

**Kinetic Modeling of Integrated Ammonia-Urea Production
Process**

by

Ang Ben Li

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Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Ang Ben Li

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Approved by,

(Dr. Periyasamy Balasubramanian)

Universiti Teknologi PETRONAS

Tronoh, Perak

August 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(ANG BEN LI)

ABSTRACT

Ammonia and urea are among the most widely produced chemicals in the world and the study of the reaction kinetics is of great interest to the industry. While much study has been performed on the each product independently, limited focus is placed on the overall kinetic study of an integrated ammonia-urea synthesis process. Therefore, the development of a mathematical model using computer software to simulate the performance of an integrated ammonia-urea converter is the main focus of the study. The mathematical model simulated contains mass balance and energy balance equations in addition to studying the effect of varying temperature on the conversion and reaction rate. The developed model provides a good match to the industrial data used as the comparison.

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TABLE OF CONTENTS

Certification of Approval	II
Certification of Originality	III
Abstract	IV
Acknowledgement	V
Chapter 1 Introduction	1
1.1 Background	1
1.2 Problem Statement	2
1.3 Objective	3
1.4 Scope of Study	3
Chapter 2 Literature Review	4
Chapter 3 Methodology	9
3.1. Research Methodology	9
3.2. Project Activities	10
3.3. Key Milestones	18
3.4. Gantt chart	20
Chapter 4 Result and Discussion	22
4.1 Ammonia Model	22
4.2 Urea Model	36
4.3 Integration of Process	41
Chapter 5 Conclusion and recommendation	43
References	44
Appendix	46

LIST OF FIGURE

Figure 2.1: Process Flow of an ammonia synthesis process	6
Figure 2.2: Process flow for a urea synthesis process	7
Figure 3.1: Mass Balance for reactor system	11
Figure 3.2: Flow chart of project activities	19
Figure 4.1: Effectiveness factor Profile - Case 1	23
Figure 4.2: Nitrogen Fractional Conversion Profile - Case 1	23
Figure 4.3: Temperature Profile - Case 1	24
Figure 4.4: Component Mole fraction Profile - Case 1	24
Figure 4.5: Hydrogen Mole Fraction Profile - Case 1	25
Figure 4.6: Ammonia Mole Fraction Profile - Case 1	25
Figure 4.7: Effectiveness Factor Profile - Case 2	26
Figure 4.8: Nitrogen Fractional Conversion Profile - Case 2	27
Figure 4.9: Temperature Profile - Case 2	27
Figure 4.10: Component Mole fraction Profile - Case 2	28
Figure 4.11: Hydrogen Mole Fraction Profile - Case 2	28
Figure 4.12: Ammonia Mole Fraction Profile - Case 2	29
Figure 4.13: Effectiveness Factor Profile - Case 3	30
Figure 4.14: Nitrogen Fractional Conversion Profile - Case 3	31
Figure 4.15: Temperature Profile - Case 3	31
Figure 4.16: Component Mole fraction Profile - Case 3	32
Figure 4.17: Hydrogen Mole Fraction Profile - Case 3	32
Figure 4.18: Ammonia Mole Fraction Profile - Case 3	33
Figure 4.19: Urea and Ammonium Carbamate and CO ₂ Flow Rate Profile	36
Figure 4.20: Ammonia Mole Fraction Profile	37
Figure 4.21: Carbon Dioxide Mole Fraction Profile	37
Figure 4.22: Ammonium Carbamate Mole Fraction Profile	38
Figure 4.23: Urea Mole Fraction Profile	38
Figure 4.24: Water Vapour Mole Fraction Profile	39
Figure 4.25: Reactor Configuration for First Possible Process Integration Method	41
Figure 4.26: Flow Chart of Second Possible Process Integration Method	42
Figure 4.27: Flow Chart of Third Possible Process Integration Method	42

LIST OF TABLES

Table 4.1: Simulation Parameters for Case 1	22
Table 4.1: Simulation Parameters for Case 2	26
Table 4.1: Simulation Parameters for Case 3	30
Table 4.4: Industrial data of ammonia reactor	34

Chapter 1

INTRODUCTION

1.1 Background

Ammonia (NH_3) is one of the most highly produced inorganic chemicals in the world, being the largest volume chemical produced from hydrocarbon based feedstock due to and more than half of the amount of ammonia produced is used for the production of urea. Ammonia is commercially produced through the reaction between hydrogen gas (H_2) and nitrogen gas (N_2) while Urea (NH_2CONH_2) is synthesized from the reaction between ammonia and carbon dioxide. Thus, being such a major chemical product signifies a great potential for the study of reaction kinetics for both reactions. While both the ammonia and urea are traditionally carried out independently on different plants, the possibility of integrating both processes into one on an industrial scale offers the attractive feature of significant economical savings. To determine the feasibility of the integration, a conceptual study regarding the possible methods of integration is to be carried out

1.2 Problem Statement

To understand the performance of the reactor converting the raw feedstock into the ammonia and urea product would require the simulation of the reaction through the development of mathematical models that are able to satisfactorily describe the reaction process. However, majority of the currently available models describe the ammonia or urea synthesis independently and thus, the models which adequately describe the integrated synthesis are lacking. Therefore, the main focus of this study is to develop a feasible mathematical model which can describe the performance of the integrated ammonia urea production process. To formulate the simulation model would require several expressions such as the individual chemical reaction steps defined by the stoichiometric equations along with the rate equations. Additionally, reaction phase equilibrium and also thermodynamics expressions are also utilized to develop the kinetic model of the ammonia and urea production process

1.3 Objective

1. To develop a kinetic model for the production of ammonia and urea in an integrated plant
2. To investigate the performance of the kinetic model developed
3. To conduct a conceptual study of an integrated ammonia-urea production process

1.4 Scope of Study

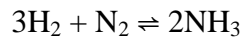
The scope covered under this conceptual kinetic model study involves:

1. Development of Mass balance equations
2. Development of Energy balance equation
3. Development of Stoichiometric equations
4. Development of Reaction rate kinetics
5. Development of Liquid-vapor system equilibrium

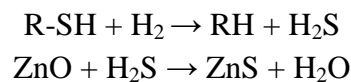
Chapter 2

LITERATURE REVIEW

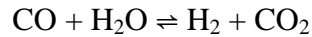
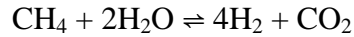
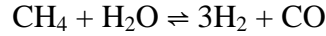
The basic ammonia reaction is the reaction between hydrogen gas and nitrogen gas to form ammonia, the stoichiometric equation is as below



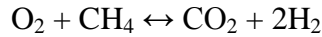
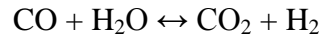
However, the feedstock to ammonia production is not just nitrogen gas and hydrogen gas. In actual fact, industrial raw feedstock of ammonia production process is natural gas and air. The natural gas is converted to synthesis gas to provide the needed hydrogen for reaction with nitrogen, which is provided by air. The conversion of hydrocarbon feedstock is performed by a process known as steam reforming. Steam reforming is the process of reacting natural gas with steam at high temperature. However, prior to performing steam reforming, the feed must first be hydrodesulfurized to remove the presence of any sulfur compounds. This is because the nickel-bearing catalysts which are used in the steam reforming process are sensitive and can be easily poisoned by the sulfur compounds. Hydrodesulfurization proceeds with the reaction as below, where R is usually a combination of cobalt-molybdenum and zinc oxide catalyst



Once the content of sulfur compound has been lowered, the natural gas feed is then passed to the primary reformer for steam reforming to take place. Here, super-heated steam is fed along with the natural gas feed which has been desulfurized. This gas mixture is then heated to 770°C. At this condition, the series of reactions below will take place with forward equilibrium



The primary reformer is only able to achieve roughly 65% conversion. The hot effluent stream leaving the primary reformer enters a secondary reformer, where it is injected with air to cause a highly exothermic reaction between oxygen and hydrocarbons, majority methane to produce more hydrogen. Notable reactions happening in the secondary reformer are as below



The natural feedstock is now converted into synthesis gas which contains hydrogen gas, carbon dioxide, carbon monoxide and water. Water and carbon oxides are a catalyst poison in the later ammonia synthesis and therefore are to be removed. The carbon oxides are removed in a process known as shift conversion while water is removed by lowering the stream temperature until it condenses to be removed.

Following the removal of water and the carbon oxides, the gas mixture of hydrogen and nitrogen is now ready to be converted into ammonia. Common ammonia converter units operate at conditions of temperatures up to 530°C and pressures ranging from 100-350bar. The formation of ammonia is a catalyzed reaction which uses iron catalysts. An ammonia reactor commonly achieves around 20-25%.

The entire process above can be illustrated by the process flow below. This ammonia synthesis process is the UDHE ammonia process, one of the many ammonia synthesis processes available. (Appl, 2007; Blanchard, Jan 11, 2011; J. C. Coplestone; Jennings, 1991)

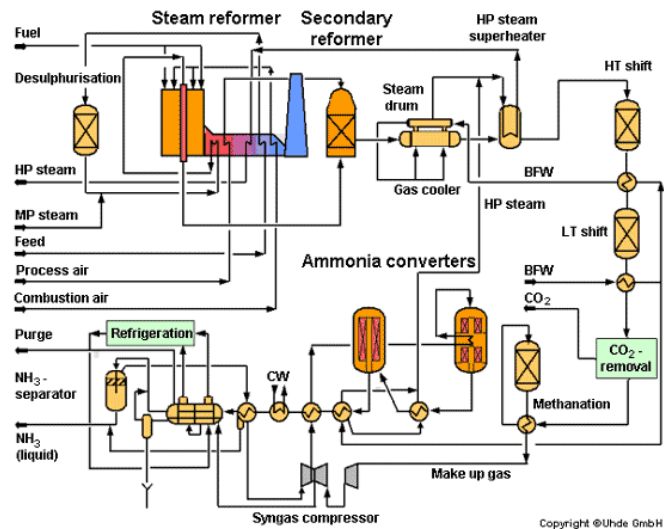
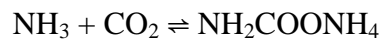


Figure 2.1: Process Flow of an ammonia synthesis process

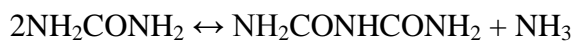
Urea synthesis on the other hand is a two-step reaction whereby in the first step, ammonia and carbon dioxide is reacted in high temperature and pressure to form ammonium carbamate. This reaction is shown below as:



The second step of the reaction to form urea is when ammonium carbamate is decomposed to form urea and water, defined by the equation below:



The decomposition of ammonium carbamate to form urea has a competing reaction in which ammonium carbamate forms biuret, an unwanted side product, described by the reaction:



The formation of biuret can be minimized by utilizing the process flow shown below

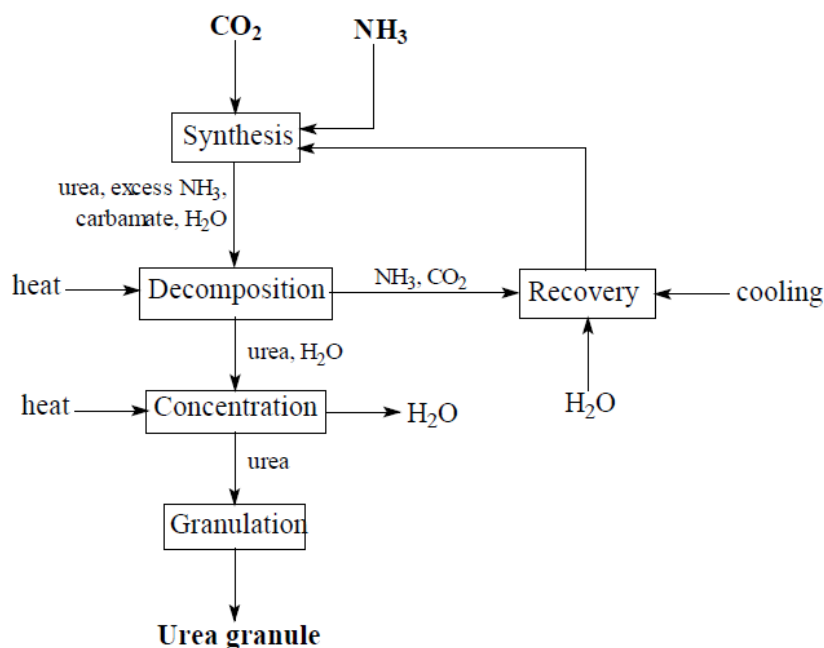


Figure 2.2: Process flow for a urea synthesis process

The formation of ammonium carbamate is fast, highly exothermic and proceeds to completion while the decomposition of ammonium carbamate is slower and is endothermic. Urea formation from ammonium carbamate also does not proceed to completion under industrial process conditions. As a result, unreacted reactants are recycled to increase the conversion. (Bhd; Snamprogetti, 10-2007; Vishnu D. Singh, Mar 30, 2010)

Once these two processes are integrated, the process flow of producing ammonia and urea slightly changes. The initial feed is then consisting of ammonia synthesis gas along with carbon dioxide. The feed would then be washed with an aqueous solution of ammonia reactant, thus removing the carbon dioxide to form the urea intermediate, ammonium carbamate. The excess ammonia will then be removed as well using water washing and removing the ammonia in aqueous form. The remainder of the feed, which now just consist of the synthesis gas for ammonia production, is passed into a converter to be reacted into ammonia. This ammonia effluent is used in the earlier mentioned carbon dioxide removal step. (Pagani & Zardi, 2003; Speth, Apr 20, 2004; Vishnu D. Singh, Mar 30, 2010)

Thus, in order to develop a model for mass balance for the reaction, we would first take a look at the rate expressions or more specifically the rate of reaction. Common standards for judging the reactor performance involves performing mass balance over the length of reactor. The mass balance is derived from the equation for rate of reaction, where the main interest is to find the change of concentration with respect to the reactor length (Butt, Jan 3 2000; Hill, October 13, 1977).

The $\frac{\Delta C}{\Delta X}$ expression is commonly derived using a modified Temkin rate expression for ammonia synthesis (Abashar, 2003; Dyson & Simon, 1968; Elnashaie, Abashar, & Al-Ubaid, 1988; Singh & Saraf, 1981). For urea synthesis, the equilibrium composition of urea along with the basic will be used to form the mass balance (Dente, Rovaglio, Bozzano, Sogaro, & Isimbaldi, 1992; Irazoqui, Isla, & Genoud, 1993; Isla, Irazoqui, & Genoud, 1993). Additional information required to complete the mass balance expression are the fugacity coefficients of the components, rate constant expression for reverse reaction, equilibrium constant and also the η effect factor, which describes the catalyst effect on the reaction. Besides the mass equations, which will provide us with the concentration profiles, the temperature and pressure profiles are also obtained by performing energy balance and momentum balance simulations respectively.

The energy balance part of the simulation model is performed by considering the temperature dependence of the heat capacities of each component and it is obtained by equating the heat of reactions to the sum of terms of sensible heat for each component.(Shah, 1967)

Chapter 3

METHODOLOGY

3.1 Research methodology

The main activities performed in this study would first be the model development of the reaction process. Once a satisfactory model is development, it would then be simulated using the MATLAB software. The model, in mathematical form would be entered into MATLAB and simulated using industry parameters. Finally, the obtained profiles would be compared to existing data to determine the model's accuracy.

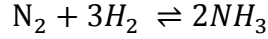
The kinetic modeling will be performed for a total of 3 configurations, which is the standalone ammonia synthesis process, the standalone urea synthesis process and finally the integrated ammonia urea synthesis process. The study of the reaction kinetics first begins with reading and studying the basic chemical reaction of the two chemical substances.

After comprehensive understanding of the reaction is obtained, the focus would then be shifted to understanding the rate laws. The rate laws would enable us to formulate the rate equation for the reaction. This expression alongside the mass balance equations will enable us to develop the model needed to simulate the reaction. Other useful expressions and equations for various parameters such as the phase equilibrium and thermodynamics will also be used in the development of the mathematical model. The mass balance equations, in addition to the energy balance would finally give us the reaction profiles of concentration and temperature to determine the performance of the integrated ammonia urea process.

3.2 Project Activities

3.2.1 Ammonia Model

The stoichiometric reaction for ammonia production is defined as



Whereby the conversion of N_2 (Limiting Reactant) is calculated by

$$X_{\text{N}_2} = \frac{F^{\circ}_{\text{N}_2} - F_{\text{N}_2}}{F^{\circ}_{\text{N}_2}}$$

β is the feed ratio of N_2 to H_2

$$\beta = \frac{F^{\circ}_{\text{N}_2}}{F^{\circ}_{\text{H}_2}}$$

The exit flow rates can be defined below

$$\begin{aligned}F_{\text{N}_2} &= F^{\circ}_{\text{N}_2} - F^{\circ}_{\text{N}_2} X_{\text{N}_2} \\F_{\text{H}_2} &= F^{\circ}_{\text{H}_2} - 3F^{\circ}_{\text{N}_2} X_{\text{N}_2} = \beta F^{\circ}_{\text{N}_2} - 3F^{\circ}_{\text{N}_2} X_{\text{N}_2} \\&= F^{\circ}_{\text{N}_2} (\beta - 3X_{\text{N}_2}) \\F_{\text{NH}_3} &= F^{\circ}_{\text{NH}_3} + 2F^{\circ}_{\text{N}_2} X_{\text{N}_2} \\F_{\text{CH}_4} &= F^{\circ}_{\text{CH}_4} \\F_{\text{Ar}} &= F^{\circ}_{\text{Ar}} \\F^{\circ}_{\text{Total}} &= F^{\circ}_{\text{N}_2} + F^{\circ}_{\text{H}_2} + F^{\circ}_{\text{NH}_3} + F^{\circ}_{\text{CH}_4} + F^{\circ}_{\text{Ar}} \\F_{\text{Total}} &= F^{\circ}_{\text{N}_2} + F^{\circ}_{\text{H}_2} + F^{\circ}_{\text{NH}_3} - 2F^{\circ}_{\text{H}_2} X_{\text{N}_2} \\&= F^{\circ}_{\text{N}_2} (1 + \beta - 2X_{\text{N}_2}) + F^{\circ}_{\text{NH}_3} + F^{\circ}_{\text{CH}_4} + F^{\circ}_{\text{Ar}}\end{aligned}$$

The mole fraction can then be calculated from flow rates

$$\begin{aligned}Y_{\text{N}_2} &= \frac{F^{\circ}_{\text{N}_2} - F^{\circ}_{\text{N}_2} X_{\text{N}_2}}{F^{\circ}_{\text{Total}}} \\Y_{\text{H}_2} &= \frac{\beta F^{\circ}_{\text{N}_2} - 3F^{\circ}_{\text{N}_2} X_{\text{N}_2}}{F^{\circ}_{\text{Total}}} \\Y_{\text{NH}_3} &= \frac{F^{\circ}_{\text{NH}_3} + 2F^{\circ}_{\text{N}_2} X_{\text{N}_2}}{F^{\circ}_{\text{Total}}} \\Y_{\text{CH}_4} &= \frac{F^{\circ}_{\text{CH}_4}}{F^{\circ}_{\text{Total}}} & Y_{\text{Ar}} &= \frac{F^{\circ}_{\text{Ar}}}{F^{\circ}_{\text{Total}}}\end{aligned}$$

The mass balance performed over a volume of the reactor

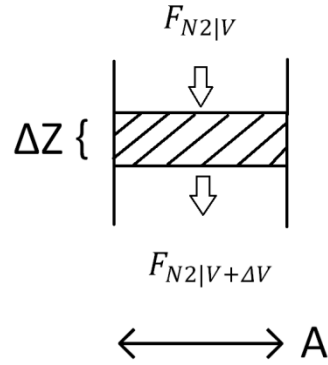


Figure 3.1: Mass balance for reactor system

$$F_{N2|V} - F_{N2|V+\Delta V} + V(r_{N2})\eta = 0$$

$$\lim_{\Delta V \rightarrow 0} \frac{F_{N2|V+\Delta V} - F_{N2|V}}{\Delta V} = \frac{dF_{N2}}{dV} = (r_{N2})\eta$$

$$\frac{dF_{NH3}}{dV} = -F_{N2}^o \frac{dX}{dV} = -\frac{1}{2}(r_{NH3})\eta$$

$$\frac{dX}{dV} = \frac{(r_{NH3})\eta}{2F_{N2}^o}$$

From the mass balance, the expression for Ammonia rate of formation can be expressed by the modified Temkin's equation

$$r_{NH3} = 2k \left[K_a^2 a_{N2} \left(\frac{a_{H2}^3}{a_{NH3}^2} \right)^\alpha - \left(\frac{a_{NH3}^2}{a_{H2}^3} \right)^{1-\alpha} \right]$$

Where k = Rate constant of reverse reaction

K_a = Equilibrium constant

a = Activity coefficient

α = Constant of value 0.5 to 0.75

The rate constant in the Temkin's equation is expressed by Arrhenius Equation

$$k = A e^{-\frac{Ea}{RT}}$$

Where A, the pre-exponential factor can be calculated using the expression

$$A = \frac{K_B T}{w} e^{\frac{\Delta S^\ddagger}{R}}$$

To determine the entropy we make use of the Yamada and Cunn (1973) correlation to calculate the molar volume

$$V_M = V_c(0.29056 - 0.08775w)^{\left(1 - \frac{T}{\eta}\right)^{\frac{2}{7}}}$$

The molar volume will then be used to calculate the absolute translational entropy using the Sackur-Tetrude equation

$$S^o_{tr} = R \ln \left(\frac{V_M}{N_a} \left(\frac{2\pi(Mw/N_A)K_B T}{h^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2}R$$

$$\Delta S^4 = \frac{1}{3}S^o_{tr}$$

The equilibrium constant can be expressed by Beattie & Gillespie equation

$$\log_{10}K_a = -2.691122\log_{10}T - 5.519265 \times 10^{-5}T + 1.848863 \times 10^{-7}T^2 + \frac{2001.6}{T} + 2.6899$$

Calculation of the Activity Coefficient using equations of state for temkins equation

$$a_{(N_2/H_2/NH_3)} = \frac{f_i}{f_i^*}$$

$$a_i = f_i = y_i \phi_i P$$

$$\phi_i P = f_i^* \text{ at reference pressure of 1 atm}$$

Where f_i = fugacity of component i

f_i^* = fugacity of component I at reference state

ϕ_i = fugacity coefficient

$$\gamma_{N_2} = 0.93431737 + 0.3101804 \times 10^{-3}T + 0.295836 \times 10^{-3}P - 0.2707279 \times 10^{-6}T^2 + 0.4775207 \times 10^{-6}P^2$$

$$\gamma_{H_2} = e^{e^{-3.8402T^{0.125} + 0.541P^2 - e^{-0.1263T^{0.5} - 15.980P^2 + 300}e^{-0.011901T - 5.941}e^{-\frac{P}{300}}^{-1}}$$

$$\gamma_{NH_3} = 0.1438996 + 0.2028538 \times 10^{-2}T - 0.4487682 \times 10^{-3}P - 0.1142945 \times 10^{-5}T^2 + 0.2761216 \times 10^{-6}P^2$$

η effect factor, which describes the effect of the catalyst is approximated by

$$\frac{d^2 x_i}{dz^2} - \left(\frac{2}{v_i + 2x_i} \right) \left(\frac{dx_i}{dz} \right)^2 + \frac{2}{z} \frac{dx_i}{dz} = - \frac{R^2}{C D_{ie}} (v_i + 2x_i)$$

Where $i = N_2, H_2, NH_3, CH_4, Ar$

$$C = \sum_{c=1}^n \frac{f_i}{RT}$$

The value of D_{ie} can be calculated using the Maxwell-Stefan diffusion equation given below

$$D_i^o = \frac{1}{\sum_{j=1, j \neq i}^n \frac{n}{d_{j,i}^o} \left(x_{j,i} - x_{i,j} \frac{Z_j}{Z_i} \right)}$$

Where $Z_1 = 0.5$

$$Z_2 = 1.5$$

$$Z_3 = -1$$

$$D_i = D_i^o \left(\frac{T}{273} \right)^{1.75} \frac{1}{P}$$

$$D_{ie} = \frac{1}{2} \Theta D_i$$

Following which the effectiveness factor can be calculated by

$$\eta = \frac{3 \left(-\frac{dx_3}{dz} \right) |_{x=1}}{\left(\frac{R^2}{C D_{3e}} \right) 2(1 + x_{3,g}) \frac{r_{NH_3}}{1 - \varepsilon}}$$

Energy Balance

At a steady state, the energy conservation is such that the summation of the energy input, energy output and energy consumed is zero.

$$F_T C p_{mix} T|_v - F_T C p_{mix} T|_{v+\Delta v} + (-\Delta H_r) r_{NH_3} \gamma \Delta v = 0$$

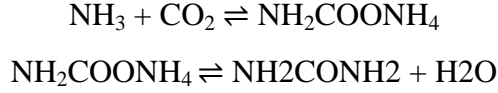
$$\lim_{\Delta v \rightarrow 0} \frac{-(F_T C p_{mix} T|_{v+\Delta v} - F_T C p_{mix} T|_v)}{\Delta v} = -(-\Delta H_r) r_{NH_3} \gamma \Delta v$$

$$F_T C p_{mix} \frac{dT}{dv} = -(-\Delta H_r) r_{NH_3} \gamma \Delta v$$

$$\frac{dT}{dv} = \frac{-(-\Delta H_r) r_{NH_3} \gamma \Delta v}{F_T C p_{mix}}$$

3.2.2. Urea Model

Following the ammonia model is the urea model, in which the stoichiometric chemical reaction is as below:



Conversion of the two individual reactions can be combined to determine the overall conversion

$$\text{Reaction 1: } \varepsilon_1 = \frac{F_{\text{carbamate}} + F_{\text{urea}}}{F^{\circ}_{\text{carbamate}} + F^{\circ}_{\text{urea}} + F^{\circ}_{\text{CO}_2}}$$

$$\text{Reaction 2: } \varepsilon_2 = \frac{F_{\text{urea}}}{F_{\text{carbamate}} + F_{\text{urea}}}$$

$$\text{Overall: } \varepsilon = \frac{F_{\text{urea}}}{F^{\circ}_{\text{carbamate}} + F^{\circ}_{\text{urea}} + F^{\circ}_{\text{CO}_2}}$$

The flow rate can be expressed in terms of a (ammonia feed ratio), b (water feed ratio), and the overall conversion

$$a = \frac{F^{\circ}_{\text{NH}_3}}{F^{\circ}_{\text{carbamate}} + F^{\circ}_{\text{urea}} + F^{\circ}_{\text{CO}_2}}$$

$$b = \frac{F^{\circ}_{\text{H}_2\text{O}}}{F^{\circ}_{\text{carbamate}} + F^{\circ}_{\text{urea}} + F^{\circ}_{\text{CO}_2}}$$

$$F^{\circ}_{\text{Total}} = F^{\circ}_{\text{NH}_3} + F^{\circ}_{\text{carbamate}} + F^{\circ}_{\text{urea}} + F^{\circ}_{\text{CO}_2} + F^{\circ}_{\text{H}_2\text{O}}$$

$$F_{\text{carbamate}} = \varepsilon_1 - \varepsilon (F^{\circ}_{\text{carbamate}} + F^{\circ}_{\text{urea}} + F^{\circ}_{\text{CO}_2})$$

$$F_{\text{urea}} = \varepsilon (F^{\circ}_{\text{carbamate}} + F^{\circ}_{\text{urea}} + F^{\circ}_{\text{CO}_2})$$

$$F_{\text{NH}_3} = a - 2\varepsilon_1 (F^{\circ}_{\text{carbamate}} + F^{\circ}_{\text{urea}} + F^{\circ}_{\text{CO}_2})$$

$$F_{\text{CO}_2} = 1 - \varepsilon_1 (F^{\circ}_{\text{carbamate}} + F^{\circ}_{\text{urea}} + F^{\circ}_{\text{CO}_2})$$

$$F_{\text{H}_2\text{O}} = b + \varepsilon (F^{\circ}_{\text{carbamate}} + F^{\circ}_{\text{urea}} + F^{\circ}_{\text{CO}_2})$$

$$F_{\text{Total}} = F_{\text{NH}_3} + F_{\text{carbamate}} + F_{\text{urea}} + F_{\text{CO}_2} + F_{\text{H}_2\text{O}}$$

$$= (1 + a + b - 2\varepsilon_1 + \varepsilon) (F^{\circ}_{\text{carbamate}} + F^{\circ}_{\text{urea}} + F^{\circ}_{\text{CO}_2})$$

$$F_N = (1 + a + b - 2\varepsilon_1 + \varepsilon)$$

The mole fractions with the use of conversion, a and b can also be expressed similarly

$$X_{\text{carbamate}} = \frac{\varepsilon_1 - \varepsilon}{F_N}$$

$$X_{\text{urea}} = \frac{\varepsilon}{F_N}$$

$$X_{\text{NH}_3} = \frac{a - 2\varepsilon_1}{F_N}$$

$$X_{\text{CO}_2} = \frac{1 - \varepsilon_1}{F_N}$$

$$X_{\text{H}_2\text{O}} = \frac{b + \varepsilon}{F_N}$$

Rate of reaction expression for 3 components

$$\begin{aligned} r_{\text{CO}_2} &= -k_{1F}[\text{C}_{\text{NH}_3}]^2[\text{C}_{\text{CO}_2}] + k_{1R}[\text{C}_{\text{carbamate}}] \\ &= -k_{1F} \left([\text{C}_{\text{NH}_3}]^2[\text{C}_{\text{CO}_2}] - \frac{[\text{C}_{\text{carbamate}}]}{k_1} \right) \end{aligned}$$

$$\begin{aligned} r_{\text{carbamate}} &= k_{1F}[\text{C}_{\text{NH}_3}]^2[\text{C}_{\text{CO}_2}] - k_{1R}[\text{C}_{\text{carbamate}}] - k_{2F}[\text{C}_{\text{carbamate}}] \\ &\quad + k_{2R}[\text{C}_{\text{urea}}][\text{C}_{\text{H}_2\text{O}}] \\ &= k_{1F} \left([\text{C}_{\text{NH}_3}]^2[\text{C}_{\text{CO}_2}] - \frac{[\text{C}_{\text{carbamate}}]}{k_1} \right) - k_{2F} \left([\text{C}_{\text{carbamate}}] \right. \\ &\quad \left. - \frac{[\text{C}_{\text{urea}}][\text{C}_{\text{H}_2\text{O}}]}{k_2} \right) \end{aligned}$$

$$\begin{aligned} r_{\text{urea}} &= k_{2F}[\text{C}_{\text{carbamate}}] - k_{2R}[\text{C}_{\text{urea}}][\text{C}_{\text{H}_2\text{O}}] \\ &= k_{2F} \left([\text{C}_{\text{carbamate}}] - \frac{[\text{C}_{\text{urea}}][\text{C}_{\text{H}_2\text{O}}]}{k_2} \right) \end{aligned}$$

Where rate constant $k_i = \frac{k_{iF}}{k_{iR}}$

Mass Balance of urea is obtained when performed over a volume of the reactor

$$\begin{aligned} F_{\text{urea}|Z} - F_{\text{urea}|Z+\Delta Z} + A\Delta Z(r_{\text{urea}}) &= 0 \\ \lim_{\Delta Z \rightarrow 0} \frac{F_{\text{urea}|Z+\Delta Z} - F_{\text{urea}|Z}}{\Delta Z} &= \frac{dF_{\text{urea}}}{dZ} = A(r_{\text{urea}}) \\ \frac{dF_{\text{urea}}}{dV} = r_{\text{urea}} &= k_{2F} \left([\text{C}_{\text{carbamate}}] - \frac{[\text{C}_{\text{urea}}][\text{C}_{\text{H}_2\text{O}}]}{k_2} \right) \end{aligned}$$

$$\frac{dF_{\text{carbamate}}}{dV} = r_{\text{carbamate}} = k_{1F} \left([C_{\text{NH}_3}]^2 [C_{\text{CO}_2}] - \frac{[C_{\text{carbamate}}]}{k_1} \right) - k_{2F} \left([C_{\text{carbamate}}] - \frac{[C_{\text{urea}}][C_{\text{H}_2\text{O}}]}{k_2} \right)$$

Similar with the ammonia mass balance, rate constant is determined by Arrhenius Equation

$$k = k_0 e^{-\frac{Ea}{RT}}$$

The liquid vapour equilibrium is expressed by the following equation of state

$$Py_i \phi_i = f_i^o X_i \gamma_i$$

Where the saturated vapour pressure is determined using the Clasius-Clapeyron equation

$$\begin{aligned} \ln(P_{s,\text{NH}_3}) &= -\frac{25.07}{T} + 56.321 \ln(T) - 0.2625T + \frac{1.753 \times 10^{-4}}{T^{-2}} - 258.139 \\ \ln(P_{s,\text{CO}_2}) &= -\frac{2370.26}{T} + 0.5911 \ln(T) - 1.178 \times 10^{-2}T + \frac{1.598 \times 10^{-5}}{T^{-2}} + 15.272 \\ \ln(P_{s,\text{H}_2\text{O}}) &= -\frac{5231.82}{T} - 6.167 \times 10^{-2} \ln(T) - 3.291 \times 10^{-3}T + \frac{1.222 \times 10^{-6}}{T^{-2}} \\ &\quad + 13.183 \end{aligned}$$

The fugacity coefficient is determined using the Redlich –Kwong equation by solving for Z

$$\ln(\hat{\phi}_i) = \left(\frac{B_i}{B}\right)(Z - 1) - \ln(Z - B) + \left(\frac{A}{B}\right) \left(\frac{B_i}{B} - Z \sqrt{\frac{A_i}{A}}\right) \ln\left(1 + \frac{B}{Z}\right)$$

$$A = \left(\sum y_i \sqrt{A_i}\right)^2$$

$$B = \sum y_i B_i$$

$$A_i = 0.42748 \frac{P_{i,\text{reduced}}}{T_{i,\text{reduced}}^{2.5}}$$

$$B_i = 0.08664 \frac{P_{i,\text{reduced}}}{T_{i,\text{reduced}}}$$

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$$

Estimation of the activity coefficient starts from determining the chemical equilibrium degree η using the conversion value and the equilibrium conversion

$$\eta = \frac{\varepsilon}{\varepsilon^*}$$

$$\begin{aligned} \varepsilon^* = & -3.4792 + 8.2677x10^{-1}a - 1.8998x10^{-2}a^2 - 2.3155x10^{-1}b \\ & - 1.144x10^{-1}\left(\frac{T}{100}\right) + 2.9879x10^{-2}ab - 1.3294x10^{-1}a\left(\frac{T}{100}\right) \\ & + 4.5348x10^{-1}\left(\frac{T}{100}\right)^2 - 5.5339x10^{-2}\left(\frac{T}{100}\right)^3 \end{aligned}$$

When the chemical equilibrium degree is determined, the activity coefficient can be calculated

$$\begin{aligned} \gamma_{NH_3} = & 0.3960 - 2.8447x10^{-3}T + 0.6111a - 0.2740a\eta + 0.8800\eta + 0.0680a^2 \\ & - 0.24894x10^{-4}Ta^2 \end{aligned}$$

$$\begin{aligned} \gamma_{CO_2} = & 0.6082 + 3.5532x10^{-4}T - 0.3681a + 0.1114b + 3.7508x10^{-4}Ta\eta \\ & - 0.10245a\eta - 4.8257x10^{-2}a^2 \end{aligned}$$

$$\gamma_{H_2O} = 22.6745 - 1.5546x10^{-2}T - 4.0697a + 2.0369\eta^2 - 15.8744\eta + 4a\eta$$

3.3 Key milestones

The key milestones in achieving the objectives of the modeling study are as follow:

1. Project title selection
2. Identifying project objective and problem statement
3. Performing literature review
4. Designing the approach to modeling
5. Develop Mathematical model for simulation
6. Input the model into MATLAB software
7. Run simulation of model using industry parameters
8. Analysis of results
9. Documentation

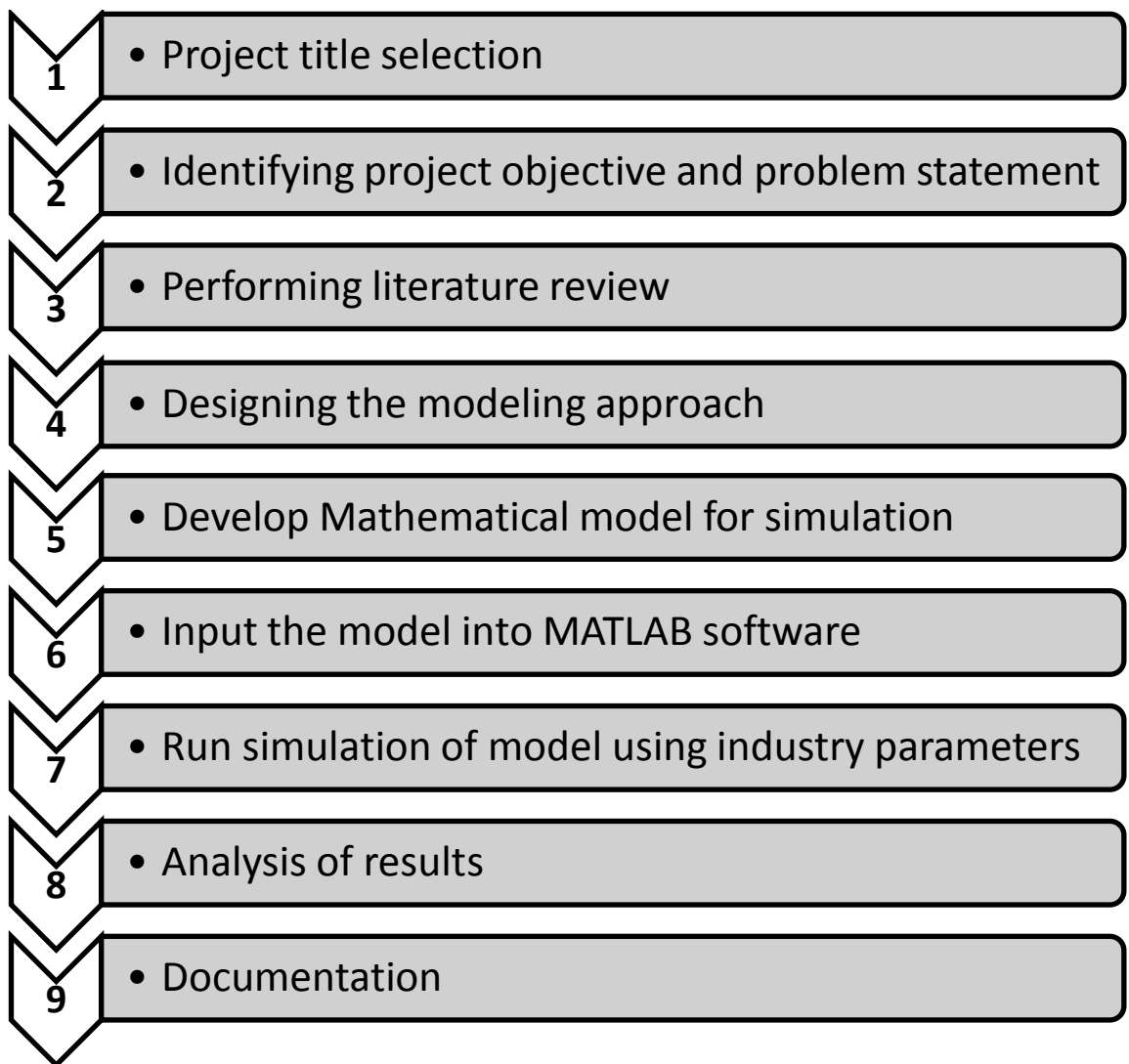


Figure 3.2: Flow chart of project activity

4.3 Gantt chart

NO	DETAIL	WEEK														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	
1	Selection of Project Topic	■	■													
2	Preliminary Research Work		■	■	■	■										
3	Submission of Extended Proposal Defense						•									
4	Proposal Defense									■	■					
5	Project Work Continues											■	■	■		
6	Submission of Interim Draft Report														•	
7	Submission of Interim Report															•

• Suggested Milestone

■ Process

NO	DETAIL	WEEK															
		1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues																
2	Submission of Progress Report								•								
3	Project Work Continues																
4	Pre-Sedex																
5	Submission of Draft Report																
6	Submission of Dissertation (Soft Bound)																
7	Submission of Technical Paper																
8	Oral Presentation																
9	Submission of Project Dissertation (Hard Bound)																

• Suggested Milestone

■ Process

Chapter 4

RESULTS AND DISCUSSION

4.1. Ammonia Model

The individual model for ammonia and urea production process has been developed into a suitable mathematical form for simulation in MATLAB. Simulation has been performed to determine the reactor performance for both the ammonia and urea production process using industrial condition to obtain the concentration profiles shown below. The simulation was carried using 3 different sets of reactor data and the results are as follow:

4.1.1. Case 1

Table 4.1: Simulation Parameters for Case 1

Total Feed Flow(Nm ³ /h)	242160				
Pressure (atm)	226				
Reactor Bed Volume Span (m ³)	4.75	7.2	7.8		
Feed Composition	N ₂	H ₂	NH ₃	CH ₄	Ar
	0.2219	0.6703	0.0276	0.0546	0.0256

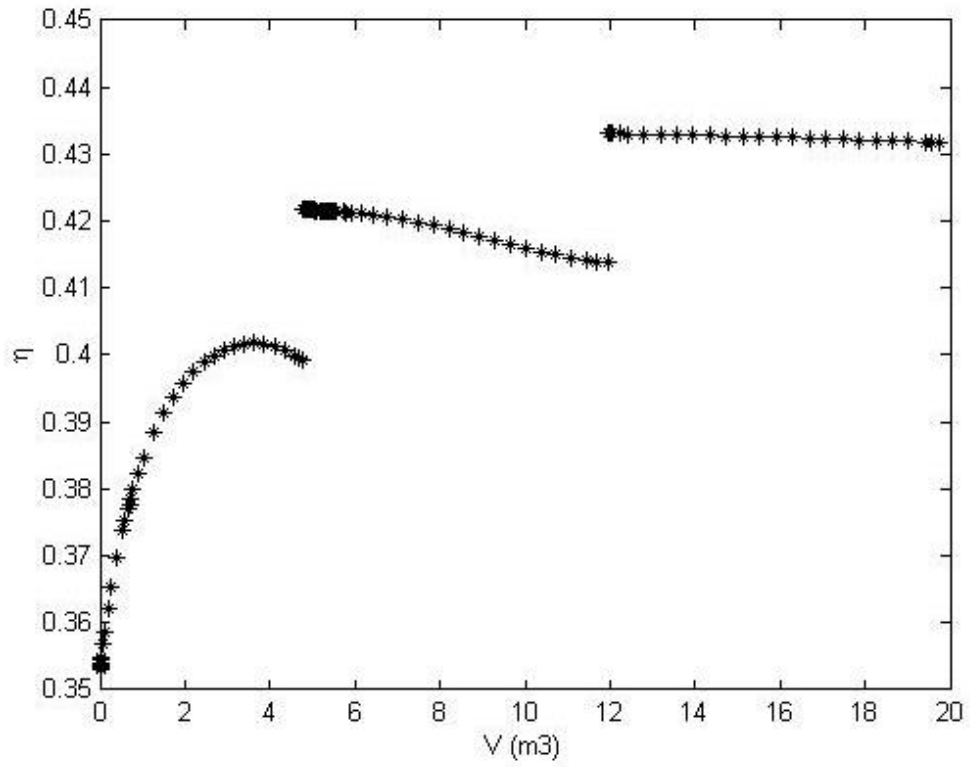


Figure 4.1: Effectiveness Factor Profile - Case 1

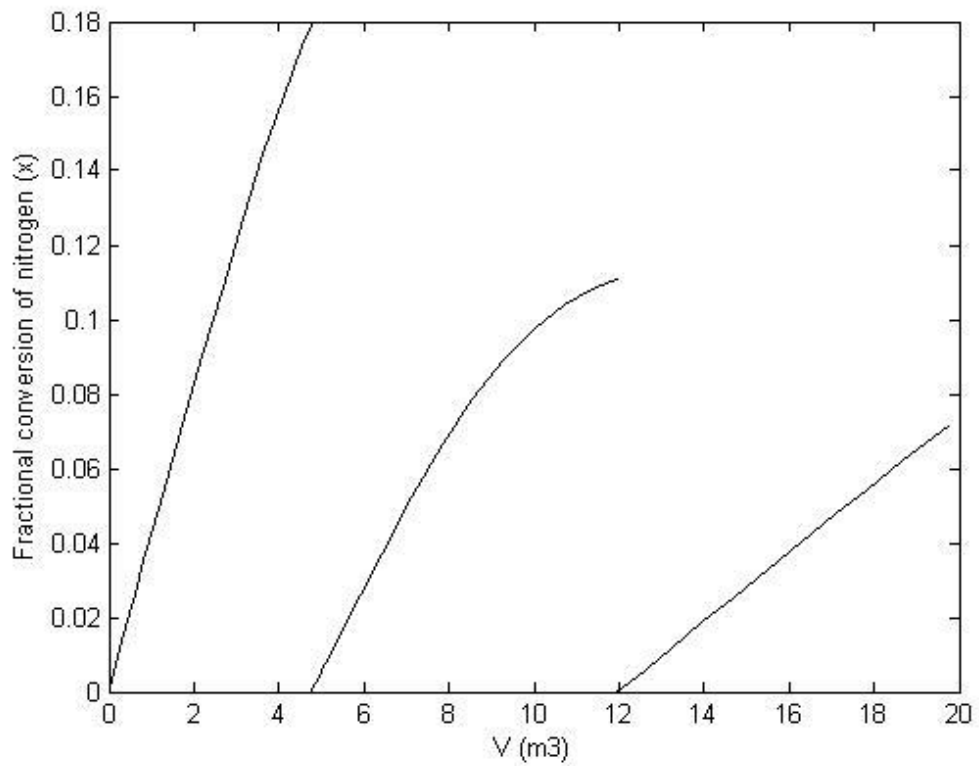


Figure 4.2: Nitrogen Fractional Conversion Profile - Case 1

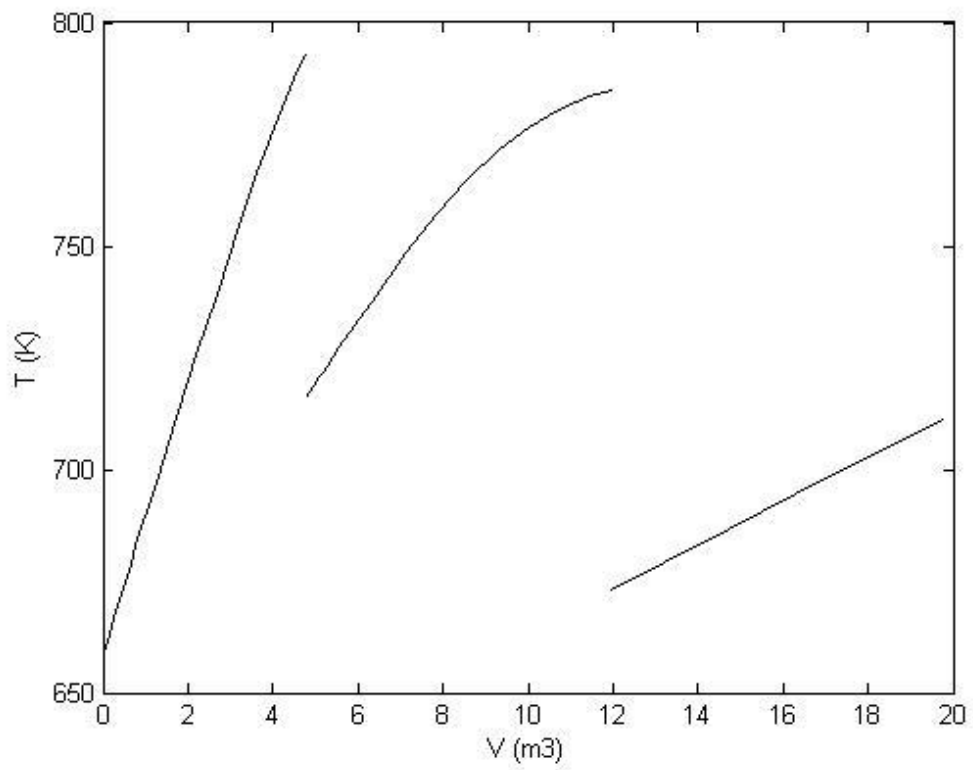


Figure 4.3: Temperature Profile - Case 1

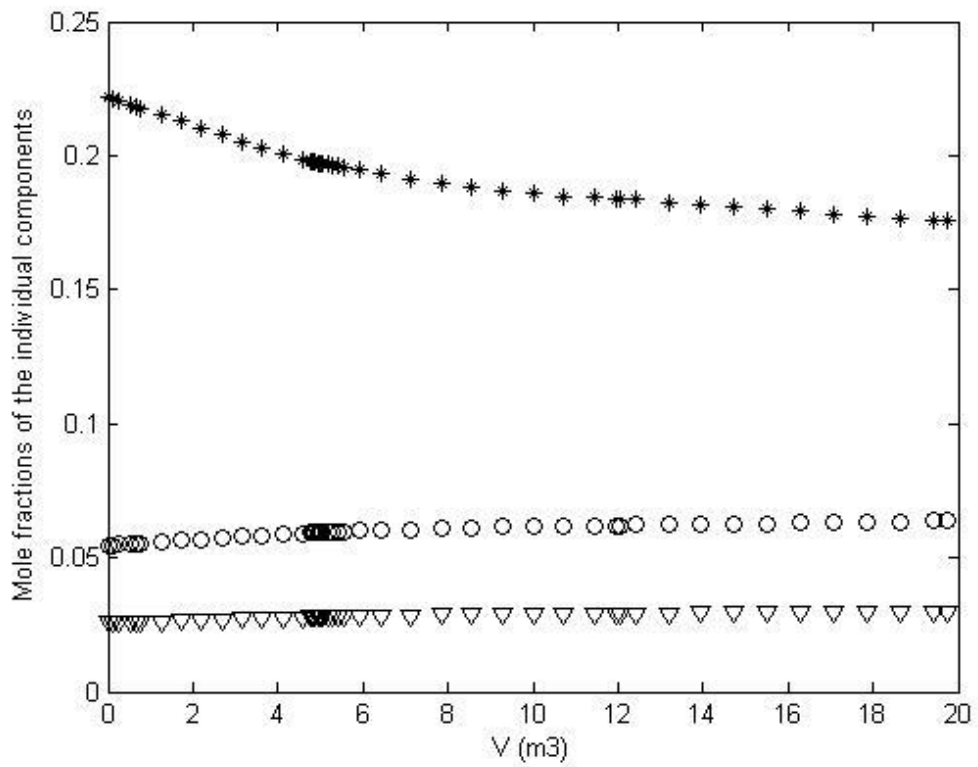


Figure 4.4: Component Mole Fraction Profile - Case 1

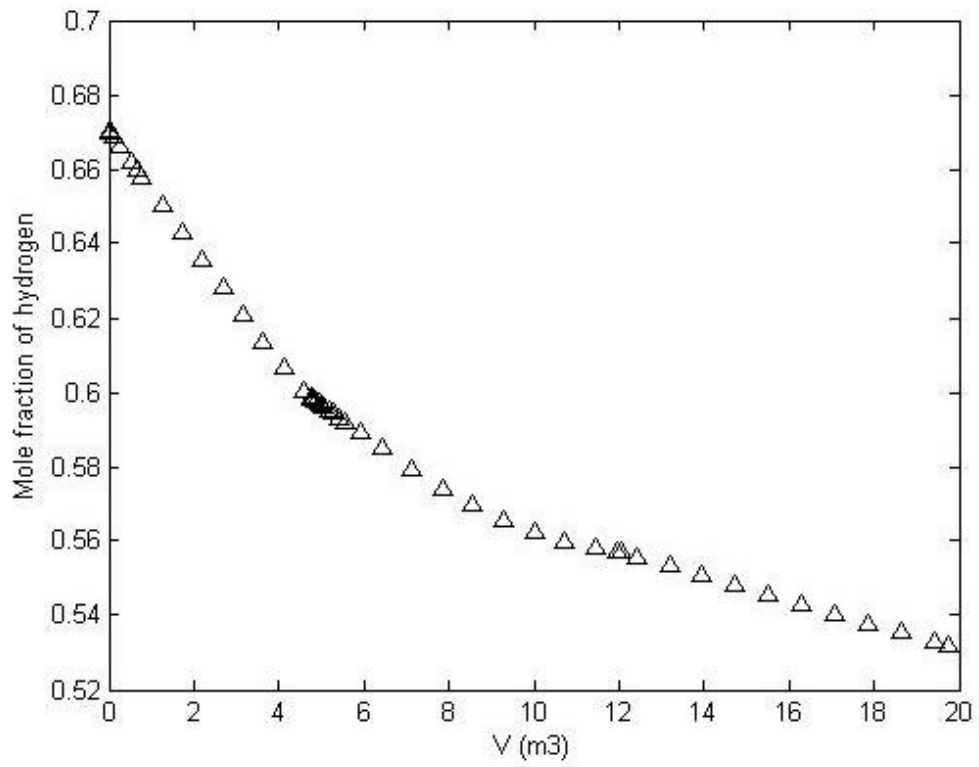


Figure 4.5: Hydrogen mole fraction Profile - Case 1

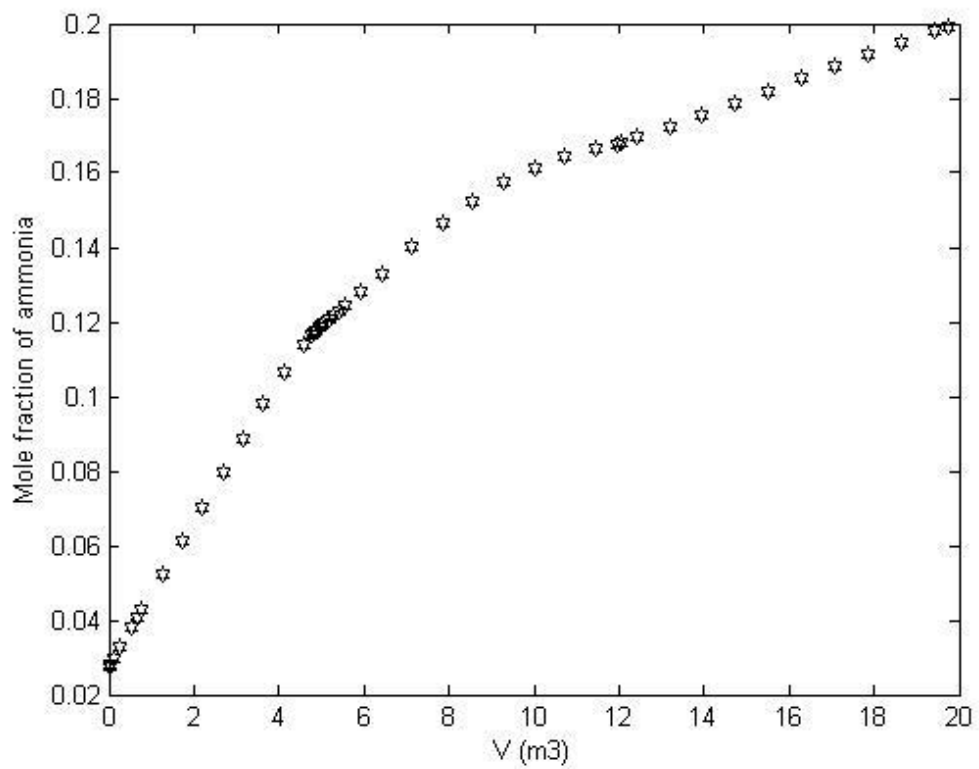


Figure 4.6: Ammonia Mole Fraction Profile - Case 1

4.1.2. Case 2

Table 4.2: Simulation Parameters for Case 2

Total Feed Flow(Nm ³ /h)	180000				
Pressure (atm)	177				
Reactor Bed Volume Span (m ³)	5.05	7.12	8.1		
Feed Composition	N ₂	H ₂	NH ₃	CH ₄	Ar
	0.1960	0.6510	0.0320	0.0740	0.0470

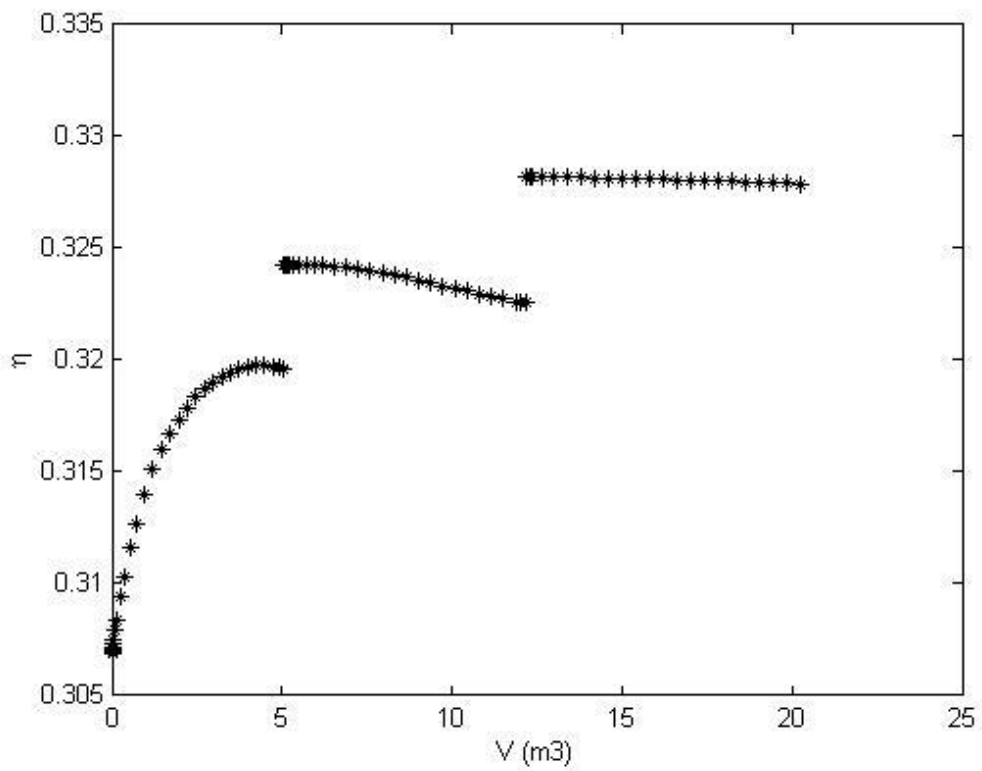


Figure 4.7: Effectiveness Factor Profile - Case 2

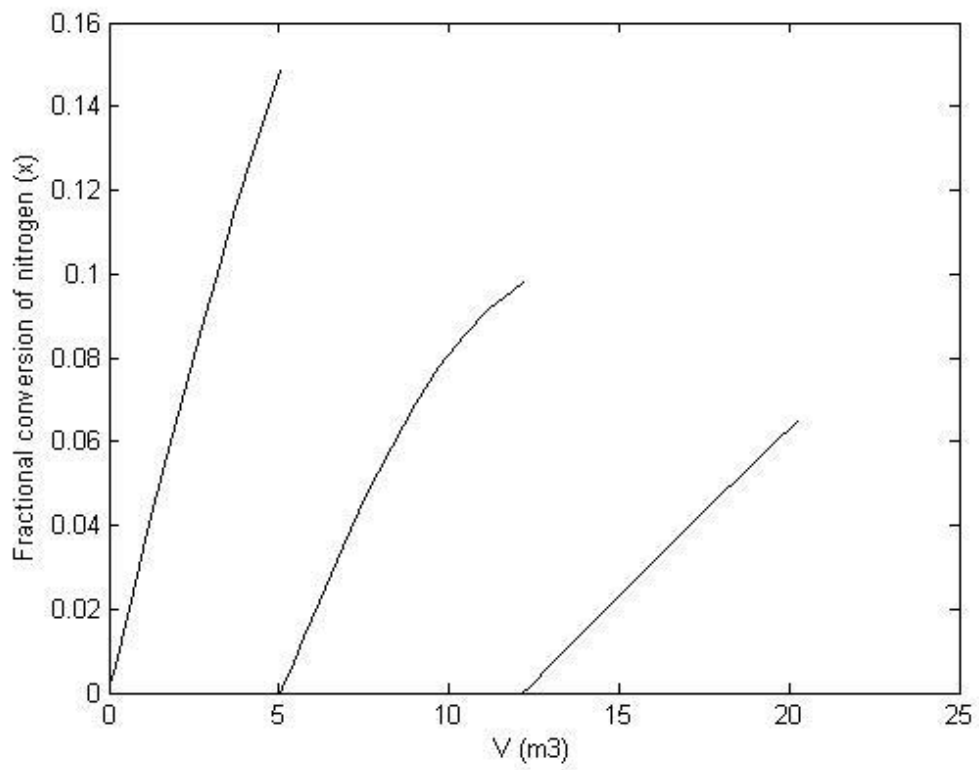


Figure 4.8: Nitrogen Fractional Conversion Profile - Case 2

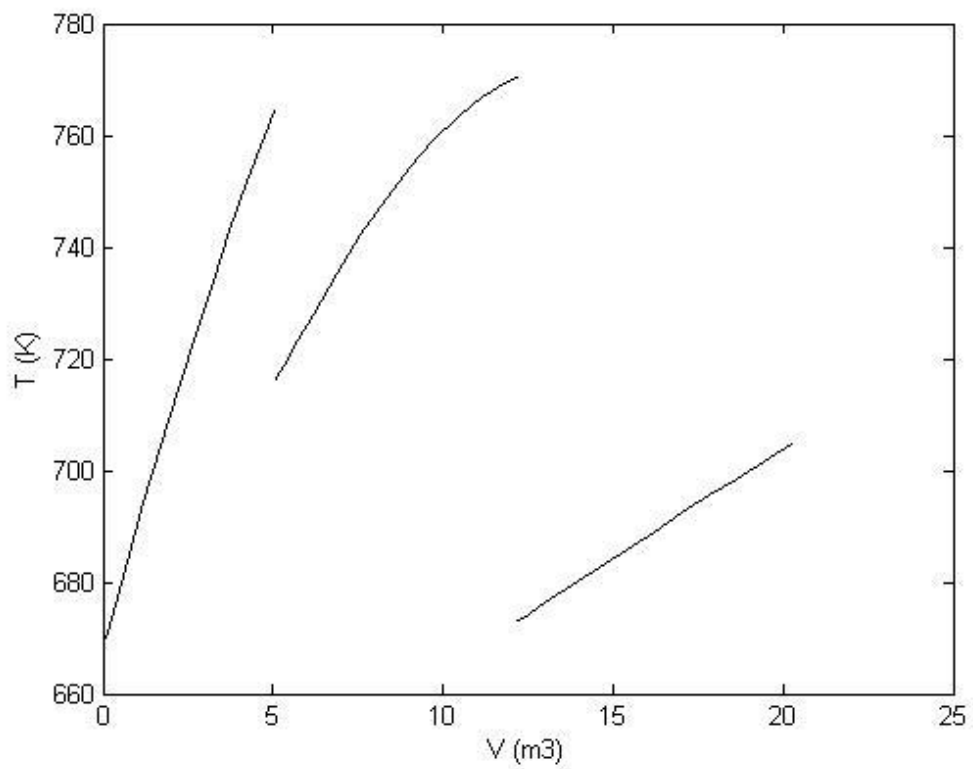


Figure 4.9: Temperature Profile - Case 2

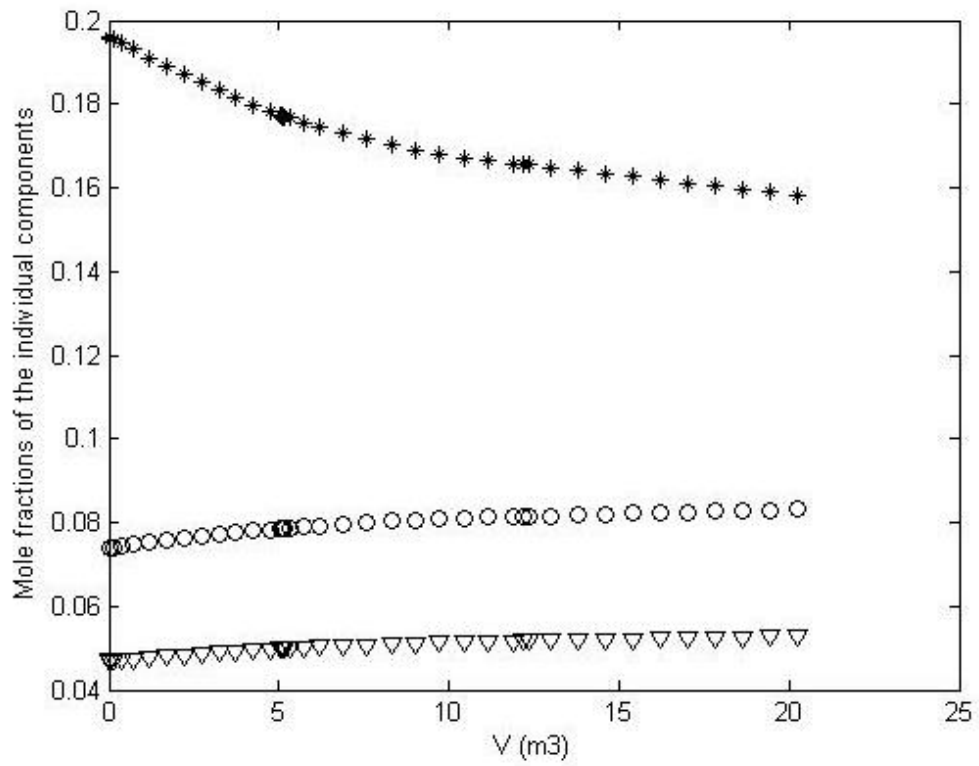


Figure 4.10: Component Mole Fraction Profile - Case 2

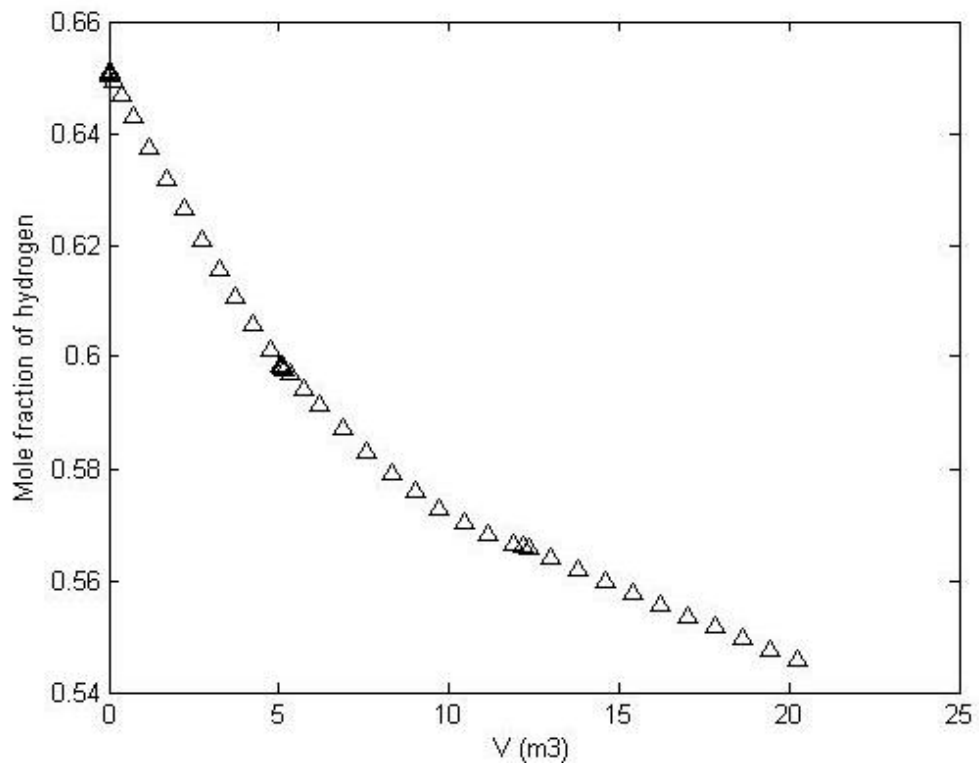


Figure 4.11: Hydrogen Mole Fraction Profile - Case 2

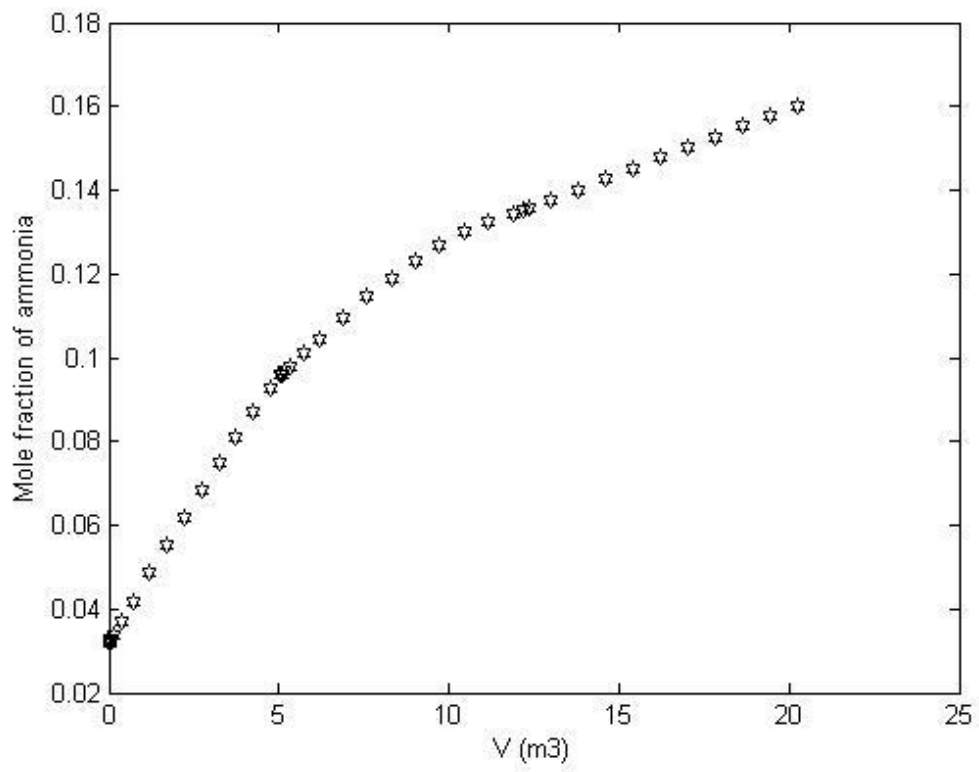


Figure 4.12: Ammonia Mole Fraction Profile – Case 2

4.1.3. Case 3

Table 4.3: Simulation Parameters for Case 3

Total Feed Flow(Nm ³ /h)	195000				
Pressure (atm)	207				
Reactor Bed Volume Span (m ³)	5.25	7.35	8.3		
Feed Composition	N ₂	H ₂	NH ₃	CH ₄	Ar
	0.2060	0.6510	0.0320	0.0730	0.0380

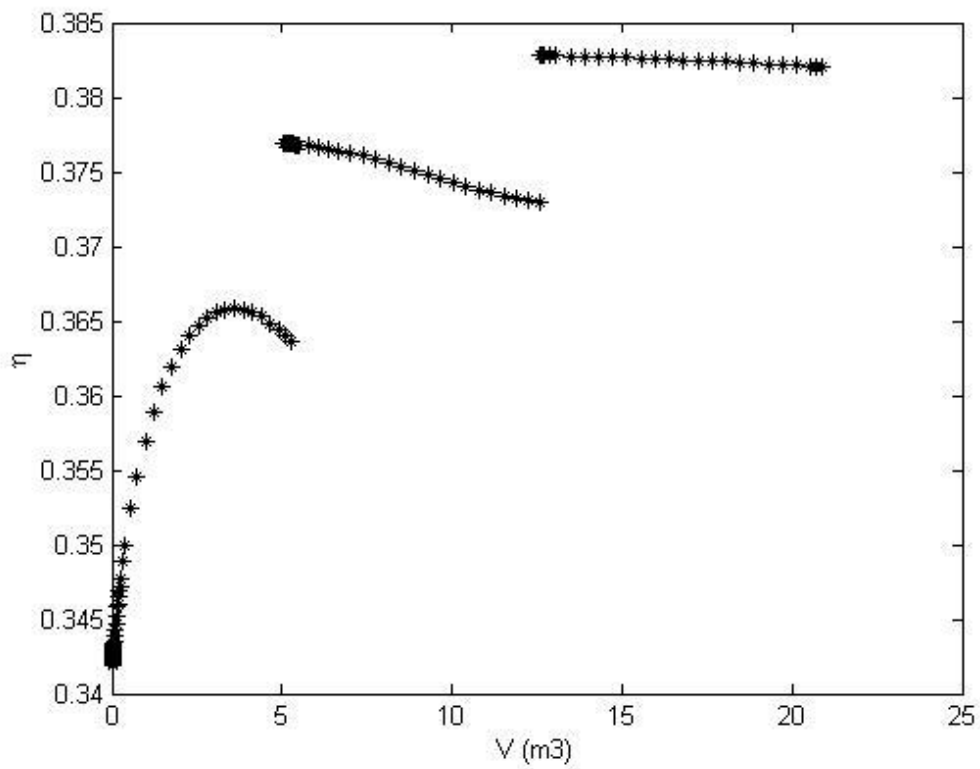


Figure 4.13: Effectiveness Factor Profile – Case 3

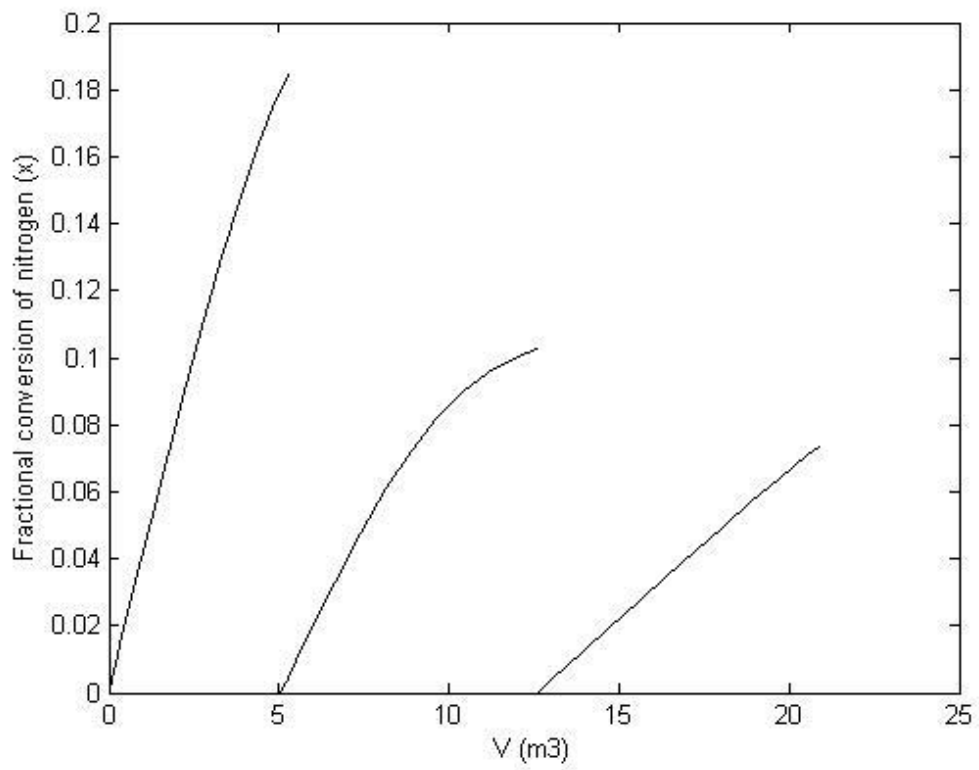


Figure 4.14: Nitrogen Fractional Conversion Profile – Case 3

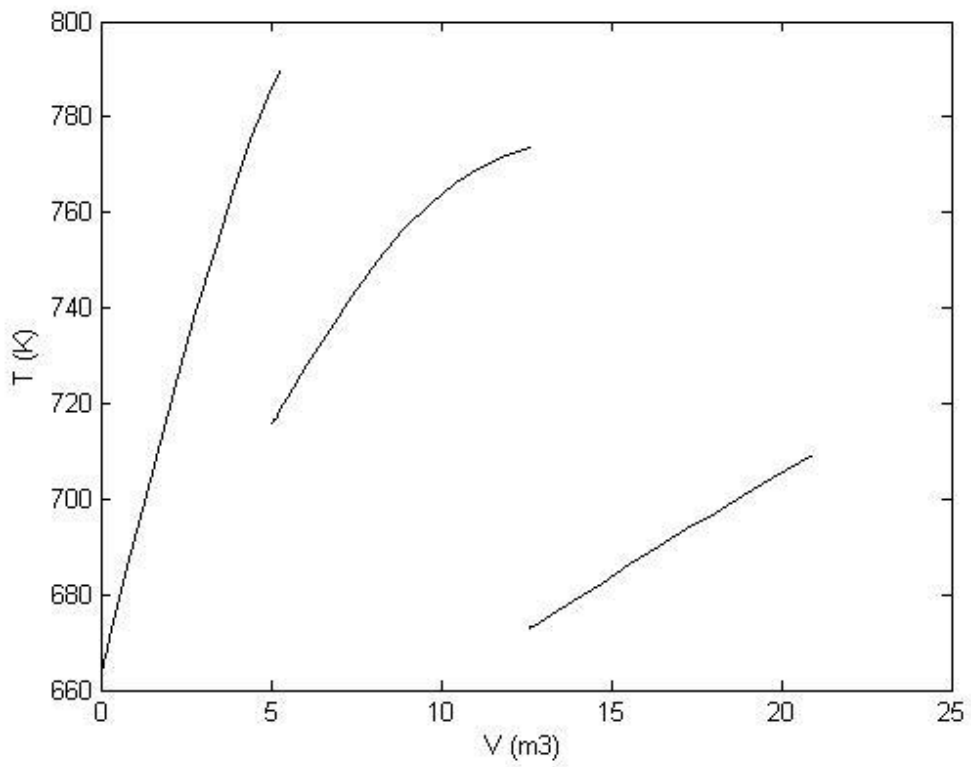


Figure 4.15: Temperature Profile – Case 3

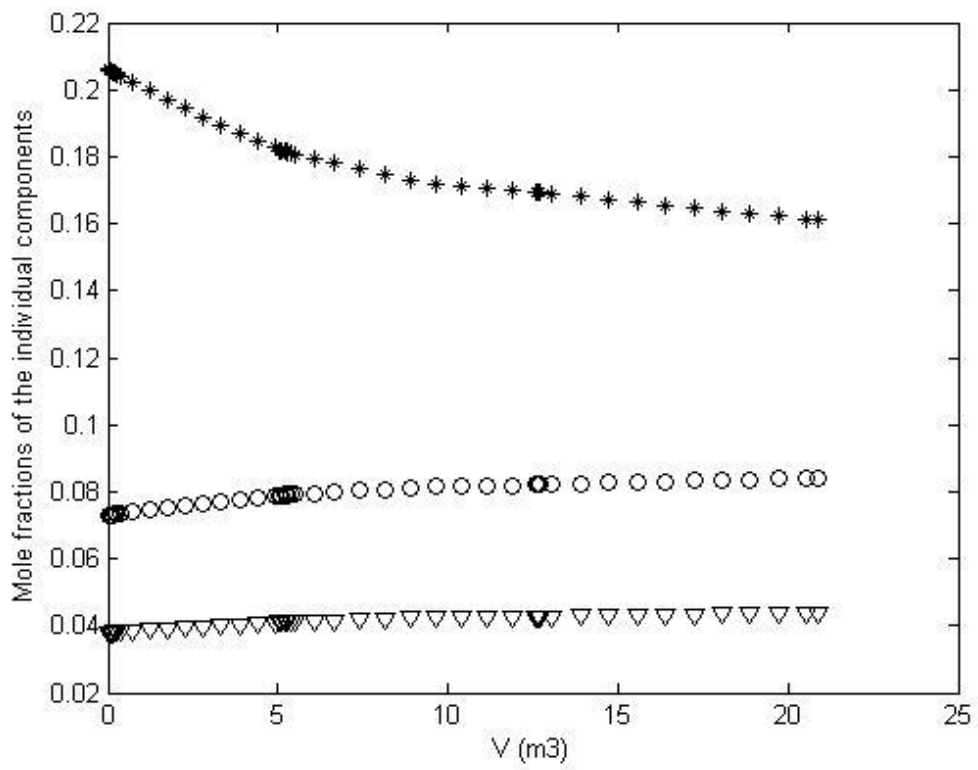


Figure 4.16: Component Mole Fraction Profile – Case 3

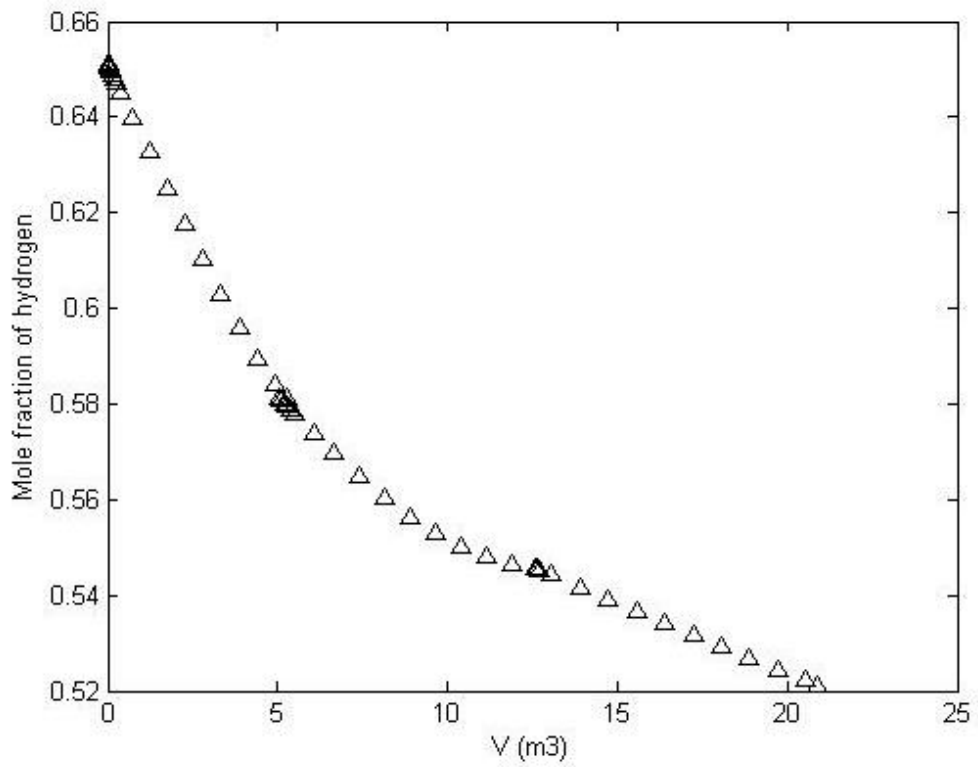


Figure 4.17: Hydrogen Mole Fraction Profile – Case 3

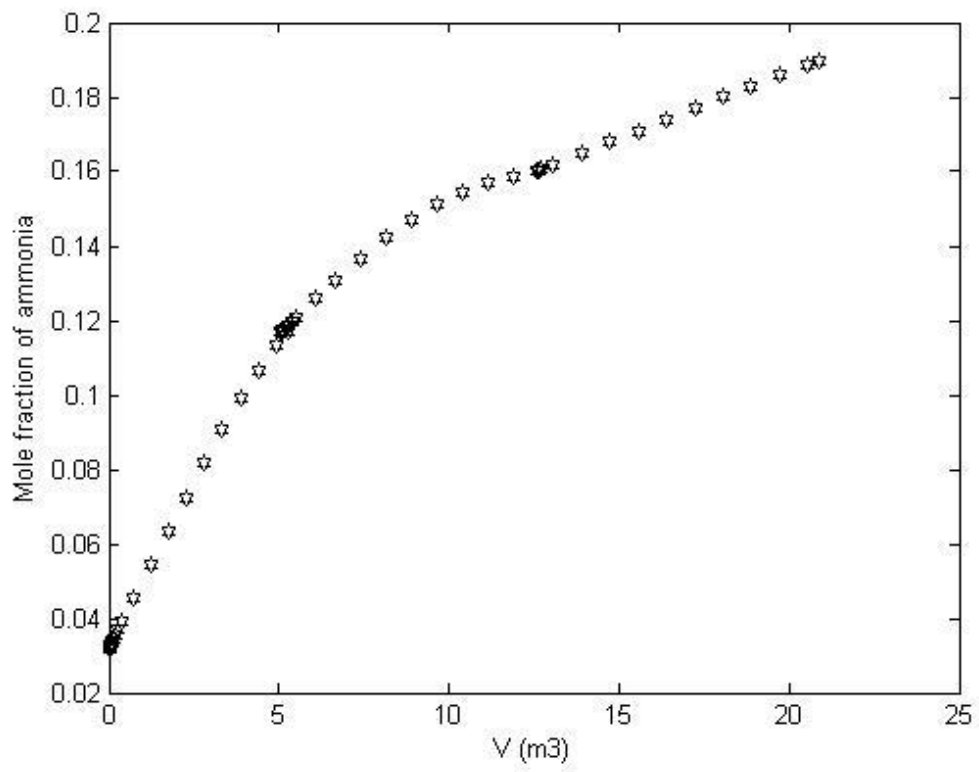


Figure 4.18: Ammonia Mole Fraction Profile – Case 3

4.1.4. Discussions

The simulation of the ammonia model provided 6 sets of profile which is the firstly, the effectiveness factor of the catalyst against the volumetric span of the reactor. The same trend is observed on all 3 simulation cases whereby the effectiveness factor of the catalyst increases with each reactor bed but decreases with volume on each individual bed. The higher the overall inlet flow rate increases the effectiveness factor as well.

The next profile obtained was the fractional conversion of nitrogen against the volumetric span of the reactor. The conversion of nitrogen decreases with each bed as the concentration of nitrogen decreases as it enters each bed. The conversion within each bed also slows down as the concentration of nitrogen decreases as the product concentration increases.

The third profile obtained is the temperature Profile against the volumetric span of the reactor. This profile is obtained from the energy balance of the system and is used to determine the performance of the model developed by the means of comparison with industrial data. Comparison shows that the model developed approximates the actual condition of the reactor adeptly. The data is as below

Table 4.4: Industrial Data of Ammonia Reactor

Case	Bed1		Bed2		Bed3	
	Inlet Temp(°C)	Outlet Temp(°C)	Inlet Temp(°C)	Outlet Temp(°C)	Inlet Temp(°C)	Outlet Temp(°C)
1	385	507	433	502	415	455
2	395	496	442	502	404	440
3	390	512	443	502	400	439

The fourth profile of the ammonia model is the component mole fraction against the volumetric span of the reactor, where the three components shown are nitrogen, methane and argon. Methane and argon, which are spectator species in the reaction, do not experience a change in concentration as the reaction progresses but

the mole fraction varies due to changes in the other species. Nitrogen, which is one of the raw material for ammonia synthesis decreases in mole fraction as the reaction medium flows through the reactor.

The fifth profile of the ammonia model is the hydrogen mole fraction against the volumetric span of the reactor whereby the same as nitrogen, is being used as raw material for ammonia conversion. The hydrogen concentration decreases as the reaction medium travels through the reactor. The last profile is that of ammonia mole fraction against the volumetric span of the reactor. Ammonia, which is the main product of the reaction increases in concentration as the reaction proceeds

4.2. Urea Model

4.2.1. Model Results

The urea model simulation was also performed to yield the following profiles:

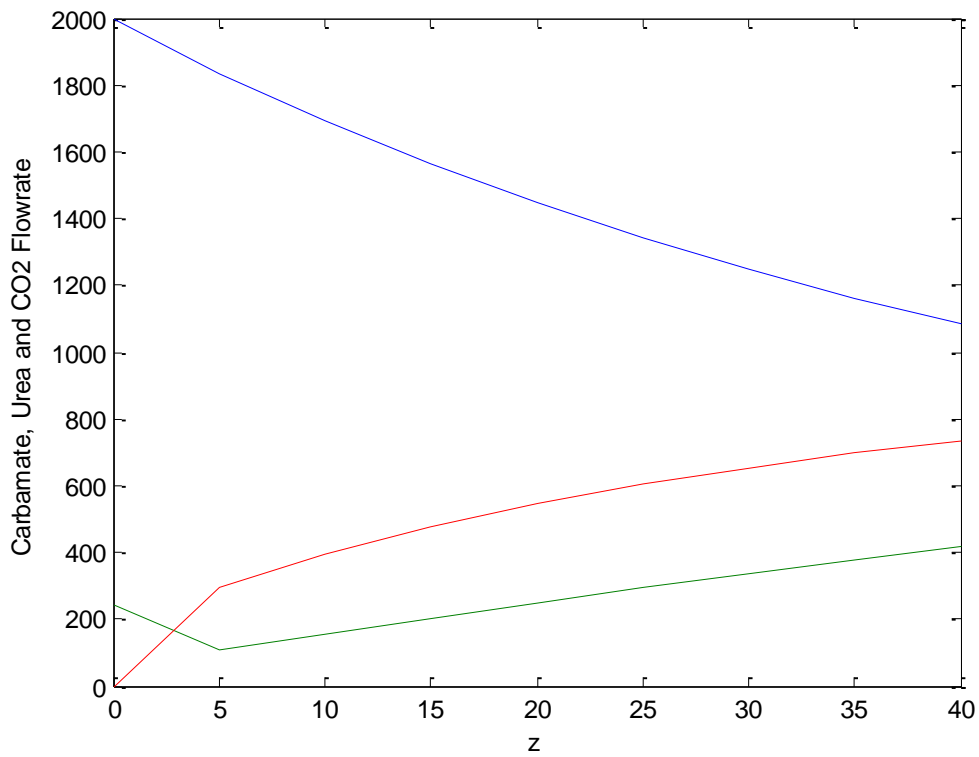


Figure 4.19: Urea, Ammonium Carbamate and CO₂ Flow Rate Profile

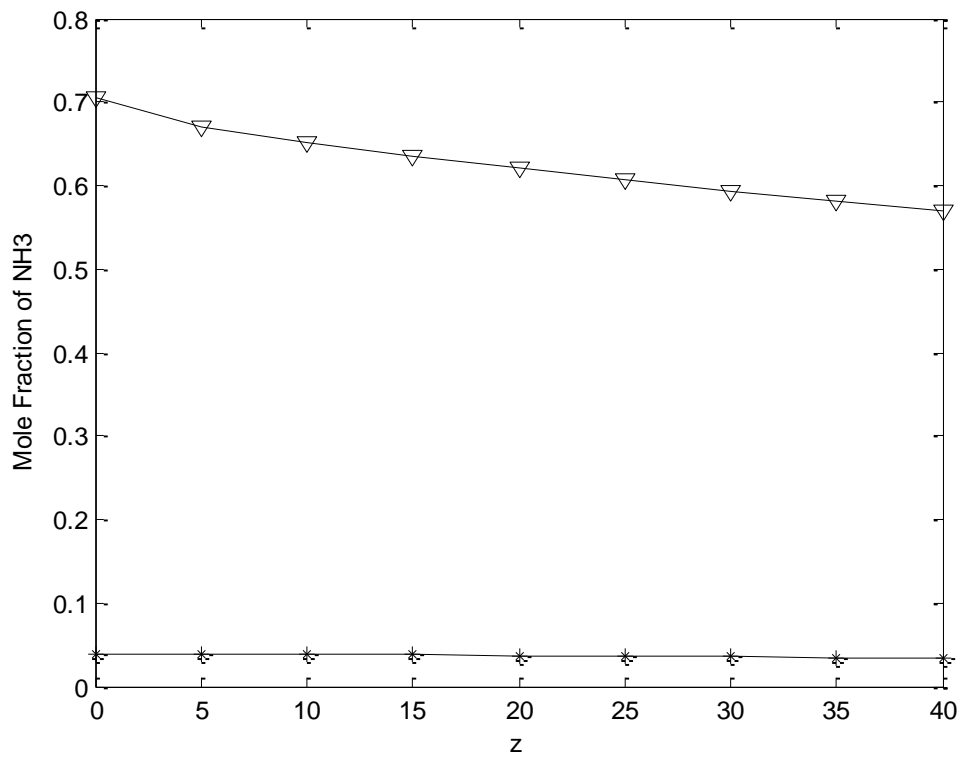


Figure 4.20: Ammonia Vapour Mole Fraction Profile

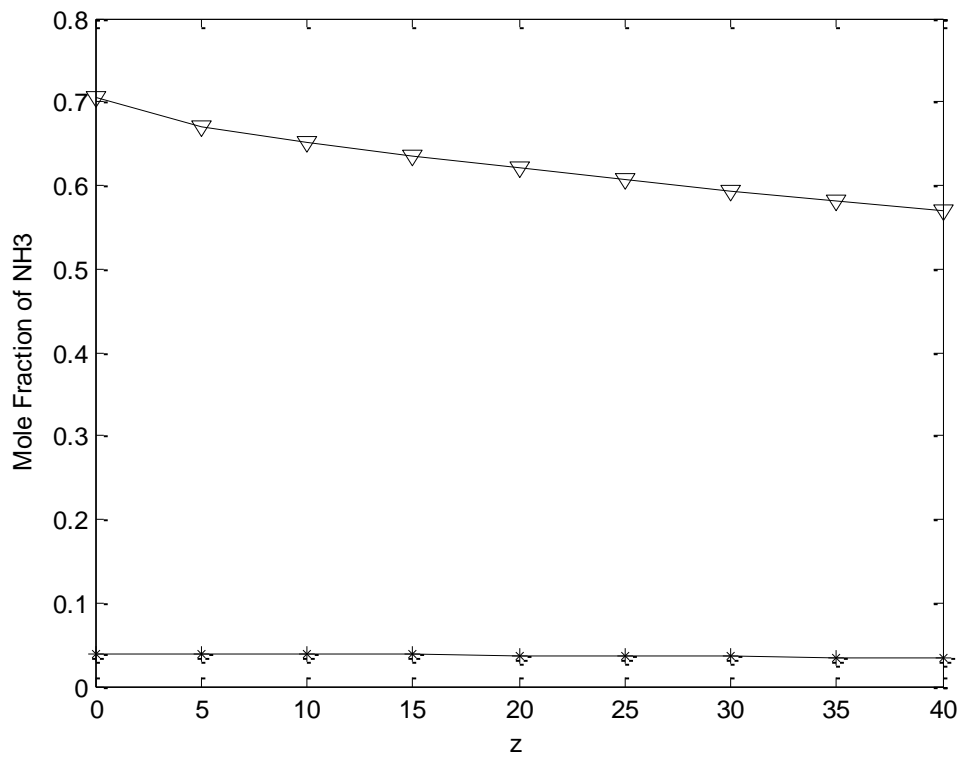


Figure 4.21: Carbon Dioxide Mole Fraction Profile

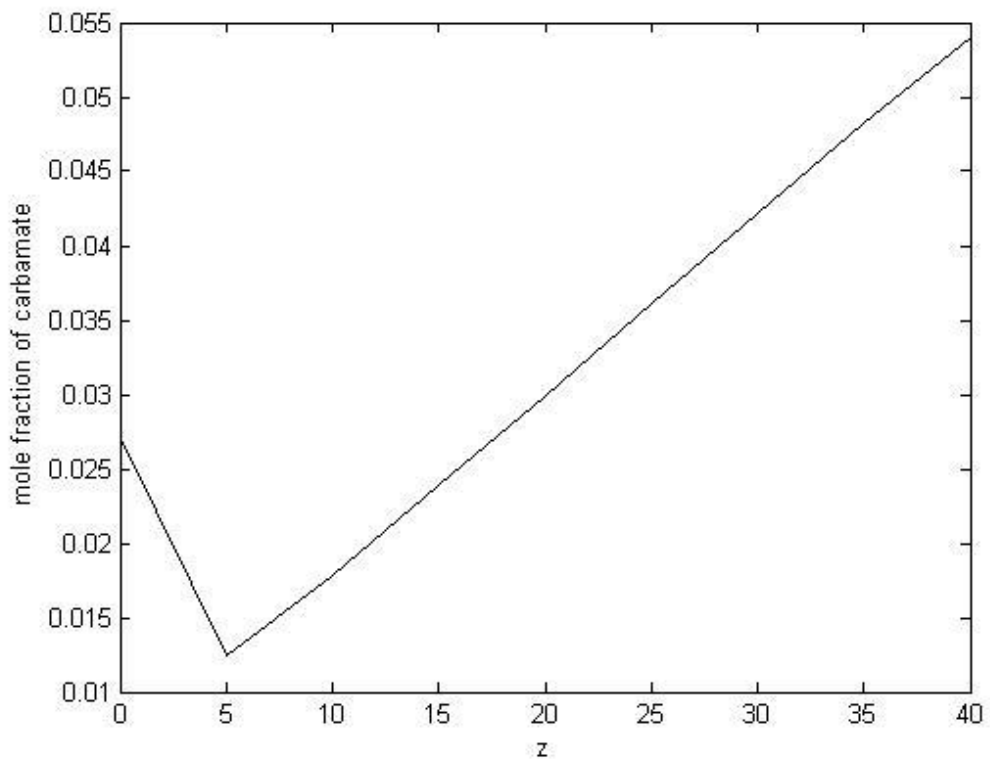


Figure 4.22: Ammonium Carbamate Mole Fraction Profile

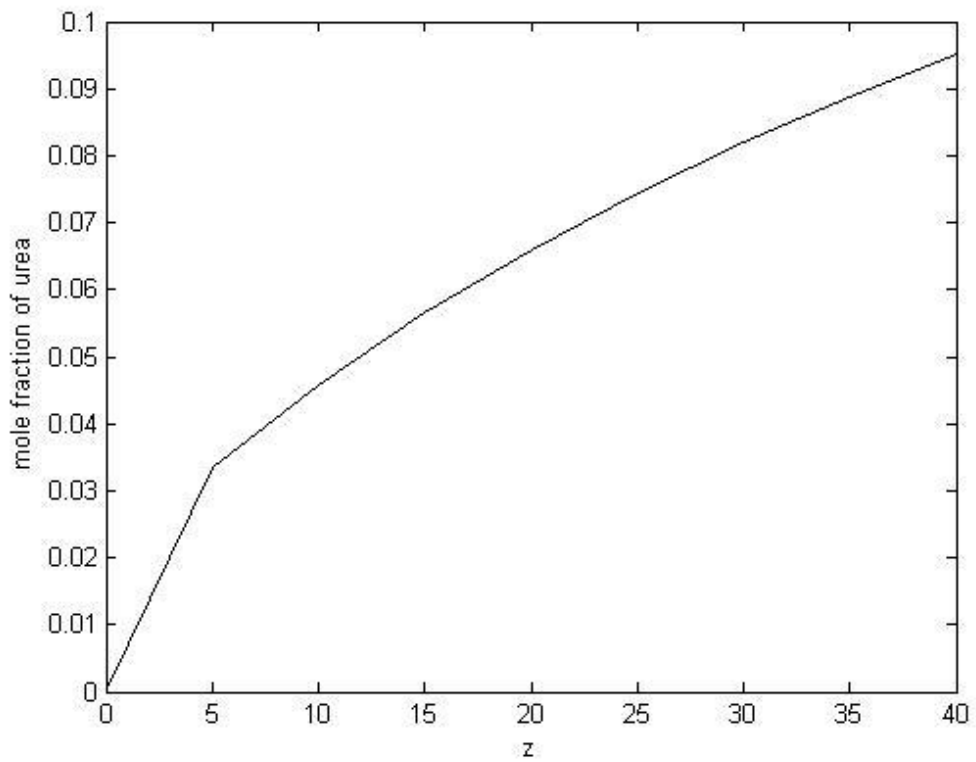


Figure 4.23: Urea Mole Fraction Profile

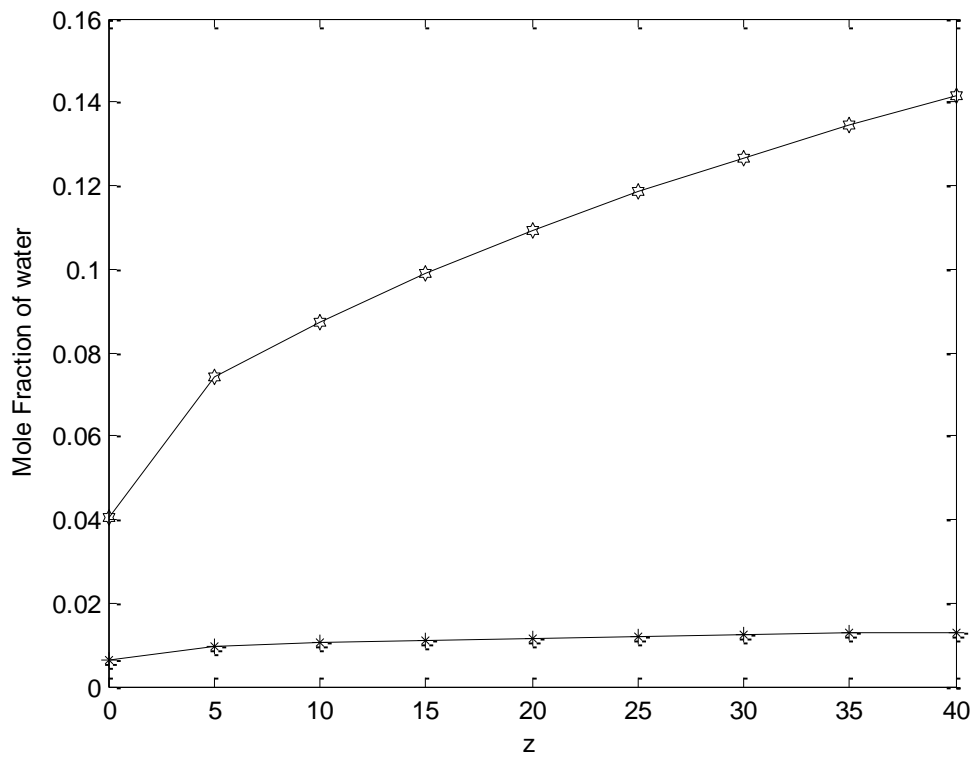


Figure 4.24: Water Mole Fraction Profile

4.2.2. Discussion

The urea model also provides 6 profiles, in which the first profile is that of component flow rate against the reactor volume span. The components shown here are carbon dioxide, ammonium carbamate and urea. The flow rate of carbon dioxide is shown by the blue lines, which indicates that it is decreasing as the reaction proceeds due to it being used as raw material for reaction. The reaction intermediate, ammonium carbamate is indicated by the green line, where by the flow of is slowly increasing. The rate of generation of ammonium carbamate is higher than the rate of consumption to form urea, hence the positive rate of flow. Urea is represented the red line on the graph and it is increasing in flow rate as it is the main product of the reaction.

The following five profiles show the individual component mole fraction against the volumetric span of the reactor. There exists a dual phase system in the urea model and therefore, for ammonia, carbon dioxide and water profile, there is a second line to describe the vapour mole fraction of said components in the system. Ammonia and both carbon dioxide, both which are reaction feeds, display a decrease in mole fraction as the reaction proceeds. Ammonium carbamate which is the reaction intermediate has a higher generation rate than consumption shows a positive increase in mole fraction. Urea which is the product, has an increasing mole fraction while water, which is formed from the decomposition of ammonium carbamate to form urea also increases in mole fraction as it is one of the final products.

The urea model has a slight error for component flow rates and mole fraction in the initial volume of reactor and this can be explained by the presence of negative values in the calculation of phase equilibria when the temperature value is subtracted. Additionally, the expression used for the ammonia vapour pressure is found to be incorrect and hence an extrapolated Antoine equation is used to provide the necessary value of the vapour pressure

4.3 Integration of process

The integration of ammonia and urea synthesis process can be done in three different ways. The first method involves using the product from the ammonia converter as feed directly to the urea converter, as in both chemical products are produced in separate converters. The flow rate of ammonia to the urea converted can be controlled by the means of a control valve and thus, in the mathematical model to describe the urea reaction, the feed flow rate is then expressed as the control model for the valve. This method of integration is the simplest as both converters are essentially still operating separately, being linked only through the control valve

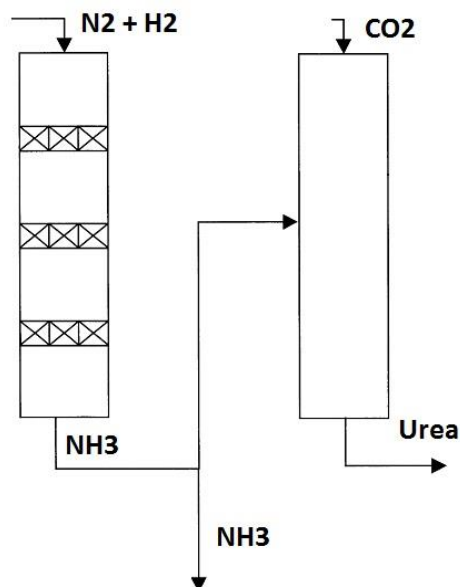


Figure 4.25: Reactor Configuration for First Possible Process Integration Method

The second method of integration can be where the feed for urea is fed along with the ammonia feed into the ammonia converter. In this scenario, the feed composition changes even before the feedstock enters the reactor as reactions such as carbamate formation occurs in the early stages of the process and thus reaction equations for the model is then separated as the synthesis of products is no longer linear. A description of the process can be as below

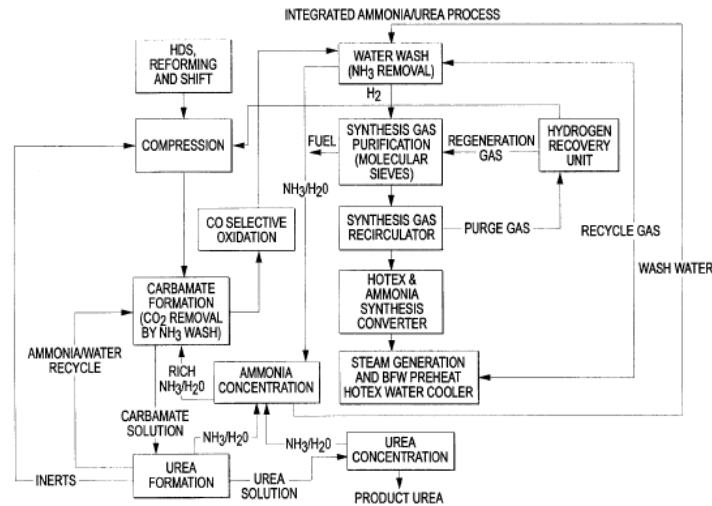


Figure 4.26: Flow Chart of Second Possible Process Integration Method

The third possible method of process integration would be to combine the processes into one multi bed reactor where the initial beds will be used for ammonia synthesis while the remaining beds will be used for urea synthesis. Mathematical modeling of this configuration would likely to follow the current ammonia model with the addition of beds to describe the urea reaction occurring in the latter beds.

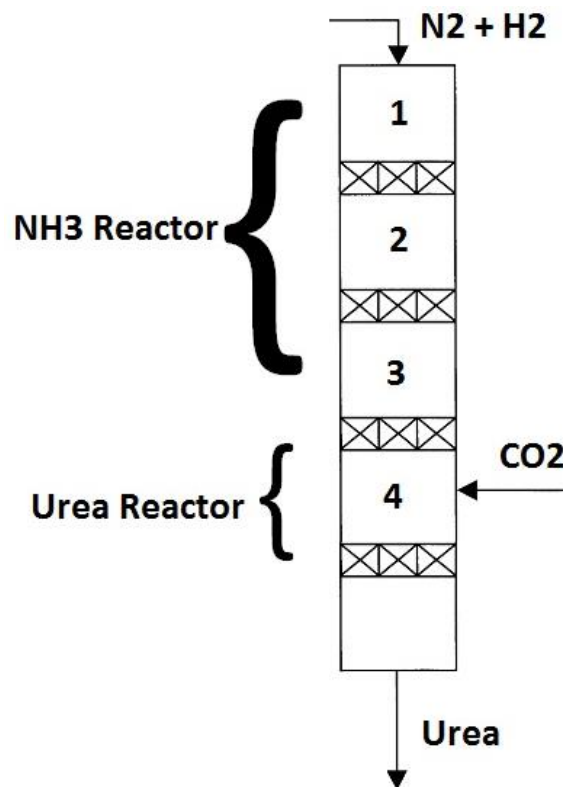


Figure 4.27: Flow Chart of Third Possible Process Integration Method

Chapter 5

CONCLUSION AND RECOMMENDATION

The simulation for the standalone ammonia and urea production process has been modeled using Matlab, providing the concentration and temperature profiles. Additionally, the effect of temperature on the conversion and reaction rate is also studied. Finally, the integration of both models is performed on a conceptual scale. Improvement to the urea model can be performed by providing a more accurate expression for determining the saturated vapour pressure of ammonia in the system and also correcting the negative value inducing temperature subtraction term.

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APPENDIX

Appendix 1: Ammonia Model MATLAB Coding - Ammonia_SimVcat_1

```
% Simulation program for Ammonia synthesis
% Adiabatic reactor simulation
clc
clear all
global Apre Eact palp Rgas P pbet FinN2 FinNH3 FinCH4 FinAr
Apre = 1.449e11*39.5;% % kgmol/m3/s
Eact = 37279; %
palp = .5;
Rgas = 1.987;
TC = 385;
Tin = TC+273 % 330 -495 deg. C
P = 1.1*226 %207; %226; %226 % 149 -309 atm
yN2in = 0.2219;
yH2in = 0.6703;
yNH3in = 0.0276
yCH4in = 0.0546;
yArin = 0.0256;
Flowin = 242160 % Nm3/h
mixMW = (yN2in*14+yH2in*2+yNH3in*17+yCH4in*16+yArin*39);
gasden = 50/mixMW; %kg/m3 ----> kgmol/m3
Ft = Flowin*gasden/3600 % m3/h ----> kgmol/m3s
% -----
% -----
% Adiabatic bed I
% -----
% -----
FinN2 = yN2in*Ft ;
FinH2 = yH2in*Ft;
FinNH3 = yNH3in*Ft;
FinCH4 = yCH4in*Ft;
FinAr = yArin*Ft;
pbet = FinH2/FinN2;
vspan = [0 4.75];
x0 =[0 Tin]
[v, x]=ode23s(@Ammonia_sys_Veq_1, vspan,x0);
output =[v x];
figure(2);clf;
plot(v,x(:,1), 'k')
hold on
xlabel('V (m3)')
ylabel('Fractional conversion of nitrogen (x)')
figure(3);clf;
plot(v,x(:,2), 'k')
hold on
xlabel('V (m3)')
ylabel('T (K)')
[nr nc] = size(output);
for i = 1:nr
    Ftot(i) = FinN2*(1+pbet-2*x(i,1))+FinNH3+FinCH4+FinAr;
    yN2(i) = FinN2*(1-x(i,1))/Ftot(i);
    yH2(i) = (pbet-3*x(i,1))*FinN2/Ftot(i);
    yNH3(i) = (FinNH3+2*x(i,1)*FinN2)/Ftot(i);
    yCH4(i) = FinCH4/Ftot(i);
    yAr(i) = FinAr/Ftot(i);
end
end
```

```

figure(4);clf;
plot(v,yN2,'*k')
hold on
plot(v,yCH4,'ok')
plot(v,yAr,'vk')
xlabel('V (m3)')
ylabel('Mole fractions of the individual components')
output1=[v x yN2' yH2' yNH3' yCH4' yAr']
save('firstbed', 'output1', '-ascii')
figure(5);clf;
plot(v,yH2,'^k')
hold on
xlabel('V (m3)')
ylabel('Mole fraction of hydrogen')
figure(6);clf;
plot(v,yNH3,'hk')
hold on
xlabel('V (m3)')
ylabel('Mole fraction of ammonia')
%-----
%-----
% Adiabatic bed II
%-----
%-----
FinN2 = yN2(nr)*Ftot(nr);
FinH2 = yH2(nr)*Ftot(nr);
FinNH3 = yNH3(nr)*Ftot(nr);
FinCH4 = yCH4(nr)*Ftot(nr);
FinAr = yAr(nr)*Ftot(nr);
pbet = FinH2/FinN2;
TC = 443;
Tin = TC+273
x0_2 =[0 Tin];
vspan = [4.75 11.95];
[v_2, x_2]=ode23s(@Ammonia_sys_Veq_1, vspan,x0_2);
output=[v_2 x_2];
figure(2);
plot(v_2,x_2(:,1),'k')
xlabel('V (m3)')
ylabel('Fractional conversion of nitrogen (x)')
figure(3);
plot(v_2,x_2(:,2),'k')
xlabel('V (m3)')
ylabel('T (K)')
[nr1 nc] = size(output);
for i = 1:nr1
    Ftot(i) = FinN2*(1+pbet-2*x_2(i,1))+FinNH3+FinCH4+FinAr;
    yN2_2(i) = FinN2*(1-x_2(i,1))/Ftot(i);
    yH2_2(i) = (pbet-3*x_2(i,1))*FinN2/Ftot(i);
    yNH3_2(i) = (FinNH3+2*x_2(i,1)*FinN2)/Ftot(i);
    yCH4_2(i) = FinCH4/Ftot(i);
    yAr_2(i) = FinAr/Ftot(i);
end
output2=[v_2 x_2 yN2_2' yH2_2' yNH3_2' yCH4_2' yAr_2']
save('Secondbed', 'output2', '-ascii')
figure(4);
plot(v_2,yN2_2,'*k')
hold on
plot(v_2,yCH4_2,'ok')
plot(v_2,yAr_2,'vk')
xlabel('V (m3)')

```

```

ylabel('Mole fractions of the individual components')
figure(5);
plot(v_2,yH2_2,'^k')
figure(6);
plot(v_2,yNH3_2,'hk')
%-----
%-----
% Adiabatic bed III
%-----
%-----
FinN2 = yN2_2(nr1)*Ftot(nr1);
FinH2 = yH2_2(nr1)*Ftot(nr1);
FinNH3 = yNH3_2(nr1)*Ftot(nr1);
FinCH4 = yCH4_2(nr1)*Ftot(nr1);
FinAr = yAr_2(nr1)*Ftot(nr1);
pbet = FinH2/FinN2;
TC = 400;
Tin = TC+273
x0_3 =[0 Tin];
vspan = [11.95 19.75];
[v_3, x_3]=ode23s(@Ammonia_sys_Veq_1, vspan,x0_3);
output =[v_3 x_3];
figure(2);
plot(v_3,x_3(:,1),'k')
xlabel('V (m3)')
ylabel('Fractional conversion of nitrogen (x)')
figure(3);
plot(v_3,x_3(:,2),'k')
xlabel('V (m3)')
ylabel('T (K)')
[nr nc] = size(output);
for i = 1:nr
    Ftot(i) = FinN2*(1+pbet-2*x_3(i,1))+FinNH3+FinCH4+FinAr;
    yN2_3(i) = FinN2*(1-x_3(i,1))/Ftot(i);
    yH2_3(i) = (pbet-3*x_3(i,1))*FinN2/Ftot(i);
    yNH3_3(i) = (FinNH3+2*x_3(i,1)*FinN2)/Ftot(i);
    yCH4_3(i) = FinCH4/Ftot(i);
    yAr_3(i) = FinAr/Ftot(i);
end
figure(4);
plot(v_3,yN2_3,'*k')
hold on
plot(v_3,yCH4_3,'ok')
plot(v_3,yAr_3,'vk')
xlabel('V (m3)')
ylabel('Mole fractions of the individual components')
figure(5)
plot(v_3,yH2_3,'^k')
figure(6)
plot(v_3,yNH3_3,'hk')
output3 =[v_3 x_3 yN2_3' yH2_3' yNH3_3' yCH4_3' yAr_3']
save('Thirdbed', 'output3', '-ascii')

```


Appendix 2: Ammonia Model MATLAB Coding - Ammonia_sys_Veq_1

```

function f = Ammonia_sys_Veq_1(v,x)
global Apre Eact palp Rgas P pbet FinN2 FinNH3 FinCH4 FinAr
global R De eps pgamN2 pgamH2 pgamNH3 Ka k palp P T
global xN2g xH2g xNH3g xCH4g xArg zspan
Ftot = FinN2*(1+pbet-2*x(1))+FinNH3+FinCH4+FinAr;
yN2 = FinN2*(1-x(1))/Ftot;
yH2 = (pbet-3*x(1))*FinN2/Ftot;
yNH3 = (FinNH3+2*x(1)*FinN2)/Ftot;
yCH4 = FinCH4/Ftot;
yAr = FinAr/Ftot;
T = x(2);
pgamN2 = 0.93431737+0.3101804e-3*T+0.295896e-3*P-0.2707279e-6*T^2+...
        0.4775207e-6*P^2;
pgamH2 = exp((P*exp(-3.8402*(T^0.125)+0.541))-(P^2)*exp(-
0.1263*(T^0.5))...
        -15.980)+300*(exp(-0.011901*T-5.941))*(exp(-P/300)-1));
pgamNH3 = 0.1438996+0.2028538e-2*T-0.4487672e-3*P-0.1142945e-
5*T^2+...
        0.2761216e-6*P^2;
actN2 = yN2*pgamN2*P;
actH2 = yH2*pgamH2*P;
actNH3 = yNH3*pgamNH3*P;
cosKa = -2.691122*log10(T)-5.519265e-5*T+1.848863e-
7*T^2+(2001.6/T)+2.6899;
Ka = 10^cosKa;
% -----
% -----
% % preexponential factor calculation:
% NA = 6.023e23;% mol
% Mw = 17;
% kb = 1.38065e-23; % J/K
% h = 6.62607e-34; %m2Kg/s2 J.s
% Tc = 405.37; % K
% Vc = 72.42; % cm3/gmol
% w = 0.2568;
% Vm = Vc;
% Vm = Vm*1e-6; %m3/mol
% st =
Rgas*log((Vm/(NA))*((2*pi*(Mw/(1000*NA))*kb*T)/h^2)^(3/2))+(5/2)*Rgas;
% Ds = (1/3)*st;
% Apre = ((kb*T)/h)*exp(Ds/Rgas)
% -----
% -----
k = Apre*exp(-Eact/(Rgas*T));
rateNH3 = 2*k*(Ka^2*actN2*(((actH2)^3)/(actNH3)^2)^palp)-...
        (((actNH3)^2)/(actH2)^3)^(1-palp));
% -----
% -----
% Effectiveness factor calculation by solving the flux equation
through
% nonlinear shooting method
R = 2.85e-3; %m
ctheta = 0.52;
eps = 0.46;
D13i = 0.161*1e-4; %m2/s
D23i = 0.629*1e-4; %m2/s

```

```

D21i = 0.571*1e-4; %m2/s
D32i = D23i;
D31i = D13i;
D12i = D21i;
xN2g = yN2;
xH2g = yH2;
xNH3g = yNH3;
xCH4g = yCH4;
xArg = yAr;
C = (actN2+actH2+actNH3)*1.013e5/(8.314*T);
% D1i = (1-xN2g)/((xH2g/D21i)+(xNH3g/D31i));
% D2i = (1-xH2g)/((xN2g/D12i)+(xNH3g/D32i));
% D3i = (1-xNH3g)/((xN2g/D13i)+(xH2g/D23i));
z1 = 1/2; z2 = 3/2; z3 = -1;
D1i = 1/((1/D21i)*(xH2g-xN2g*(z2/z1))+(1/D31i)*(xNH3g-xN2g*(z3/z1)));
D2i = 1/((1/D12i)*(xN2g-xH2g*(z1/z2))+(1/D32i)*(xNH3g-xH2g*(z3/z2)));
D3i = 1/((1/D13i)*(xN2g-xNH3g*(z1/z3))+(1/D23i)*(xH2g-xNH3g*(z2/z3)));
D1 = D1i*((T/273)^1.75)*(1/P);
D2 = D2i*((T/273)^1.75)*(1/P);
D3 = D3i*((T/273)^1.75)*(1/P);
D1e = (1/2)*ctheta*D1;
D2e = (1/2)*ctheta*D2;
D3e = (1/2)*ctheta*D3;
De = [D1e D2e D3e];
% zspan = [1.0:-0.01:0.85];
% zspan = [1.0 0.85];
zspan = [0.825 1];
% za0 = [0.0320 0.0728 -0.1732 0.0000 0.1559];
za0 = [0.20 0.60 0.20 0.06 0.02];
options = optimset('Tolx', 1e-6, 'TolFun', 1e-6, 'MaxIter', 5000);
yin = fsolve(@residual_isocatsph_eq,za0,options);
% y0 = [xN2g yin(1) xH2g yin(2) xNH3g yin(3) xCH4g yin(4) xArg
yin(5)];
y0 = [yin(1) 0 yin(2) 0 yin(3) 0 yin(4) 0 yin(5) 0];
% options = odeset('Events', @isocat_event1);
[z,y]=ode23s(@isocatsph_eq,zspan,y0,options);
zf = length(z);
% etanum = -3*y(1,6);
etanum = -3*y(zf,6);
etaden = ((R^2/(C*D3e))*rateNH3*((2+2*xNH3g)/(1-eps)));
eta = etanum/etaden;
figure(1)
plot(v,eta,'*k')
hold on
xlabel('V (m3)')
ylabel('\eta')
% -----
% -----
% delH = (-9184.0-7.2949*T+0.34996e-2*T^2+0.033563e-5*T^3-...
% 0.11625e-9*T^4+(-6329.3-3.1619*P)+(14.3595+4.4552e-3*P)*T-
T^2*...
% (18.3395e-3+1.928e-6*P)-51.21+0.14215*P);
delH = (9157.0+(0.54526+(840.6/T)+(4.59734/T^3))*P+5.4365*T+...
2.2525e-4*T^2-1.6917e-6*T^3);
cpN2 = (6.903-0.03753e-2*T+0.1930e-5*T^2-0.6891e-9*T^3);
cpH2 = (6.952-0.04576e-2*T+0.09563e-5*T^2-0.2079e-9*T^3);
cpNH3 = (6.5846+0.61251e-2*T+0.23663e-5*T^2-1.5981e-9*T^3+...
(96.1678-0.067571*P+(-0.222502+1.6847e-4*P)*T+...

```

```

        (1.289044e-4-1.009514e-7*P)*T^2));
cpCH4 = (4.750+1.2e-2*T+0.3030e-5*T^2-2.630e-9*T^3);
cpAr = 4.9675;
cpmix = yN2*cpN2+yH2*cpH2+yNH3*cpNH3+yCH4*cpCH4+yAr*cpAr;
% a = Ftot*cpmix
% FN2 = FinN2*(1-x(1));
% FH2 = FinN2*(pbet-3*x(1));
% FNH3 = FinNH3+2*x(1)*FinN2;
% FCH4 = FinCH4;
% FAr = FinAr;
% mcp = FN2*cpN2+FH2*cpH2+FNH3*cpNH3+FCH4*cpCH4+FAr*cpAr
f(1) = rateNH3*eta/(2*FinN2); % mass balance
f(2) = delH*(rateNH3)*eta/(Ftot*cpmix); % energy balance
% f(2) = delH*rateNH3*eta/mcp;
f = f';

```

Appendix 3: Ammonia Model MATLAB Coding - isocatsph_eq

```

function f = isocatsph_eq(z,y)
global R De eps pgamN2 pgamH2 pgamNH3 Ka k palp P T
% y(1) = x1 mole fraction of nitrogen in the catalyst pellet
% y(2) = dx1/dz
% y(3) = x2 mole fraction of hydrogen in the catalyst pellet
% y(4) = dx2/dz
% y(5) = x3 mole fraction of ammonia in the catalyst pellet
% y(6) = dx3/dz
% y(7) = x4 mole fraction of methane in the catalyst pellet
% y(8) = dx4/dz
% y(9) = x5 mole fraction of methane in the catalyst pellet
% y(10) = dx5/dz
% -----
% -----
yN2 = y(1);
yH2 = y(3);
yNH3 = y(5);
actN2 = yN2*pgamN2*P;
actH2 = yH2*pgamH2*P;
actNH3 = yNH3*pgamNH3*P;
rateNH3 = 2*k*(Ka^2*actN2*(((actH2)^3)/(actNH3)^2)^palp)-...
          (((actNH3)^2)/(actH2)^3)^(1-palp));
C = (actN2+actH2+actNH3)*1.013e5/(8.314*T);
% -----
% -----
% Integration from z = 1 to z = 0
f(1) = y(2);
f(2) = ((2*y(2)^2)/(-1+2*y(1)))-(2*y(2)/z)-(R^2/(C*De(1)))*...
      ((-1+2*y(1))*rateNH3/(1-eps));
f(3) = y(4);
f(4) = ((2*y(4)^2)/(-3+2*y(3)))-(2*y(4)/z)-(R^2/(C*De(2)))*...
      ((-3+2*y(3))*rateNH3/(1-eps));
f(5) = y(6);
f(6) = ((2*y(6)^2)/(2+2*y(5)))-(2*y(6)/z)-(R^2/(C*De(3)))*...
      ((2+2*y(5))*rateNH3/(1-eps));
f(7) = y(8);
f(8) = ((y(8)^2)/y(7))-(2*y(8)/z);
f(9) = y(10);
f(10) = ((y(10)^2)/y(9))-(2*y(9)/z);
% Integration from z = 0 to 1
% if z == 0
%   f(1) = y(2);
%   f(2) = (1/3)*(((2*y(2)^2)/(-1+2*y(1)))-(R^2/(C*De(1)))*...
%           ((-1+2*y(1))*rateNH3/(1-eps)));
%   f(3) = y(4);
%   f(4) = (1/3)*(((2*y(4)^2)/(-3+2*y(3)))-(R^2/(C*De(2)))*...
%           ((-3+2*y(3))*rateNH3/(1-eps)));
%   f(5) = y(6);
%   f(6) = (1/3)*(((2*y(6)^2)/(2+2*y(5)))-(R^2/(C*De(3)))*...
%           ((2+2*y(5))*rateNH3/(1-eps)));
%   f(7) = y(8);
%   f(8) = (1/3)*((y(8)^2)/y(7));
%   f(9) = y(10);
%   f(10) = (1/3)*((y(10)^2)/y(9));
% else
%   f(1) = y(2);
%   f(2) = ((2*y(2)^2)/(-1+2*y(1)))-(2*y(2)/z)-(R^2/(C*De(1)))*...

```

```

%      ((-1+2*y(1))*rateNH3/(1-eps));
%      f(3) = y(4);
%      f(4) = ((2*y(4)^2)/(-3+2*y(3)))-(2*y(4)/z)-(R^2/(C*De(2)))*...
%      ((-3+2*y(3))*rateNH3/(1-eps));
%      f(5) = y(6);
%      f(6) = ((2*y(6)^2)/(2+2*y(5)))-(2*y(6)/z)-(R^2/(C*De(3)))*...
%      ((2+2*y(5))*rateNH3/(1-eps));
%      f(7) = y(8);
%      f(8) = ((y(8)^2)/y(7))-(2*y(8)/z);
%      f(9) = y(10);
%      f(10) = ((y(10)^2)/y(9))-(2*y(9)/z);
% end
f = f';

```

Appendix 4: Ammonia Model MATLAB Coding - residual_isocatsph_eq

```
function f = residual_isocatsph_eq(za)
global xN2g xH2g xNH3g xCH4g xArg zspan
% y0 = [xN2g za(1) xH2g za(2) xNH3g za(3) xCH4g za(4) xArg za(5)];
y0 = [za(1) 0 za(2) 0 za(3) 0 za(4) 0 za(5) 0];
options = optimset('Tolx', 1e-6, 'TolFun', 1e-6, 'MaxIter', 8000);
% options = odeset('Events', @isocat_event);
[z,y]=ode23s(@isocatsph_eq,zspan,y0,options);
% Integration from z = 1 to 0
% f(1) = y(length(z),2); % dx1/dz
% f(2) = y(length(z),4); % dx1/dz
% f(3) = y(length(z),6); % dx1/dz
% f(4) = y(length(z),8); % dx1/dz
% f(5) = y(length(z),10); % dx1/dz
% % Integration from z = 0 to 1
f(1) = y(length(z),1)-xN2g; % dx1/dz
f(2) = y(length(z),3)-xH2g; % dx1/dz
f(3) = y(length(z),5)-xNH3g; % dx1/dz
f(4) = y(length(z),7)-xCH4g; % dx1/dz
f(5) = y(length(z),9)-xArg; % dx1/dz
```

Appendix 5: Ammonia Model MATLAB Coding – ureasim

```

% Urea synthesis reactions
% Simulation program
clc
clear
global FDin FCin FUin A a b T K Apre Ea Rgas den P Pref cbet
global xNH3 xCO2 xH2O epu_1 P T a b
% parameters
FDin = 2000;
FCin = 0.12*FDin;
FUin = 0.0*FDin;
d = 2.5;
A =pi*(d^2)/4;
% A = 2*pi*(d/2)*L;
a = 3; % 2-6, 2.3-3.6
b = 0.16; % 0 -1.2, 0.1-0.6
T = 463 % in K, 433-483 K, 433-463 K
K = [12.5 65.6];
Apre =[5.75e6 2.5e8]*3600; % per h per s
Ea = [139500 98500]; % J/mol
Rgas = 8.314; % J/mol/K
den = 260; %260;
P = 25; % 14-25 Mpa
Pref = 25;
cbet = 1.526;
nk = length(Apre);
for i = 1:nk
% k(i) = Apre(i)*exp(-Ea(i)/(Rgas*T))*(P/Pref)^cbet;
k(i) = Apre(i)*exp(-Ea(i)/(Rgas*T));
end
k
% Initial guess
Fin = [FDin FCin FUin];
zspan = [0:5:40];
% ODE solver
% options = odeset('RelTol', 1e-6,'AbsTol',1e-9);
options =[];
[z, F] = ode23s(@urea_eq,zspan,Fin,options);
z
F
[nr nc] =size(z);
for i = 1:nr
ep1(i) = (F(i,2)+F(i,3))/(FCin+FUin+FDin);
epu(i) = F(i,3)/(FCin+FUin+FDin);
FN(i) = 1+a+b-2*ep1(i)+epu(i);
xA(i) = (a-2*ep1(i))/FN(i);
xD(i) = (1-ep1(i))/FN(i);
xC(i) = (ep1(i)-epu(i))/FN(i);
xU(i) = epu(i)/FN(i);
xW(i) = (b+epu(i))/FN(i);
end
disp('NH3 CO2 Carbamide Urea Water')
output_1=[xA' xD' xC' xU' xW']
ep1
epu
figure(1);clf;
plot(z,F)
xlabel('z')

```

```

ylabel('FCO2, Fcarbamate and FUrea')
figure(2); clf
plot(z,xA,'v-k')
xlabel('z')
ylabel(' mole fraction of NH3')
hold on
figure(3); clf;
plot(z,xD,'p-k')
xlabel('z')
ylabel(' mole fraction of CO2')
hold on
figure(4); clf;
plot(z,xC,'k')
xlabel('z')
ylabel(' mole fraction of carbamate')
figure(5); clf;
plot(z,xU,'k')
xlabel('z')
ylabel(' mole fraction of urea')
figure(6); clf;
plot(z,xW,'h-k')
xlabel('z')
ylabel(' mole fraction of water')
hold on
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
output2 =[xA' xD' xW']
[npt nc]=size(output2);
%calculating vapour fraction Y
for j=1:npt
    for i=1:nc
        Yassum(i)=0.15;
    end
    xNH3 = xA(j);
    xCO2 = xD(j);
    xH2O = xW(j);
    epu_1 =epu(j);
    Y = fsolve(@urea_eq_2,Yassum);
    Yassum = Y;
    yNH3(j)= Y(1);
    yCO2(j) = Y(2);
    yH2O(j) = Y(3);
end
output3 =[yNH3' yCO2' yH2O']
figure(2);
plot(z,yNH3,'*-k')
xlabel('z')
ylabel(' YNH3')
figure(3);
plot(z,yCO2,'*-k')
xlabel('z')
ylabel(' YCO2')
figure(6);
plot(z,yH2O,'*-k')
xlabel('z')
ylabel(' YH2O')

```


Appendix 6: Ammonia Model MATLAB Coding - urea_eq

```

% Urea synthesis reactor equations
function f =urea_eq(z, F)
global FDin FCin FUin A a b T K Apre Ea Rgas den P Pref cbet
ep1 = (F(2)+F(3))/(FCin+FUin+FDin);
epu = F(3)/(FCin+FUin+FDin);
% molar flow rate
FD = (1-ep1)*(FCin+FUin+FDin);
FA = (a-2*ep1)*(FCin+FUin+FDin);
FC = (ep1-epu)*(FCin+FUin+FDin);
FU = epu*(FCin+FUin+FDin);
FW = (b+epu)*(FCin+FUin+FDin);
% liquid phase composition
% FN = 1+a+b-2*ep1+epu;
% xA = (a-2*ep1)/FN;
% xD = (1-ep1)/FN;
% xC = (ep1-epu)/FN;
% xU = epu/FN;
% xW = (b+epu)/FN;
% urea synthesis rate expression
FN = 1+a+b-2*ep1+epu;
v0 = FN*(FCin+FUin+FDin)/den;
Ca = FA/v0;
Cd = FD/v0;
Cc = FC/v0;
Cu = FU/v0;
Cw = FW/v0;
nk = length(Apre);
for i = 1:nk
%     k(i) = Apre(i)*exp(-Ea(i)/(Rgas*T))*(P/Pref)^cbet;
    k(i) = Apre(i)*exp(-Ea(i)/(Rgas*T));
end
rd = -k(1)*(Cd*Ca^2-Cc/K(1));
rc = k(1)*(Cd*Ca^2-Cc/K(1))-k(2)*(Cc-Cu*Cw/K(2));
ru = k(2)*(Cc-(Cu*Cw/K(2)));
% differential equations
% Kinetic equation for co2
f(1) = A*rd;
% Kinetic equation for ammonium carbamate
f(2) = A*rc;
% Kinetic equation for urea
f(3) = A*ru;
f = f';

```

Appendix 7: Ammonia Model MATLAB Coding - urea_eq_2

```

% Vapour phase mole fraction calculator
function f =urea_eq_2(Yassum)
global xNH3 xCO2 xH2O epu_1 P T a b
yNH3 =Yassum(1);
yCO2 =Yassum(2);
yH2O=Yassum(3);
PcritNH3 = 11.28;
PcritCO2 = 7.38;
PcritH2O = 22.06;
TcritNH3 = 405.6;
TcritCO2 = 304.19;
TcritH2O = 647.096;
PredNH3=P/PcritNH3;
PredCO2=P/PcritCO2;
PredH2O=P/PcritH2O;
TredNH3=T/TcritNH3;
TredCO2=T/TcritCO2;
TredH2O=T/TcritH2O;
E = epu_1;
%

```

```

% Clasius-clayperon eq
%LnPsNH3=(-25.07/T)+(56.321*log(T))-0.2625*T+(1.753e-4/T^2)-258.139;
%PsNH3 = exp(LnPsNH3)

% Antoine coefficients From Hysys
%LnPsNH3=59.655+(-4261.5/T)+(-6.90480*log(T))+(0.0000100170*T^2);
%PNH3kpa=exp(LnPsNH3);
%PsNH3 =PNH3kpa/1000

%Antoine coefficients from internet
LnPsNH3=4.86886-(1113.928/(T-10.409));
PNH3bar = exp(LnPsNH3);
PsNH3 = PNH3bar/10

% Thermodynamic property of ammonia
%F=(1/TredNH3)*((-7.296510*(1-TredNH3))+(1.618053*(1-
TredNH3)^1.5)+(-1.956546*(1-TredNH3)^2.5)+(-2.114118*(1-
TredNH3)^5));
%PsNH3=exp(F)/PcritNH3

% Lee-Kesler Equation
%F0=5.92714-(6.09648/TredNH3)-
(1.28862*log(TredNH3))+(0.169347*(TredNH3)^6);
%F1=15.2518-(15.6875/TredNH3)-
(13.4721*log(TredNH3))+(0.43577*(TredNH3)^6);
%LnPsNH3=F0+0.25*F1;
%Test=exp(LnPsNH3);
%PsNH3=Test/1000

% Corresponding state principle
%LnPred0=5.790206+(6.251894*((1-TredNH3)^1.89))+(11.65859*((1-
TredNH3)^5.67))*log(TredNH3);
%LnPred1=4.888195+(15.08591*((1-TredNH3)^1.89))+(46.78273*((1-
TredNH3)^5.67))*log(TredNH3);
%LnPred2=33.91196+(-315.0248*((1-TredNH3)^1.89))+(-1672.179*((1-
TredNH3)^5.67))*log(TredNH3);

```

```

%Zc=(PcritNH3*1000)/(8.314472*235*TcritNH3);
%Afactor=(Zc-0.29)^2;
%LnPred=LnPred0+(0.25*LnPred1)+(Afactor*LnPred2)
%Pred123=exp(LnPred);
%PsNH3=(Pred123*PcritNH3*1000)/1000
%


---


LnPsCO2=(-2370.26/T)-(0.5911*log(T))-1.178e-2*T+(1.598e-
5*T^2)+15.272;
PsCO2 = exp(LnPsCO2)
LnPsH2O=(-5231.82/T)-(6.167e-2*log(T))-3.291e-3*T+(1.222e-
6*T^2)+13.183;
PsH2O = exp(LnPsH2O);

% Fugacity Coefficient, Phi
ANH3= 0.42748*(PredNH3/((TredNH3)^2.5));
ACO2= 0.42748*(PredCO2/((TredCO2)^2.5));
AH2O= 0.42748*(PredH2O/((TredH2O)^2.5));
BNH3= 0.08664*(PredNH3/TredNH3);
BCO2= 0.08664*(PredCO2/TredCO2);
BH2O= 0.08664*(PredH2O/TredH2O);
%
A = ((yNH3*sqrt(ANH3))+(yCO2*sqrt(ACO2))+(yH2O*sqrt(AH2O)))^2;
B = (yNH3*ANH3)+(yCO2*ACO2)+(yH2O*AH2O);
p = [1 -1 (A-B-B^2) -(A*B)];
r = roots(p);
z = max(r);
% Z = max(Z2)
lnphiNH3 = (BNH3/B)*(z-1)-log(z-B)+(A/B)*((BNH3/B)-
2*sqrt(ANH3/A))*(log(1+B/z));
FugCoNH3=exp(lnphiNH3)
%FugCoNH3= 0.1438996+(0.2028538e-2*T)-(0.4487672e-3*P)-(0.1142945e-
5*T^2)+(0.2791216e-6*P^2)
lnphiCO2 = (BCO2/B)*(z-1)-log(z-B)+(A/B)*((BCO2/B)-
2*sqrt(ACO2/A))*(log(1+B/z));
FugCoCO2 =exp(lnphiCO2);
lnphiH2O = (BH2O/B)*(z-1)-log(z-B)+(A/B)*((BH2O/B)-
2*sqrt(AH2O/A))*(log(1+B/z));
FugCoH2O =exp(lnphiH2O);
%Activity Coefficient, Gamma
Estar= -3.4792+8.2677e-1*a-1.8998e-2*a^2-2.3155e-1*b-1.144e-
1*(T/100)+....
2.9879e-2*a*b-1.3294e-1*a*(T/100)+4.5348e-1*(T/100)^2-5.5339e-
2*(T/100)^3;
%E= (Fin-F)/Fin which component to put for conversion calculation
N =E/Estar;
GammaNH3 = 0.3960-2.8447e-3*T+0.6111*a-
0.2740*a*N+0.8800*N+0.0680*a^2-...
0.24894e-4*T*a^2;
GammaCO2 = 0.6082+3.5532e-4*T-0.3681*a+0.1114*b+3.37508e-4*T*a*N-...
0.10245*a*N-4.8257e-2*a^2+1.7667e-4*T*a^2;
GammaH2O = 22.6745-1.5546e-2*T-4.0697*a+2.0369*N^2-15.8744*N+4*a*N;
%Liquid-Vapour Equilibrium Equation
yNH3cal = (PsNH3*GammaNH3*xNH3)/(P*FugCoNH3);
yCO2cal = (PsCO2*GammaCO2*xCO2)/(P*FugCoCO2);
yH2Ocal = (PsH2O*GammaH2O*xH2O)/(P*FugCoH2O);
%
f(1) = yNH3-yNH3cal;
f(2) = yCO2-yCO2cal;
f(3) = yH2O-yH2Ocal;

```