lower risk to achieve profit less the targeted one than deterministic method at same targeted profit. However, consideration of both deterministic and stochastic analyses can provide more effective results.

Table 5.1 Concluded information and key parameters of manufacturing process

No.	Description	results
	Ammonia manufacturing process	
1	Ammonia capacity	3,870 TPD
2	Raw materials	Hydrogen from Natural gas, Nitrogen from Air
3	Process Units	22 units
4	Overall Energy Consumption	3,585 MMKJ/hr. 9.49×10^4 kW
5	Annual Operating Expenditure (OPEX)	231,860,129 $
6	Product specifications	Ammonia purity 99.90 % Temperature -33.3 ^{o}C Pressure 320 psia
	Urea manufacturing process	
7	Urea capacity	5,472 TPD
8	Raw materials	Ammonia, Carbon dioxide
9	Process Units	21 units
10	Overall Energy Consumption	Hot utilities 427 MMKJ/hr. Cold utilities 493 MMKJ/hr. Shaft work 9.52×10^4 kW
11	Annual Operating Expenditure (OPEX)	146,182,569 $
12	Product specifications	Granulated urea purity 99.90 % Temperature 93.33 ^{o}C
	Techno economic assessment	
13	Plant lifetime	10 years
14	Overall Capital Expenditure (CAPEX)	233,988,848 $
15	Products price	Ammonia 206 $/ton Urea 288 $/ton
16	Payback period	5.4 year (at 10 % interest)
17	Net present value	197,175,232 $

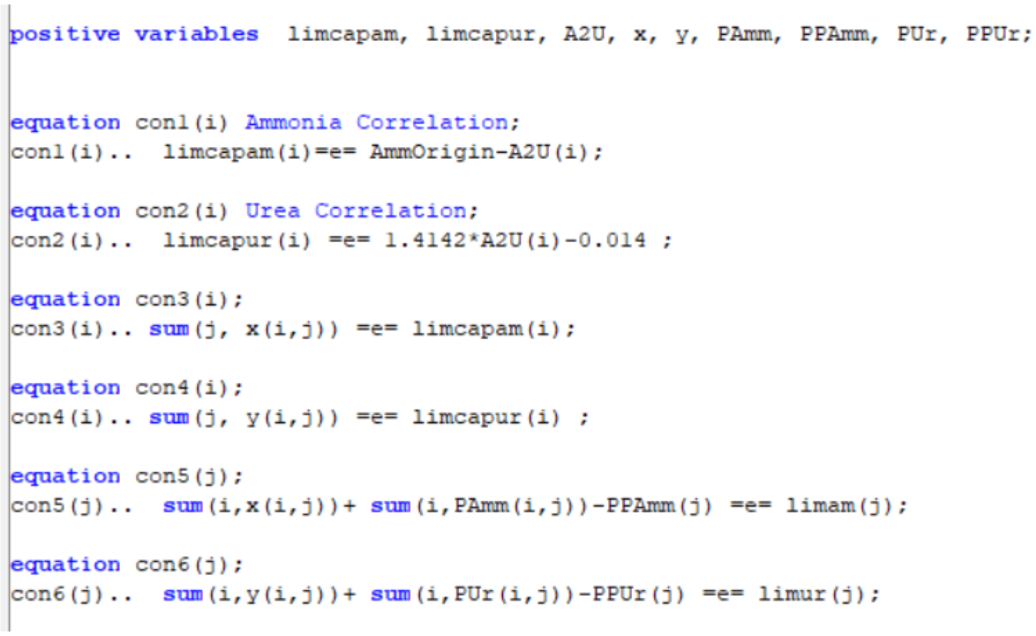
Table 5.2 Concluded information and key parameters of supply chain optimization

	Ammonia (t/d)			Urea (t/d)			Ammonia production rate (t/d)	Urea production rate (t/d)	Σ Profit in 30 days ($)
	(j1)	(j2)	(j3)	(j1)	(j2)	(j3)			
Average	813	679	814	673	565	664			
Mean	800	700	800	650	500	650			
SD	100	300	100	100	200	100			
Fixed production rate									
Deterministic	813	679	830	673	565	951	2,322	2,189	4,417,229
Stochastic No.12	836	629	857	694	667	828	2,322	2,189	4,619,053
Stochastic No.13	770	730	822	798	693	698	2,322	2,189	4,622,681
Varied production rate									
Deterministic	813	679	814	673	565	1,025	2,306	2,263	4,610,028
Stochastic No.9	825	674	743	771	805	777	2,242	2,353	4,850,215
Stochastic No.12	836	680	857	694	667	807	2,373	2,168	4,863,511
Stochastic No.23	864	633	904	731	633	764	2,401	2,128	4,806,255

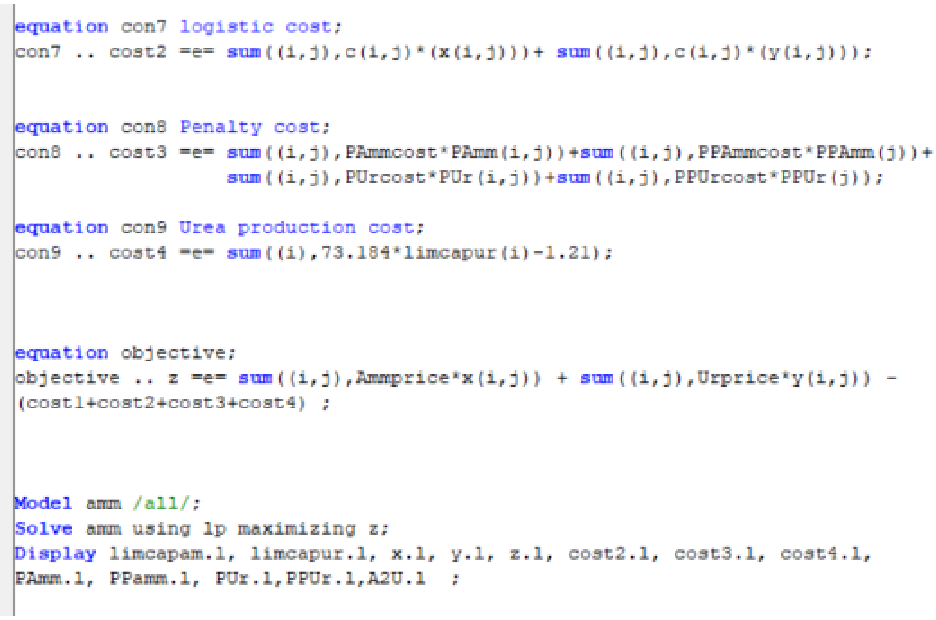


```
----     77 VARIABLE x.L  Ammonia sale product

            j1          j2          j3

i1     813.000     679.000     830.000


----     77 VARIABLE y.L  Urea sale product

            j1          j2          j3

i1     673.000     565.000     951.000


----     77 VARIABLE z.L                  =   191285.500  Profit
            VARIABLE cost2.L              =   100520.500  logistic cost
            VARIABLE cost3.L              =    21488.000  Penalty cost

----     77 VARIABLE PAmm.L  lack Ammonia

                      ( ALL       0.000 )


----     77 VARIABLE PPAmm.L  Waste Ammonia

j3 16.000


----     77 VARIABLE PUr.L  lack Urea

                      ( ALL       0.000 )


----     77 VARIABLE PPUr.L  Waste Urea

j3 287.000
```

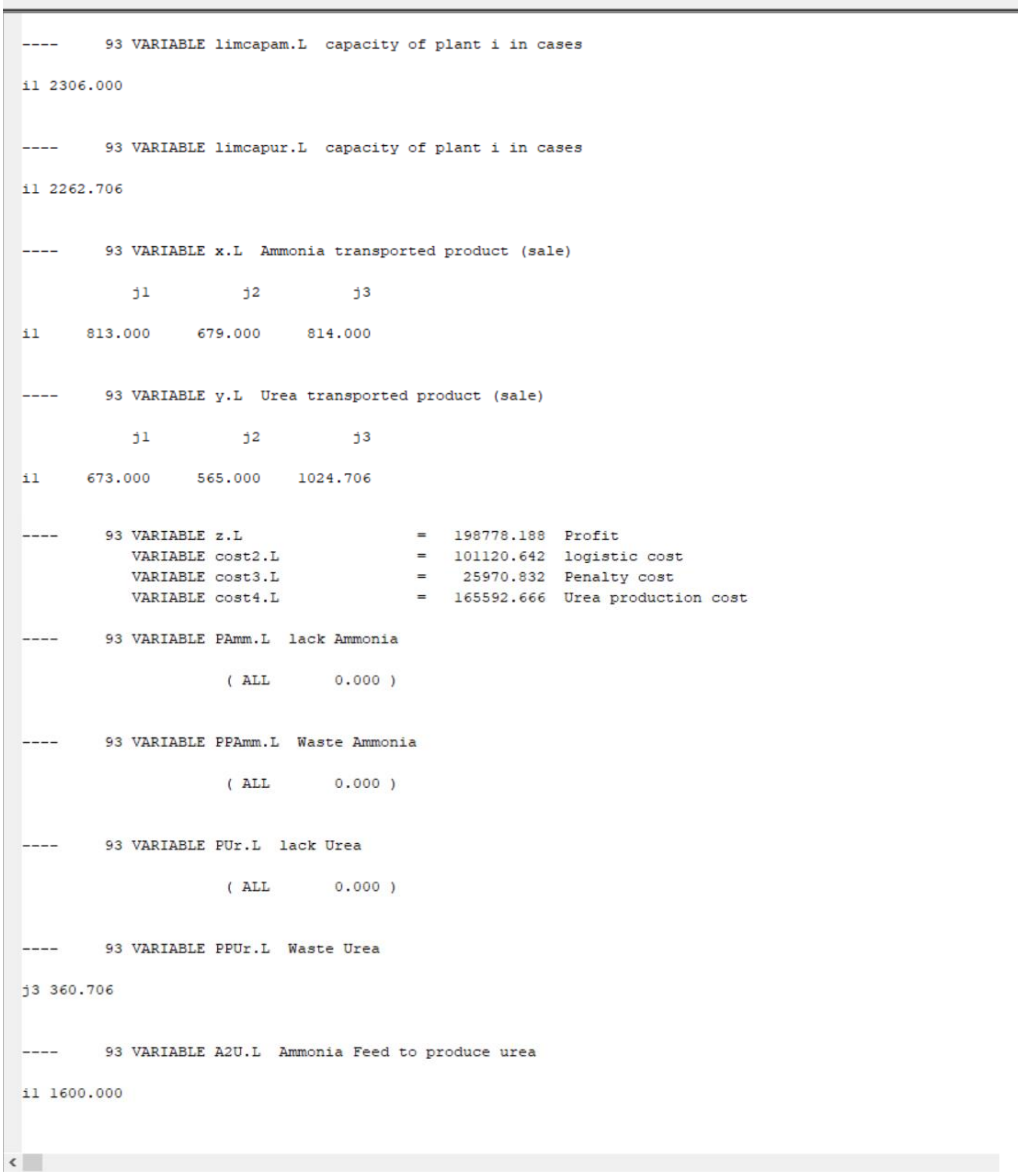
Figure A GAMS programing of ammonia and urea plant with improved deterministic supply chain under fixed production rate.



```
positive variables  limcapam, limcapur, A2U, x, y, PAmm, PPAmm, PUr, PPUr;


equation con1(i) Ammonia Correlation;
con1(i)..  limcapam(i)=e= AmmOrigin-A2U(i);

equation con2(i) Urea Correlation;
con2(i)..  limcapur(i) =e= 1.4142*A2U(i)-0.014 ;

equation con3(i);
con3(i).. sum(j, x(i,j)) =e= limcapam(i);

equation con4(i);
con4(i).. sum(j, y(i,j)) =e= limcapur(i) ;

equation con5(j);
con5(j)..  sum(i,x(i,j))+ sum(i,PAmm(i,j))-PPAmm(j) =e= limam(j);

equation con6(j);
con6(j)..  sum(i,y(i,j))+ sum(i,PUr(i,j))-PPUr(j) =e= limur(j);
```



```
equation con7 logistic cost;
con7 .. cost2 =e= sum((i,j),c(i,j)*(x(i,j)))+ sum((i,j),c(i,j)*(y(i,j)));


equation con8 Penalty cost;
con8 .. cost3 =e= sum((i,j),PAmmcost*PAmm(i,j))+sum((i,j),PPAmmcost*PPAmm(j))+
                  sum((i,j),PUrcost*PUr(i,j))+sum((i,j),PPUrcost*PPUr(j));

equation con9 Urea production cost;
con9 .. cost4 =e= sum((i),73.184*limcapur(i)-1.21);



equation objective;
objective .. z =e= sum((i,j),Ammprice*x(i,j)) + sum((i,j),Urprice*y(i,j)) -
(cost1+cost2+cost3+cost4) ;



Model amm /all/;
Solve amm using lp maximizing z;
Display limcapam.l, limcapur.l, x.l, y.l, z.l, cost2.l, cost3.l, cost4.l,
PAmm.l, PPamm.l, PUr.l,PPUr.l,A2U.l  ;
```



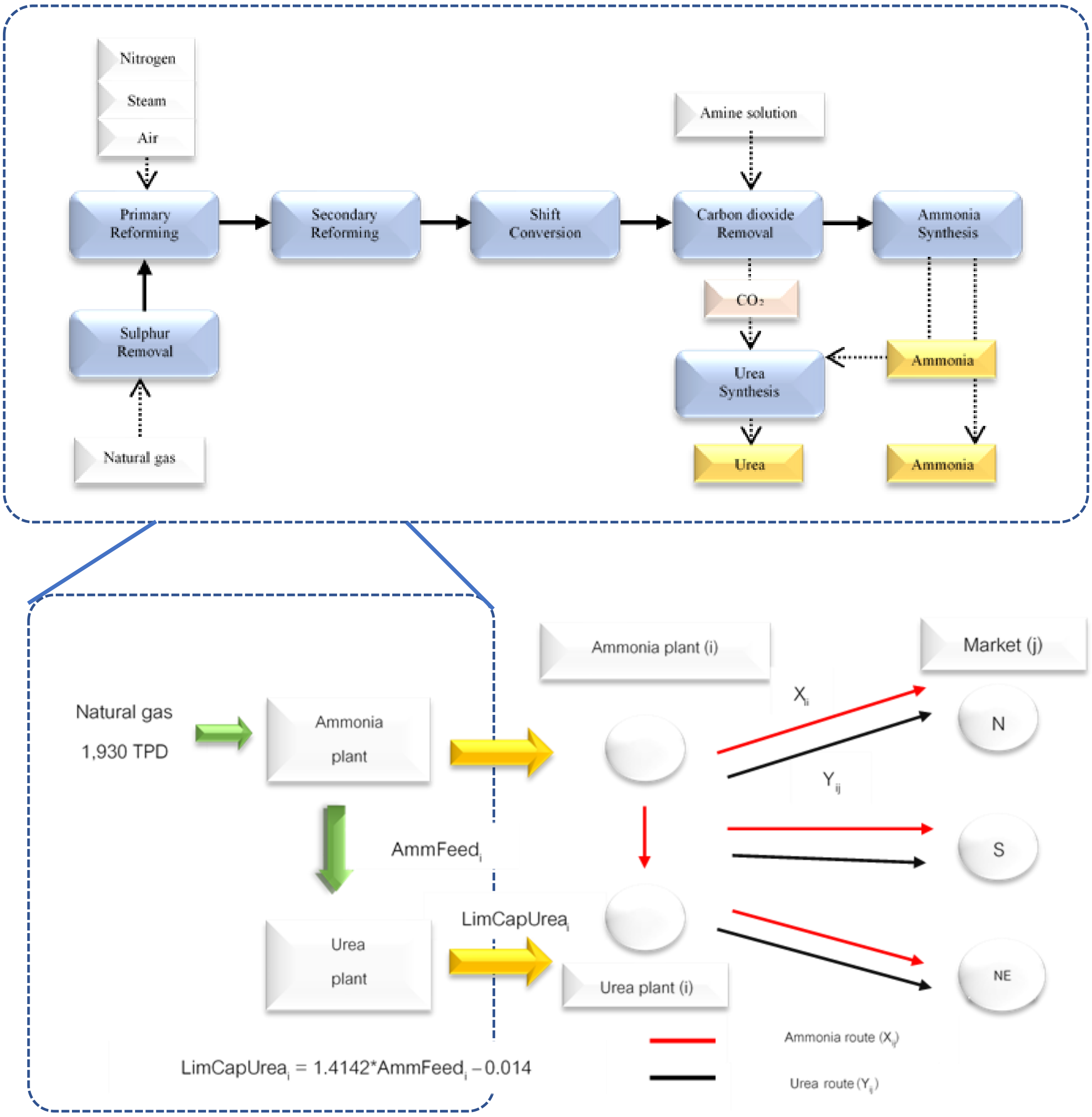
```
----     93 VARIABLE limcapam.L  capacity of plant i in cases

i1 2306.000


----     93 VARIABLE limcapur.L  capacity of plant i in cases

i1 2262.706


----     93 VARIABLE x.L  Ammonia transported product (sale)

            j1          j2          j3

i1     813.000     679.000     814.000


----     93 VARIABLE y.L  Urea transported product (sale)

            j1          j2          j3

i1     673.000     565.000    1024.706


----     93 VARIABLE z.L                   =   198778.188  Profit
            VARIABLE cost2.L               =   101120.642  logistic cost
            VARIABLE cost3.L               =    25970.832  Penalty cost
            VARIABLE cost4.L               =   165592.666  Urea production cost

----     93 VARIABLE PAmm.L  lack Ammonia

                      ( ALL       0.000 )


----     93 VARIABLE PPAmm.L  Waste Ammonia

                      ( ALL       0.000 )


----     93 VARIABLE PUr.L  lack Urea

                      ( ALL       0.000 )


----     93 VARIABLE PPUr.L  Waste Urea

j3 360.706


----     93 VARIABLE A2U.L  Ammonia Feed to produce urea

i1 1600.000
```

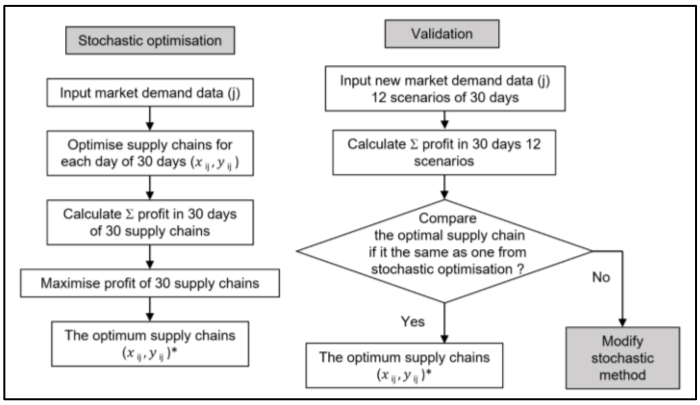
Figure B GAMS programing ammonia and urea plant with improved deterministic supply chain under varied production rate.

APPENDICES / APPENDIX

Appendix A

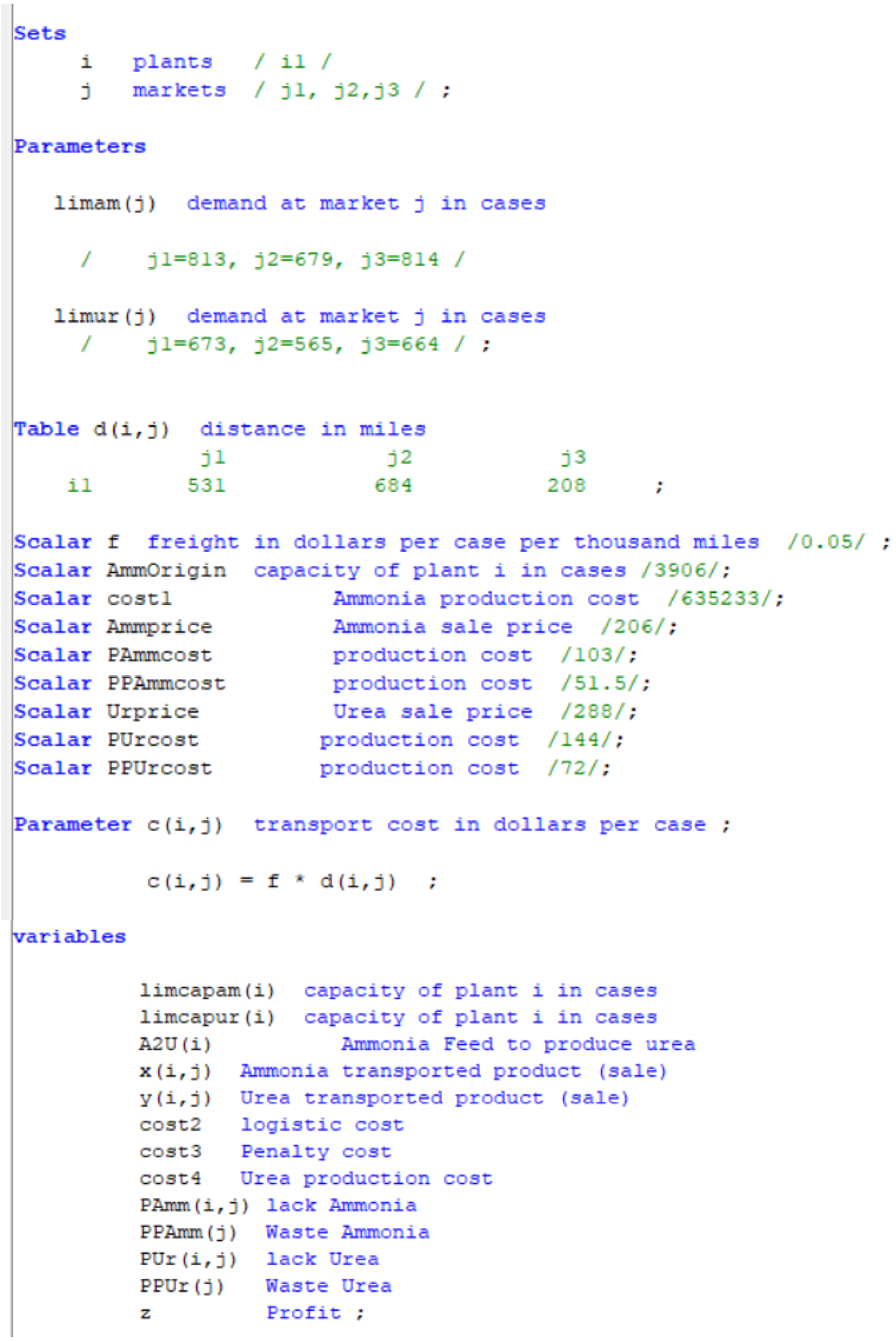
GRAPHICAL ABSTRACT





Appendix B Aaaaa Aaaaaa Aaaaaa

GAMS programing of ammonia and urea plant with improved deterministic supply chain under varied production rate



```
Sets
     i    plants    / i1 /
     j    markets   / j1, j2,j3 / ;

Parameters

   limam(j)   demand at market j in cases

     /    j1=813, j2=679, j3=814 /

   limur(j)   demand at market j in cases
     /    j1=673, j2=565, j3=664 / ;


Table d(i,j)  distance in miles
              j1            j2            j3
    i1       531           684           208     ;

Scalar f  freight in dollars per case per thousand miles  /0.05/ ;
Scalar AmmOrigin  capacity of plant i in cases /3906/;
Scalar cost1            Ammonia production cost  /635233/;
Scalar Ammprice         Ammonia sale price  /206/;
Scalar PAmmcost         production cost  /103/;
Scalar PPAmmcost        production cost  /51.5/;
Scalar Urprice          Urea sale price  /288/;
Scalar PUrcost         production cost  /144/;
Scalar PPUrcost        production cost  /72/;

Parameter c(i,j)  transport cost in dollars per case ;

          c(i,j) = f * d(i,j)   ;

variables

         limcapam(i)  capacity of plant i in cases
         limcapur(i)  capacity of plant i in cases
         A2U(i)          Ammonia Feed to produce urea
         x(i,j)  Ammonia transported product (sale)
         y(i,j)  Urea transported product (sale)
         cost2   logistic cost
         cost3   Penalty cost
         cost4   Urea production cost
         PAmm(i,j) lack Ammonia
         PPAmm(j)  Waste Ammonia
         PUr(i,j)  lack Urea
         PPUr(j)   Waste Urea
         z         Profit ;
```

Appendix C Aaaaa Aaaaaaa Aaaaaa

Excel programing results of ammonia and urea plant with improved stochastic supply chain under fixed production rate (XY 1-6 of 30)

XY1	Ammonia			Urea			Penalty cost									Transportation Cost				
Day	N	S	NE	N	S	NE	N	S	NE	N	S	NE	Amm	Urea	Sum	Amm	Urea	Sum	Sale	Profit
1	677	762	851	687	581	634	0	0	1648	0	0	20664	1648	20664	22312	53218	47688	100906	1108764	190076
2	834	1262	801	478	632	558	16171	51500	4223	15048	7344	26136	71894	48528	120422	53218	47688	100906	1108764	91966
3	878	38	790	575	366	634	20703	37286	4790	8064	15480	20664	62779	44208	106987	53218	47688	100906	1108764	105401
4	777	700	773	614	513	692	10300	3193	5665	5256	4896	16488	19158	26640	45798	53218	47688	100906	1108764	166590
5	828	758	759	621	575	706	15553	206	6386	4752	432	15480	22145	20664	42809	53218	47688	100906	1108764	169579
6	987	637	784	712	494	695	31930	6438	5099	3600	6264	16272	43466	26136	69602	53218	47688	100906	1108764	142786
7	790	711	801	640	702	731	11639	2627	4223	3384	17424	13680	18489	34488	52977	53218	47688	100906	1108764	159411
8	911	675	748	623	475	511	24102	4481	6953	4608	7632	29520	35535	41760	77295	53218	47688	100906	1108764	135093
9	825	674	743	771	805	604	15244	4532	7210	12096	32256	22824	26986	67176	94162	53218	47688	100906	1108764	118226
10	888	829	895	723	737	628	21733	6901	1236	5184	22464	21096	29870	48744	78614	53218	47688	100906	1108764	133774
11	782	288	891	750	823	497	10815	24411	824	9072	34848	30528	36050	74448	110498	53218	47688	100906	1108764	101890
12	836	680	857	694	667	724	16377	4223	1339	1008	12384	14184	21939	27576	49515	53218	47688	100906	1108764	162873
13	770	956	822	798	693	564	9579	19982	3142	15984	16128	25704	32703	57816	90519	53218	47688	100906	1108764	121869
14	743	791	816	701	232	607	6798	2987	3451	2016	25128	22608	13236	49752	62988	53218	47688	100906	1108764	149400
15	815	667	642	528	588	940	14214	4893	12412	11448	1008	2736	31518	15192	46710	53218	47688	100906	1108764	165678
16	812	722	1040	779	643	777	13905	2060	16171	13248	8928	10368	32136	32544	64680	53218	47688	100906	1108764	147708
17	935	999	771	653	493	678	26574	24411	5768	2448	6336	17496	56753	26280	83033	53218	47688	100906	1108764	129355
18	776	439	766	676	644	719	10197	16635	6026	792	9072	14544	32857	24408	57265	53218	47688	100906	1108764	155123
19	997	375	743	701	648	570	32960	19931	7210	2016	9648	25272	60101	36936	97037	53218	47688	100906	1108764	115351
20	751	815	842	588	876	736	7622	5459	2112	7128	42480	13320	15193	62928	78121	53218	47688	100906	1108764	134267
21	932	625	868	679	486	610	26265	7056	773	576	6840	22392	34093	29808	63901	53218	47688	100906	1108764	148487
22	887	578	783	613	548	578	21630	9476	5150	5328	2376	24696	36256	32400	68656	53218	47688	100906	1108764	143732
23	864	633	904	731	633	692	19261	6644	2163	6336	7488	16488	28068	30312	58380	53218	47688	100906	1108764	154008
24	612	599	827	674	357	799	3348	8395	2884	936	16128	8784	14626	25848	40474	53218	47688	100906	1108764	171914
25	955	844	721	605	295	692	28634	8446	8343	5904	20592	16488	45423	42984	88407	53218	47688	100906	1108764	123981
26	913	509	908	766	355	634	24308	13030	2575	11376	16272	20664	39913	48312	88225	53218	47688	100906	1108764	124163
27	627	610	822	769	431	627	2575	7828	3142	11808	10800	21168	13545	43776	57321	53218	47688	100906	1108764	155067
28	726	677	686	830	303	693	5047	4378	10146	20592	20016	16416	19570	57024	76594	53218	47688	100906	1108764	135794
29	690	772	871	485	438	703	1339	1030	618	14544	10296	15696	2987	40536	43523	53218	47688	100906	1108764	168865
30	580	756	901	716	904	701	4996	309	1854	4176	46512	15840	7159	66528	73687	53218	47688	100906	1108764	138701
Sum																				4261121

XY2	Ammonia			Urea			Penalty cost									Transportation Cost				
Day	N	S	NE	N	S	NE	N	S	NE	N	S	NE	Amm	Urea	Sum	Amm	Urea	Sum	Sale	Profit
1	677	762	851	687	581	634	8086	7725	5150	30096	3672	32040	20961	65808	86769	53969	45527	99495	1108764	127030
2	834	1262	801	478	632	558	0	59225	0	0	0	37512	59225	37512	96737	53969	45527	99495	1108764	117062
3	878	38	790	575	366	634	4532	33424	567	13968	19152	32040	38522	65160	103682	53969	45527	99495	1108764	110117
4	777	700	773	614	513	692	2936	1339	1442	19584	8568	27864	5717	56016	61733	53969	45527	99495	1108764	152066
5	828	758	759	621	575	706	309	7313	2163	20592	4104	26856	9785	51552	61337	53969	45527	99495	1108764	152462
6	987	637	784	712	494	695	15759	2575	876	33696	9936	27648	19210	71280	90490	53969	45527	99495	1108764	123309
7	790	711	801	640	702	731	2266	2472	0	23328	10080	25056	4738	58464	63202	53969	45527	99495	1108764	150597
8	911	675	748	623	475	511	7931	618	2730	20880	11304	40896	11279	73080	84359	53969	45527	99495	1108764	129440
9	825	674	743	771	805	604	464	670	2987	42192	24912	34200	4120	101304	105424	53969	45527	99495	1108764	108375
10	888	829	895	723	737	628	5562	14626	9682	35280	15120	32472	29870	82872	112742	53969	45527	99495	1108764	101057
11	782	288	891	750	823	497	2678	20549	9270	39168	27504	41904	32497	108576	141073	53969	45527	99495	1108764	72726
12	836	680	857	694	667	724	206	361	5768	31104	5040	25560	6335	61704	68039	53969	45527	99495	1108764	145760
13	770	956	822	798	693	564	3296	27707	2163	46080	8784	37080	33166	91944	125110	53969	45527	99495	1108764	88689
14	743	791	816	701	232	607	4687	10712	1545	32112	28800	33984	16944	94896	111840	53969	45527	99495	1108764	101959
15	815	667	642	528	588	940	979	1030	8189	7200	3168	10008	10197	20376	30573	53969	45527	99495	1108764	183226
16	812	722	1040	779	643	777	1133	3605	24617	43344	1584	21744	29355	66672	96027	53969	45527	99495	1108764	117772
17	935	999	771	653	493	678	10403	32136	1545	25200	10008	28872	44084	64080	108164	53969	45527	99495	1108764	105635
18	776	439	766	676	644	719	2987	12772	1803	28512	1728	25920	17562	56160	73722	53969	45527	99495	1108764	140077
19	997	375	743	701	648	570	16789	16068	2987	32112	2304	36648	35844	71064	106908	53969	45527	99495	1108764	106891
20	751	815	842	588	876	736	4275	13184	4223	15840	35136	24696	21682	75672	97354	53969	45527	99495	1108764	116445
21	932	625	868	679	486	610	10094	3193	6901	28944	10512	33768	20188	73224	93412	53969	45527	99495	1108764	120387
22	887	578	783	613	548	578	5459	5614	927	19440	6048	36072	12000	61560	73560	53969	45527	99495	1108764	140239
23	864	633	904	731	633	692	3090	2781	10609	36432	144	27864	16480	64440	80920	53969	45527	99495	1108764	132879
24	612	599	827	674	357	799	11433	4532	2678	28224	19800	20160	18643	68184	86827	53969	45527	99495	1108764	126972
25	955	844	721	605	295	692	12463	16171	4120	18288	24264	27864	32754	70416	103170	53969	45527	99495	1108764	110629
26	913	509	908	766	355	634	8137	9167	11021	41472	19944	32040	28325	93456	121781	53969	45527	99495	1108764	92018
27	627	610	822	769	431	627	10661	3966	2163	41904	14472	32544	16789	88920	105709	53969	45527	99495	1108764	108090
28	726	677	686	830	303	693	5562	515	5923	50688	23688	27792	12000	102168	114168	53969	45527	99495	1108764	99631
29	690	772	871	485	438	703	7416	8755	7210	1008	13968	27072	23381	42048	65429	53969	45527	99495	1108764	148370
30	580	756	901	716	904	701	13081	7107	10300	34272	39168	27216	30488	100656	131144	53969	45527	99495	1108764	82655
Sum																				3612559

XY3	Ammonia			Urea			Penalty cost									Transportation Cost				
Day	N	S	NE	N	S	NE	N	S	NE	N	S	NE	Amm	Urea	Sum	Amm	Urea	Sum	Sale	Profit
1	677	762	851	687	581	634	10352	74572	28583	16128	30960	44208	113506	91296	204802	39233	40763	79996	1108764	28496
2	834	1262	801	478	632	558	2266	126072	31158	6984	38304	49680	159496	94968	254464	39233	40763	79996	1108764	-21165
3	878	38	790	575	366	634	0	0	31724	0	0	44208	31724	44208	75932	39233	40763	79996	1108764	157366
4	777	700	773	614	513	692	5202	68186	32600	5616	21168	40032	105987	66816	172803	39233	40763	79996	1108764	60495
5	828	758	759	621	575	706	2575	74160	33321	6624	30096	39024	110056	75744	185800	39233	40763	79996	1108764	47499
6	987	637	784	712	494	695	11227	61697	32033	19728	18432	39816	104957	77976	182933	39233	40763	79996	1108764	50365
7	790	711	801	640	702	731	4532	69319	31158	9360	48384	37224	105009	94968	199977	39233	40763	79996	1108764	33322
8	911	675	748	623	475	511	3399	65611	33887	6912	15696	53064	102897	75672	178569	39233	40763	79996	1108764	54729
9	825	674	743	771	805	604	2730	65508	34145	28224	63216	46368	102382	137808	240190	39233	40763	79996	1108764	-6892
10	888	829	895	723	737	628	1030	81473	26317	21312	53424	44640	108820	119376	228196	39233	40763	79996	1108764	5103
11	782	288	891	750	823	497	4944	25750	26523	25200	65808	54072	57217	145080	202297	39233	40763	79996	1108764	31002
12	836	680	857	694	667	724	2163	66126	28274	17136	43344	37728	96563	98208	194771	39233	40763	79996	1108764	38528
13	770	956	822	798	693	564	5562	94554	30076	32112	47088	49248	130192	128448	258640	39233	40763	79996	1108764	-25342
14	743	791	816	701	232	607	6953	77559	30385	18144	9648	46152	114897	73944	188841	39233	40763	79996	1108764	44458
15	815	667	642	528	588	940	3245	64787	39346	3384	31968	22176	107378	57528	164906	39233	40763	79996	1108764	68393
16	812	722	1040	779	643	777	3399	70452	18849	29376	39888	33912	92700	103176	195876	39233	40763	79996	1108764	37422
17	935	999	771	653	493	678	5871	98983	32703	11232	18288	41040	137557	70560	208117	39233	40763	79996	1108764	25182
18	776	439	766	676	644	719	5253	41303	32960	14544	40032	38088	79516	92664	172180	39233	40763	79996	1108764	61118
19	997	375	743	701	648	570	12257	34711	34145	18144	40608	48816	81113	107568	188681	39233	40763	79996	1108764	44618
20	751	815	842	588	876	736	6541	80031	29046	1872	73440	36864	115618	112176	227794	39233	40763	79996	1108764	5505
21	932	625	868	679	486	610	5562	60461	27707	14976	17280	45936	93730	78192	171922	39233	40763	79996	1108764	61376
22	887	578	783	613	548	578	927	55620	32085	5472	26208	48240	88632	79920	168552	39233	40763	79996	1108764	64747
23	864	633	904	731	633	692	721	61285	25853	22464	38448	40032	87859	100944	188803	39233	40763	79996	1108764	44495
24	612	599	827	674	357	799	13699	57783	29819	14256	648	32328	101301	47232	148533	39233	40763	79996	1108764	84766
25	955	844	721	605	295	692	7931	83018	35278	4320	5112	40032	126227	49464	175691	39233	40763	79996	1108764	57608
26	913	509	908	766	355	634	3605	48513	25647	27504	792	44208	77765	72504	150269	39233	40763	79996	1108764	83029
27	627	610	822	769	431	627	12927	58916	30076	27936	9360	44712	101919	82008	183927	39233	40763	79996	1108764	49372
28	726	677	686	830	303	693	7828	65817	37080	36720	4536	39960	110725	81216	191941	39233	40763	79996	1108764	41357
29	690	772	871	485	438	703	9682	75602	27553	6480	10368	39240	112837	56088	168925	39233	40763	79996	1108764	64374
30	580	756	901	716	904	701	15347	73954	26008	20304	77472	39384	115309	137160	252469	39233	40763	79996	1108764	-19170
Sum																				1272161

Appendix D Aaaaaa Aaaaaaaa Aaaaaaaaa

Excel programing results of ammonia and urea plant with improved stochastic supply chain under varied production rate (XY 1-6 of 30)

XY1	Ammonia			Urea			Penalty cost									Transportation Cost			Urea		
Day	N	S	NE	N	S	NE	N	S	NE	N	S	NE	Amm	Urea	Sum	Amm	Urea	Sum	cost	Sale	Profit
1	677	762	851	687	581	634	0	0	0	0	0	27600	0	27600	27600	52885	48690	101575	167249	1129916	198259
2	834	1262	801	478	632	558	16171	51500	2575	15048	7344	33072	70246	55464	125710	52885	48690	101575	167249	1129916	100149
3	878	38	790	575	366	634	20703	37286	3142	8064	15480	27600	61131	51144	112274	52885	48690	101575	167249	1129916	113584
4	777	700	773	614	513	692	10300	3193	4017	5256	4896	23424	17510	33576	51086	52885	48690	101575	167249	1129916	174773
5	828	758	759	621	575	706	15553	206	4738	4752	432	22416	20497	27600	48097	52885	48690	101575	167249	1129916	177762
6	987	637	784	712	494	695	31930	6438	3451	3600	6264	23208	41818	33072	74890	52885	48690	101575	167249	1129916	150969
7	790	711	801	640	702	731	11639	2627	2575	3384	17424	20616	16841	41424	58264	52885	48690	101575	167249	1129916	167594
8	911	675	748	623	475	511	24102	4481	5305	4608	7632	36456	33887	48696	82583	52885	48690	101575	167249	1129916	143276
9	825	674	743	771	805	604	15244	4532	5562	12096	32256	29760	25338	74112	99450	52885	48690	101575	167249	1129916	126409
10	888	829	895	723	737	628	21733	6901	4532	5184	22464	28032	33166	55680	88846	52885	48690	101575	167249	1129916	137013
11	782	288	891	750	823	497	10815	24411	4120	9072	34848	37464	39346	81384	120730	52885	48690	101575	167249	1129916	105129
12	836	680	857	694	667	724	16377	4223	618	1008	12384	21120	21218	34512	55730	52885	48690	101575	167249	1129916	170129
13	770	956	822	798	693	564	9579	19982	1494	15984	16128	32640	31055	64752	95806	52885	48690	101575	167249	1129916	130052
14	743	791	816	701	232	607	6798	2987	1803	2016	25128	29544	11588	56688	68275	52885	48690	101575	167249	1129916	157583
15	815	667	642	528	588	940	14214	4893	10764	11448	1008	5568	29870	18024	47894	52885	48690	101575	167249	1129916	177965
16	812	722	1040	779	643	777	13905	2060	19467	13248	8928	17304	35432	39480	74912	52885	48690	101575	167249	1129916	150947
17	935	999	771	653	493	678	26574	24411	4120	2448	6336	24432	55105	33216	88321	52885	48690	101575	167249	1129916	137538
18	776	439	766	676	644	719	10197	16635	4378	792	9072	21480	31209	31344	62553	52885	48690	101575	167249	1129916	163306
19	997	375	743	701	648	570	32960	19931	5562	2016	9648	32208	58453	43872	102324	52885	48690	101575	167249	1129916	123534
20	751	815	842	588	876	736	7622	5459	464	7128	42480	20256	13545	69864	83408	52885	48690	101575	167249	1129916	142450
21	932	625	868	679	486	610	26265	7056	1751	576	6840	29328	35072	36744	71815	52885	48690	101575	167249	1129916	154043
22	887	578	783	613	548	578	21630	9476	3502	5328	2376	31632	34608	39336	73944	52885	48690	101575	167249	1129916	151915
23	864	633	904	731	633	692	19261	6644	5459	6336	7488	23424	31364	37248	68611	52885	48690	101575	167249	1129916	157247
24	612	599	827	674	357	799	3348	8395	1236	936	16128	15720	12978	32784	45762	52885	48690	101575	167249	1129916	180097
25	955	844	721	605	295	692	28634	8446	6695	5904	20592	23424	43775	49920	93695	52885	48690	101575	167249	1129916	132164
26	913	509	908	766	355	634	24308	13030	5871	11376	16272	27600	43209	55248	98456	52885	48690	101575	167249	1129916	127402
27	627	610	822	769	431	627	2575	7828	1494	11808	10800	28104	11897	50712	62608	52885	48690	101575	167249	1129916	163250
28	726	677	686	830	303	693	5047	4378	8498	20592	20016	23352	17922	63960	81882	52885	48690	101575	167249	1129916	143977
29	690	772	871	485	438	703	1339	1030	2060	14544	10296	22632	4429	47472	51901	52885	48690	101575	167249	1129916	173958
30	580	756	901	716	904	701	4996	309	5150	4176	46512	22776	10455	73464	83918	52885	48690	101575	167249	1129916	141940
Sum																					4474415

XY2	Ammonia			Urea			Penalty cost									Transportation Cost			Urea		
Day	N	S	NE	N	S	NE	N	S	NE	N	S	NE	Amm	Urea	Sum	Amm	Urea	Sum	cost	Sale	Profit
1	677	762	851	687	581	634	8086	16971	5150	30096	3672	10944	30206	44712	74918	67803	40109	107912	122070	1042048	101916
2	834	1262	801	478	632	558	0	17559	0	0	0	0	17559	0	17559	67803	40109	107912	122070	1042048	159275
3	878	38	790	575	366	634	4532	54257	567	13968	19152	10944	59355	44064	103419	67803	40109	107912	122070	1042048	73415
4	777	700	773	614	513	692	2936	20164	1442	19584	8568	19296	24541	47448	71989	67803	40109	107912	122070	1042048	104845
5	828	758	759	621	575	706	309	17177	2163	20592	4104	21312	19649	46008	65657	67803	40109	107912	122070	1042048	111177
6	987	637	784	712	494	695	15759	23408	876	33696	9936	19728	40043	63360	103403	67803	40109	107912	122070	1042048	73431
7	790	711	801	640	702	731	2266	19597	0	23328	10080	24912	21863	58320	80183	67803	40109	107912	122070	1042048	96651
8	911	675	748	623	475	511	7931	21451	2730	20880	11304	3384	32112	35568	67680	67803	40109	107912	122070	1042048	109154
9	825	674	743	771	805	604	464	21503	2987	42192	24912	6624	24953	73728	98681	67803	40109	107912	122070	1042048	78153
10	888	829	895	723	737	628	5562	13520	9682	35280	15120	10080	28764	60480	89244	67803	40109	107912	122070	1042048	87590
11	782	288	891	750	823	497	2678	41382	9270	39168	27504	4392	53330	71064	124394	67803	40109	107912	122070	1042048	52440
12	836	680	857	694	667	724	206	21194	5768	31104	5040	23904	27168	60048	87216	67803	40109	107912	122070	1042048	89618
13	770	956	822	798	693	564	3296	6980	2163	46080	8784	864	12439	55728	68167	67803	40109	107912	122070	1042048	108667
14	743	791	816	701	232	607	4687	15477	1545	32112	28800	7056	21709	67968	89677	67803	40109	107912	122070	1042048	87157
15	815	667	642	528	588	940	979	21863	8189	7200	3168	55008	31030	65376	96406	67803	40109	107912	122070	1042048	80428
16	812	722	1040	779	643	777	1133	19031	24617	43344	1584	31536	44781	76464	121245	67803	40109	107912	122070	1042048	55589
17	935	999	771	653	493	678	10403	4765	1545	25200	10008	17280	16713	52488	69201	67803	40109	107912	122070	1042048	107633
18	776	439	766	676	644	719	2987	33605	1803	28512	1728	23184	38395	53424	91819	67803	40109	107912	122070	1042048	85015
19	997	375	743	701	648	570	16789	36901	2987	32112	2304	1728	56677	36144	92821	67803	40109	107912	122070	1042048	84013
20	751	815	842	588	876	736	4275	14241	4223	15840	35136	25632	22739	76608	99347	67803	40109	107912	122070	1042048	77487
21	932	625	868	679	486	610	10094	24026	6901	28944	10512	7488	41021	46944	87965	67803	40109	107912	122070	1042048	88869
22	887	578	783	613	548	578	5459	26447	927	19440	6048	2880	32833	28368	61201	67803	40109	107912	122070	1042048	115633
23	864	633	904	731	633	692	3090	23614	10609	36432	144	19296	37313	55872	93185	67803	40109	107912	122070	1042048	83649
24	612	599	827	674	357	799	11433	25365	2678	28224	19800	34704	39476	82728	122204	67803	40109	107912	122070	1042048	54630
25	955	844	721	605	295	692	12463	12748	4120	18288	24264	19296	29331	61848	91179	67803	40109	107912	122070	1042048	85655
26	913	509	908	766	355	634	8137	30000	11021	41472	19944	10944	49158	72360	121518	67803	40109	107912	122070	1042048	55316
27	627	610	822	769	431	627	10661	24799	2163	41904	14472	9936	37622	66312	103934	67803	40109	107912	122070	1042048	72900
28	726	677	686	830	303	693	5562	21348	5923	50688	23688	19440	32833	93816	126649	67803	40109	107912	122070	1042048	50185
29	690	772	871	485	438	703	7416	16456	7210	1008	13968	20880	31082	35856	66938	67803	40109	107912	122070	1042048	109896
30	580	756	901	716	904	701	13081	17280	10300	34272	39168	20592	40661	94032	134693	67803	40109	107912	122070	1042048	42141
Sum																					2582525

XY3	Ammonia			Urea			Penalty cost									Transportation Cost			Urea		
Day	N	S	NE	N	S	NE	N	S	NE	N	S	NE	Amm	Urea	Sum	Amm	Urea	Sum	cost	Sale	Profit
1	677	762	851	687	581	634	10352	74572	6283	16128	30960	110608	91207	157696	248903	32827	50354	83180	227691	1247469	52462
2	834	1262	801	478	632	558	2266	126072	1133	6984	38304	116080	129471	161368	290839	32827	50354	83180	227691	1247469	10526
3	878	38	790	575	366	634	0	0	0	0	0	110608	0	110608	110608	32827	50354	83180	227691	1247469	190757
4	777	700	773	614	513	692	5202	68186	876	5616	21168	106432	74263	133216	207479	32827	50354	83180	227691	1247469	93886
5	828	758	759	621	575	706	2575	74160	1597	6624	30096	105424	78332	142144	220476	32827	50354	83180	227691	1247469	80889
6	987	637	784	712	494	695	11227	61697	309	19728	18432	106216	73233	144376	217609	32827	50354	83180	227691	1247469	83756
7	790	711	801	640	702	731	4532	69319	1133	9360	48384	103624	74984	161368	236352	32827	50354	83180	227691	1247469	65013
8	911	675	748	623	475	511	3399	65611	2163	6912	15696	119464	71173	142072	213245	32827	50354	83180	227691	1247469	88120
9	825	674	743	771	805	604	2730	65508	2421	28224	63216	112768	70658	204208	274866	32827	50354	83180	227691	1247469	26499
10	888	829	895	723	737	628	1030	81473	10815	21312	53424	111040	93318	185776	279094	32827	50354	83180	227691	1247469	22271
11	782	288	891	750	823	497	4944	25750	10403	25200	65808	120472	41097	211480	252577	32827	50354	83180	227691	1247469	48788
12	836	680	857	694	667	724	2163	66126	6901	17136	43344	104128	75190	164608	239798	32827	50354	83180	227691	1247469	61567
13	770	956	822	798	693	564	5562	94554	3296	32112	47088	115648	103412	194848	298260	32827	50354	83180	227691	1247469	3105
14	743	791	816	701	232	607	6953	77559	2678	18144	9648	112552	87190	140344	227534	32827	50354	83180	227691	1247469	73831
15	815	667	642	528	588	940	3245	64787	7622	3384	31968	88576	75654	123928	199582	32827	50354	83180	227691	1247469	101783
16	812	722	1040	779	643	777	3399	70452	25750	29376	39888	100312	99601	169576	269177	32827	50354	83180	227691	1247469	32188
17	935	999	771	653	493	678	5871	98983	979	11232	18288	107440	105833	136960	242793	32827	50354	83180	227691	1247469	58572
18	776	439	766	676	644	719	5253	41303	1236	14544	40032	104488	47792	159064	206856	32827	50354	83180	227691	1247469	94509
19	997	375	743	701	648	570	12257	34711	2421	18144	40608	115216	49389	173968	223357	32827	50354	83180	227691	1247469	78008
20	751	815	842	588	876	736	6541	80031	5356	1872	73440	103264	91928	178576	270504	32827	50354	83180	227691	1247469	30861
21	932	625	868	679	486	610	5562	60461	8034	14976	17280	112336	74057	144592	218649	32827	50354	83180	227691	1247469	82716
22	887	578	783	613	548	578	927	55620	361	5472	26208	114640	56908	146320	203228	32827	50354	83180	227691	1247469	98137
23	864	633	904	731	633	692	721	61285	11742	22464	38448	106432	73748	167344	241092	32827	50354	83180	227691	1247469	60273
24	612	599	827	674	357	799	13699	57783	3811	14256	648	98728	75293	113632	188925	32827	50354	83180	227691	1247469	112440
25	955	844	721	605	295	692	7931	83018	3554	4320	5112	106432	94503	115864	210367	32827	50354	83180	227691	1247469	90998
26	913	509	908	766	355	634	3605	48513	12154	27504	792	110608	64272	138904	203176	32827	50354	83180	227691	1247469	98189
27	627	610	822	769	431	627	12927	58916	3296	27936	9360	111112	75139	148408	223547	32827	50354	83180	227691	1247469	77818
28	726	677	686	830	303	693	7828	65817	5356	36720	4536	106360	79001	147616	226617	32827	50354	83180	227691	1247469	74748
29	690	772	871	485	438	703	9682	75602	8343	6480	10368	105640	93627	122488	216115	32827	50354	83180	227691	1247469	85250
30	580	756	901	716	904	701	15347	73954	11433	20304	77472	105784	100734	203560	304294	32827	50354	83180	227691	1247469	-2929
Sum																					2075029

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