CHAPTER I

INTRODUCTION

1.1. Background

Indonesia is an agricultural country where many individuals work in the farming industry. Agriculture is a crucial component of the economy, particularly the use of chemicals in farming. The Indonesian government has a food strategy that prioritizes increasing food production and improving the food production process. The goal is to produce enough food to sustain the population. This will be achieved by ensuring good quality seeds are available for planting, using fertilizers to stimulate plant growth, and developing pest control methods. These efforts have also contributed to the growth of the chemical industry, including the production of more pesticides. The aim is to meet the increasing demand for materials that support different sectors by building new factories, such as a hexamethylenetetramine plant.

Hexamine was first synthesized in 1859. It is a white crystalline powder with a mild amine smell. It can dissolve in water, alcohol, and chloroform, but not in ether. When dissolved in water, its solubility decreases as temperature increases. It becomes less soluble in hot water. When an aqueous solution of hexamine is cooled below 14°C, it forms a hydrate called (CH2)6N4·6H2O through crystallization (Riegel, 2003).

Hexamethylenetetramine, also known as hexamine, has various applications in different industries. It can solidify certain types of resins, stick rubber to textiles, and alter the properties of proteins. It is used in making powerful explosives and fuel tablets that burn easily. In the rubber industry, it helps make rubber stronger. It can also be used to kill fungi, protect against rusting, prevent clothes from shrinking, and fight bacteria. Hexamine is also used in making new compounds and is an ingredient in medicines (Swart *et al.*, 1996)

Based on the multiple uses of hexamine in various industries and its importance in Indonesia's expanding industrial sector, having a hexamine production plant is necessary for several reasons, including:

a. The primary aim of the plant is to reduce reliance on foreign suppliers, meet domestic demand for hexamethylenetetramine, and generate significant economic benefits, thereby conserving the country's foreign exchange reserves.
b. The plant can take advantage of Indonesia's abundant raw materials, such as locally produced formaldehyde and ammonia, to ensure a stable, efficient, and reliable supply.
c. The plant's construction will encourage technical developments and innovation in Indonesia's chemical industrial sector. It would improve the country's chemical engineering and industrial capacities by facilitating the transfer of knowledge, skills, and advanced technologies.
d. By exporting high-quality hexamethylenetetramine products, the plant could contribute significantly to the country's income through exports, provided it meets international standards.
e. Relations between both local and foreign companies would be promoted, which would allow the exchange of knowledge and market growth in Indonesia's chemical sector. This will encourage sector growth and development by using the skills and resources of several stakeholders.

1.2. Literature Review

1.2.1. Hexamethylenetetramine

Hexamethylenetetramine is a chemical that is made by combining formaldehyde and ammonia. It is often used to create thermosetting plastic materials. This chemical is usually produced by evaporating a mixture of a watery solution of formaldehyde and ammonia, which is done through a batch process. The reaction that occurs can be described as follows:

$$6\ CH_2O\ (l) + 4\ NH_3\ (g) \rightarrow\ C_6H_{12}N_4\ (l) +\ 6\ H_2O$$

(Swart *et al*., 1996)

Hexamine is highly soluble in water, and the reaction is quite exothermic, implying the possibility for high yields under quite a few operating conditions. However, effective results are heavily dependent on elements such as the physical condition and concentration of the reactants, which allow for simple and comprehensive control of the reaction temperature. (Lefebvre *et al*., 1966).

Uses of Hexamethylenetetramine include:

- Medical Uses: Hexamethylenetetramine was previously used as an antiseptic for the reproductive system to help prevent and cure infections.
- Chemical Substitute: Hexamethylenetetramine is utilized in the synthesis of other chemicals. For instance, it is a key component in the production of resins, plastics, rubber additives, and pharmaceuticals.
- Fuel Additive: Hexamethylenetetramine is used as a fuel additive in some applications to improve the combustion qualities of certain fuels.
- Explosive: Some explosive formulations contain hexamethylenetetramine, which is able to stabilise and improve the explosive qualities.
- Food Preservation: Food Preservation: Hexamethylenetetramine is used in multiple food preservation processes to prevent some foods from spoiling.

1.2.2. Ammonia

The discovery of ammonia dates back over two centuries, with its gaseous form first isolated by the English chemist Joseph Priestley in 1774. The French chemist Claude Louis Berthollet determined the composition of ammonia in 1785. Notably, in 1898, Adolph Frank and Nikodem Caro made a significant breakthrough by discovering that nitrogen (N_2) could be converted into calcium cyanamide using calcium carbide. The resultant calcium cyanamide could then be hydrolysed with water, forming ammonia (Pattabathula & Richardson, 2016).

1.2.3. Formaldehyde

Formaldehyde (CH2O) goes by various names, including methanal, methylene oxide, oxyethylene, methyl aldehyde, oxo methane, and formic aldehyde. It appears as a colourless gas with a strong, irritating odour at room temperature. This compound is highly reactive, tends to undergo polymerization, is easily flammable, and can create explosive mixtures when mixed with air. It dissolves easily in water, alcohol, and other polar solvents. In water solutions, formaldehyde forms hydrates and polymers, and it can exist in various forms like methylene glycol, and polyoxymethylene (Liteplo *et al*., 2002).

1.3. Review of Thermodynamics

To determine whether the process is endothermic or exothermic, measure the heat with the standard heat of formation at atmospheric pressure and 298 K. The reaction that occurs:

$$6\ CH_2O + 4\ NH_3 \rightarrow C_6H_{12}N_4 + 6\ H_2O$$

The below table contains the heat of formation data for each component in the hexamine production process at 298 K:

Component	ΔHf 298 (kJ/mol K)
NH3	-46.11
CH2O	-108.57
H2O	-285.83
CH3OH	-201.3
C6H12N4	760.68

(Yaws, 1999)

Calculation:

$$\Delta H°f\ 298\ K = \Delta H°f_{\ Product} - \Delta H°f_{\ Reactant}$$

- $\Delta H°f_{\ Product} = [\ (\Delta H°f\ C_6H_{12}N_4) + (6 \times \Delta H°f\ H_2O)]$
  $= (760{,}68 + (6 \times -285{,}83))$ kJ/mol
  $= -954{,}3$ kJ/mol
- $\Delta H°f_{\ Reactant} = [\ (\ 6\ x\ \Delta H°f\ CH_2O) + (4 \times \Delta H°f\ NH_3)]$
  $= ((6 \times -108{,}57) + (4 \times -46{,}11))$
  $= -835{,}\ 86$ kJ/mol
- $\Delta H°f\ 298\ K = \Delta H°f_{\ Product} - \Delta H°f_{\ Reactant}$
  $\Delta H°f\ 298\ K = -954{,}3$ kJ/mol $- (-835{,}86$ kJ/mol)
  $\Delta H°f\ 298\ K = -118\ 44$ kJ/mol
  $\Delta H°f\ 298\ K = -28{,}\ 3078$ kcal/mol

The calculation of ΔH°f for the following process, which equals a negative number, indicates that the reaction is exothermic. Thus, the reaction produces heat.

The equilibrium constant (K) value defines whether a reaction is reversible or irreversible. The energy of each chemical is shown in the table below:

Component	ΔGf 298 (kJ/mol K)
NH3	-16.4
CH2O	-109.91
H2O	-228.642
CH3OH	-202.64
C6H12N4	410.8

(Yaws, 1999)

Calculation:

$$\underline{\Delta G^\circ = \Sigma\,(n\,\Delta G^\circ f\ product) - \Sigma\,(n\,\Delta G^\circ f\ reactant)}$$

$$\underline{\Delta G^\circ = -RT\ ln\ K}$$

$$\underline{K = \exp(-\Delta G^\circ/RT)}$$

Index:

ΔG° : Standard Gibbs free energy change for the reaction.

R : Universal gas constant (approximately 8.314 J/(mol·K)).

T : Absolute temperature in kelvin (K).

K : Equilibrium constant for the reaction.

(Smith *et al*., 2018)

- $\Delta G^\circ f$ Product = [($\Delta G^\circ f$ $C_6H_{12}N_4$) + (6 x $\Delta G^\circ f$ H_2O)]

  = (410,80 + (6 x – 228,6418)) kJ/mol

  = (410,80) -1371,8508

  = - 961,0508 kJ/mol

- $\Delta G°f$ $_{\text{Reactant}}$ = [(6 x $\Delta G°f$ CH_2O) + (4 x $\Delta G°f$ NH_3)]

  = ((6 x -109,91) + (4 x -16,4))

  =-659,46 + (-65,6)

  = - 725, 06 kJ/mol

- $\Delta G°f$ 298 K = $\Delta G°f$ $_{\text{Product}}$ - $\Delta G°f$ $_{\text{Reactant}}$

  $\Delta G°f$ 298 K = - 961,0508 kJ/mol – (- 725,06 kJ/mol)

  $\Delta G°f$ 298 K = - 235, 9908 kJ/mol

  $\Delta G°f$ 298 $K =$ - 56, 4031 kcal/mol

- K_{298} → Standard Temperature

  $$K298 = \exp \frac{\Delta G°f\ 298}{RT}$$

  $$K298 = \exp \frac{-56{,}4031}{-1{,}987\frac{kcal}{mol}K\ X\ 298\ K}$$

  $$K298 = \exp \frac{-56{,}4031}{-592{,}126}$$

  K298 = exp (0,0952)

  K298 = $e^{0{,}0952}$

  K298 = 1,0998

- K operation → K 313

  $$\frac{K\ operation}{K298} = exp\ \frac{-\Delta\ H°f\ 298}{Ra}[\frac{1}{Toperation} - \frac{1}{T298}]$$

  $$\frac{K\ operation}{1{,}0998} = exp\ \frac{-28{,}3078}{1{,}987}[\frac{1}{313} - \frac{1}{298}]$$

  $$\frac{K\ operation}{1{,}0998} = \ e^{-0{,}00235}$$

  $K\ operation$ = 0,9977 x 1,0998

  K 313 = 1,075

- ΔG_{313} = - RT ln K_{313}

  = - 1,987 x 313 ln 1,075

  = - 44,978 kcal/mol

When G° is negative, it indicates that K is higher than one. If K is higher than one, the reaction favours product production and is called irreversible.

1.4. Review of Reaction Kinetics

a. Temperature = 40°C

b. Pressure = 1 atm

c. Phase = Liquid: Liquid

d. Ratio (CH_2O : NH_3) = 3 : 2

This reaction is involved in the production of hexamine using formaldehyde and ammonia as raw materials is as follows:

$$6\ CH_2O\ (l) + 4\ NH_3\ (g) \rightarrow C_6H_{12}N_4\ (l) + 6\ H_2O$$

From a kinetic perspective, this reaction can be defined as follows:

$$A + B \rightarrow C$$

The previous equation shows that the process of producing hexamine is a third-order reaction. The reaction rate equation and kinetic equation appear as follows:

$-r_A = kC_A C_B^2$

$K = 1{,}42 \times 10^3\ exp(-3090/T)$ (Froment *et al*., 2011).

Index:

rA : Rate of disappearance of A (formaldehyde).

K : Rate constant.

CA : Concentration of A (formaldehyde).

CB : Concentration of B (ammonia).

K : Equilibrium constant.

T : Temperature.

The reaction rate constant (k) is calculated to be 0.0736 (L^2/s.mol^2) under the reactor's operating conditions of T = 313 K.

1.5. Production Capacity

a. Hexamethylenetetramine Import of Indonesia

The capacity of the hexamine factory depends on the annual demand in Indonesia. Data on hexamine imports in Indonesia is provided by *Badan Pusat Statistik.* The table below shows hexamine import data for Indonesia.

Table 1 Import in Indonesia

Year	Total (Kgs/Yr)
2017	19407198
2018	20460250
2019	20422007
2020	20604284
2021	25180194

(BPS, 2022)

A polynomial regression of order 3 is calculated and graphed based on Table 1 to predict the future trend of hexamine imports in Indonesia.

Figure 1 shows a graph and equation describing the link between annual hexamine imports.

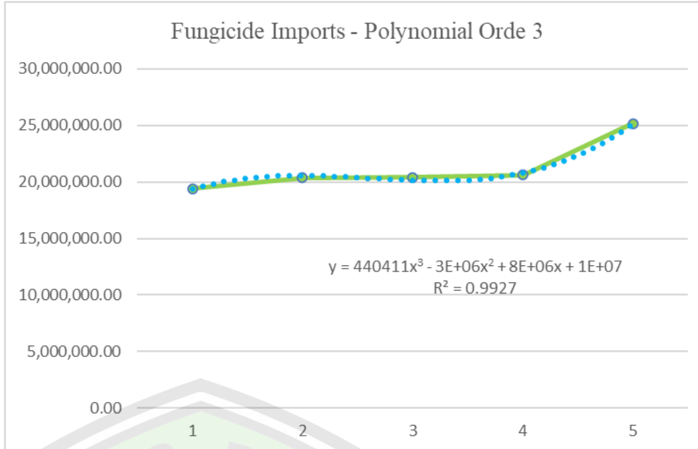

Figure 1 Polynomial Approximation Import Graph

Calculation:

- y $= 440411\ x^3 - 3e + 06x^2 + 8e + 06x + 1e + 07$
  R^2 = 0,9927
  x = 2026-2021
  x = 5

- M1 $= 440411\ x^3 - 3e + 06x^2 + 8e + 06x + 1e + 07$
  $= 440411\ (5)^3 - 3e + 06(5)^2 + 8e + 06(5) + 1e + 07$
  = 55.051.578,309 Kgs/year
  = 55.051,578 tonnes/year

b. Hexamine Factory in Indonesia

Several countries-built hexamine manufacturing plants to meet their special needs. Based on local demand, PT. Kaltim Hexamindo Wiratama in Indonesia produces about 3,000 metric tonnes of hexamine per year.

c. Hexamethylenetetramine Export of Indonesia

Hexamine exports in Indonesia have been evolving, according to statistics from *Badan Pusat Statistik*. The table below shows hexamine export data for Indonesia.

Table 2 Export in Indonesia

Year	Total (Kgs/Yr)
2017	1614831
2018	1506305.97
2019	1271163.99
2020	1303147.82
2021	1584569.42

(BPS, 2022)

Based on Table 2, a graph was made to predict the future track of hexamine exports in Indonesia. Figure 2 displays a graph and equation that show the relationship between hexamine export data over the years.

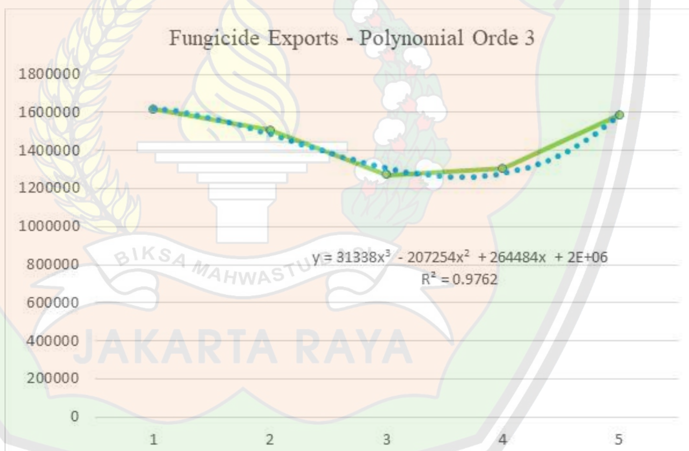

Figure 2 Polynomial Approximation Export Graph

Calculation:

- y $= 31338\ x^3 - 207254x^2 + 264484x + 2e + 06$
  $R^2 = 0{,}9762$
  x = 2026-2021
  x = 5
- M4 $= 31338\ x^3 - 207254x^2 + 264484x + 2e + 06$

$= 31338\ (5)^3 – 207254(5)^2 + 264484(5) + 2e + 06$
= 58.331,436 Kgs/year
= 58,331 tonnes/year

d. Domestic Demand in Indonesia

Domestic demand in Indonesia has changed, according to Indexbox statistics. The following table shows Indonesian domestic demand:

Table 3 Domestic Demand in Indonesia

Year	Kgs/Yr
2010	7,376,319.00
2011	9,685,436.00
2012	8,095,854.00
2013	11,042,289.00
2014	11,576,251.00

(Indexbox, 2022)

Table 3 was used to make a graph that predicts the trend of domestic demand in Indonesia over the next several years. Figure 3 displays a graph and equation that show the relationship between domestic demand statistics over the years.

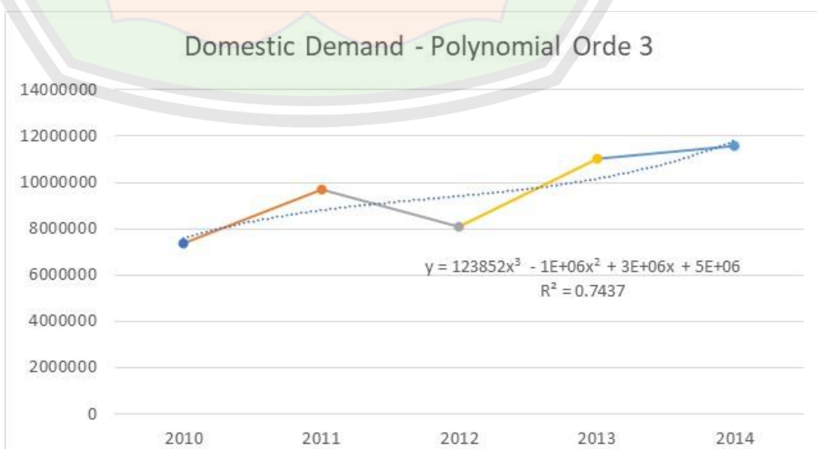

Figure 3 Polynomial Approximation Domestic Demand Graph

Calculation:

- $y = 123852\ x^3 - 1e + 06x^2 + 3e + 06x + 5e + 06$

  $R^2 = 0{,}9473$

  x = 2026-2014

  x = 12

- M5 $= 123852\ x^3 - 1e + 06x^2 + 3e + 06x + 5e + 06$

  = 123852 (12)3 – 1e + 06(12)2 + 3e + 06(12) + 5e + 06

  = 214017000 Kgs/year

  = 214017 tonnes/year

The production capacity of hexamethylenetetramine in 2025 can be calculated using the formula equation:

M1 + M2 + M3 = M4 + M5

M3 = (M4 + M5) – (M1 + M2)

(Kusnarjo, 2010)

Index:

m1 : Imported Amount in the Year of Factory Establishment

m2 : Current Domestic Production

m3 : Planned Factory's Capacity

m4 : Exported Amount in the Year of Factory Establishment

m5 : Domestic Consumption Amount

M3 = (M4 + M5) – (M1 + M2)

= (58,331 + 214,017) – (55,051.578+3000)

= 156,023.753 Tonnes/Year

The fulfilment of 15% of the available capacity,

= 15% x 156,023.753 Tonnes/Year

= 23,403.5595 Tonnes/Year

≈ 24.000 Tonnes/Year

Therefore, the hexamine factory planned for establishment in 2026 will have an annual production capacity of 24,000 tonnes.