Simulation and Energy Optimization of Ammonia Synthesis Loop
Ashutosh Desai#1, Shreyans Shah#2, Sanchit Goyal#3
Under the guidance of,
Prof. Arvind Prasad
Department of chemical engineering, Dwarkadas.J.Sanghavi college of Engineering,
Plot U-15, Bhaktivedanta swami marg, Ville parle (W), Mumbai-56, India.

Abstract
In this study, a flow sheet representing Ammonia Synthesis Loop for industrial production of Ammonia referred from the literature has been optimized by proposing a rigorous kinetic model for a plug flow reactor. The kinetic model proposed is developed on Scilab and the flow sheet is simulated using Cape-Open to Cape-Open Simulator. Various output parameters and corresponding operational profits have been analyzed for different input feed flow rates.

Keywords: ammonia, optimization, SciLab, reactor, modelling, simulation.

I. INTRODUCTION

Industrial ammonia is sold either as ammonia liquor (usually 28% ammonia in water) or as pressurized or refrigerated anhydrous liquid ammonia transported in tank cars or cylinders. (Bland, 2015)

In most commercial plants, either steam reforming of methane or gasification of coal is used as the source of nitrogen and hydrogen gas for the Haber-Bosch synthesis loop. The nitrogen and hydrogen gas mixture, which is called synthetic gas, is first compressed to 120-220 bars, depending on the particular plant, before it enters the ammonia synthesis loop. Only a fraction of the synthetic gas is converted to ammonia in a single pass through the converter due to thermodynamic equilibrium of the ammonia synthesis reaction as shown

\[
\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3 \quad \Delta H=46.22 \text{ kJ/mol}
\]

The converter typically contains a catalyst of iron promoted with K2O and Al2O3 to speed the reaction and to increase the amount of ammonia produced during each pass. The gaseous ammonia and unconverted gas then enters the ammonia recovery portion of the synthesis loop. The Haber-Bosch process continues to be improved, mostly through changes in the catalyst and heat recovery. One catalytic improvement that is starting to be used commercially is a ruthenium-based catalyst instead of an iron-based catalyst. An improved catalyst allows more ammonia to be produced per pass through the converter at lower temperatures and pressures. As a result, less energy is consumed in the production of ammonia.

A. Kinetic Model

The rate expression of Temkin-Phyzhez has been widely accepted to represent the synthesis of ammonia over wide ranging conditions, a modified form of the Temkin-Phyzhez equation expressed in terms of activities as developed by (Dyson & Simon, 1968) was used in this work.

The rate expression is given by:

\[
R_{\text{NH}_3} = 2k \left( \frac{K_a^2 a_{\text{N}_2}}{a_{\text{NH}_3}} \frac{a_{\text{H}_2}}{a_{\text{NH}_3}}^{\alpha} - \frac{a_{\text{H}_2}}{a_{\text{NH}_3}}^{1-\alpha} \right)
\] (1)

Where \(k\) is the rate constant for the reverse reaction, \(K_a\) is the equilibrium constant, \(a_i\) is the activity of component \(i\) and \(\alpha\) is a constant which takes a value from 0.5 to 0.75.

The rate equation for the reactants was determined using the stoichiometry of the reaction

\[
\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3
\]

And used to relate the individual rates of reaction as follows

\[
\frac{R_{\text{N}_2}}{-1} = \frac{R_{\text{H}_2}}{-3} = \frac{R_{\text{NH}_3}}{2}
\] (2)

B. Mass Balance

As the feed gas passes over the catalyst bed it reacts. The moles of nitrogen, hydrogen and ammonia change. If \(N\) is the total molar flow over the catalyst bed then,

\[
N_i = x_i \times N
\] (3)

\(N_i\) is the flow rate of individual component over the bed. For a packed bed the change in moles of any component per unit time over a differential volume of bed is
The change of moles of nitrogen per unit time over a differential volume of bed is
\[
\frac{dN_2}{dV} = R_1 \tag{4}
\]

The change in molar concentration of nitrogen over a differential volume of bed is
\[
\frac{dN_2}{dV} = -R_{N_2} \tag{5}
\]

The change in molar concentrations of hydrogen and ammonia over a differential volume of bed are
\[
\frac{dN_2}{dV} = \frac{\left(\frac{1}{2}R_{NH_3}\right) - \left(x_{NH_3} \frac{dN}{dV}\right)}{N} \tag{6}
\]
\[
\frac{dN_2}{dV} = \left(x_{NH_3} \frac{dN}{dV}\right) \tag{7}
\]

The change in temperature of gas over an infinitesimal catalyst bed is
\[
\frac{dT}{dV} = \frac{R_{N_2} \left (-\Delta H_{RT} \right )}{N + Cpmix} \tag{10}
\]

**II. DETERMINATION OF PARAMETERS**

**A. Specific Heat Capacity**
(Gunorubon & Raphael, 2014)

The heat capacities of the components of the reactant gases were obtained with the expression:
\[
C_p = 4.1884(a_1 + b_1T + c_1T^2 + d_1T^3) \tag{11}
\]
(Refer Table 1, Page 10)

The heat capacity of the ammonia is given by,
\[
C_{PNH_3} = (6.5846 - 0.61251 \times 10^{-2}T + 0.23663 \times 10^{-5}T^2 + 1.5981 \times 10^{-9}T^3 + 96.1678 - 0.067571T + (0.2225 + 1.6847 \times 10^{-4}P)T + (1.289 \times 10^{-4} - 1.0095 \times 10^{-7}P)T^2) \tag{12}
\]

**B. Effectiveness Factor (ƞ)**
(Gunorubon & Raphael, 2014)

To investigate the effects of temperature and density of the catalyst interior and the difference between these parameters with those of the catalyst surface, an effectiveness factor called ƞ has been defined. The general form of the equation defining this effectiveness factor has been given below.
\[
ƞ = b_0 + b_1T + b_2X + b_3T^2 + b_4X^2 + b_5T^3 + b_6X^3 \tag{13}
\]
(Refer Table 2, Page 10)

**C. Equilibrium Constant (K_a)**
The equilibrium constant was obtained using the expression in (Gunorubon & Raphael, 2014)
\[
\log K_a = \left(-2.69112 \log T - 5.51925 \times 10^{-5}T + 1.848863 \times 10^{-7}T^2 + \frac{2003.6}{T} + 2.689\right) \tag{14}
\]

**D. Rate Constant (k)**
The rate constant values were obtained using Arrhenius relation with values for synthesis relation obtained from (Gunorubon & Raphael, 2014)
\[
k = k_s \exp \left(\frac{-E}{RT}\right) \tag{15}
\]

**E. Component Fugacity Coefficient**
The fugacity coefficients for all the components were determined using the expressions given by (Ukpaka & Izonowei, 2017) as
\[
\phi_{N_2} = \left(\exp\left(\exp(-3.802T^{0.125} + 0.541)P - \exp(-0.1263T^{0.5} - 15.98)P^2 + \left(300\exp(-0.011901T - 5.941)\left(\exp\left(\frac{P}{300}\right)\right)\right)\right)\right) \tag{16}
\]
\[
\phi_{NH_3} = \left(0.93431737 + 0.295896 \times 10^{-3}P - 0.270727 \times 10^{-6}T^2 + 0.4775207 \times 10^{-9}P^2\right) \tag{17}
\]
\[
\phi_{N_2} = \left(0.1438996 + 0.2028538 \times 10^{-3}T + 0.4487672 \times 10^{-7}P - 0.1142945 \times 10^{-9}T^2 + 0.276121 \times 10^{-6}P^2\right) \tag{18}
\]
III. SIMULATION

The topography of the process used in the referred paper was simulated. This flowsheet closely represents an industrial unit. Araujo et al simulated this flowsheet using Aspen Plus®. In this work the flowsheet was simulated using COFE (Cape Open Flowsheet Environment) Simulator.

The catalytic bed in the reference flowsheet were replaced by our own PFR models which were designed using SciLab. The designed PFR models were incorporated in SciLab unit operation of COFE (Cape Open Flowsheet Environment) Simulator.

IV. MODELLING OF THE REACTOR

A 3-Bed PFR was modelled using the Scilab Unit operation. Modelling of the reactor was done by using all the necessary equations mentioned in the above section. The equations were written as a part of the code in Scilab and the program was run accordingly. The code for a particular bed was used for all three beds and introduced in the Scilab Unit Operation in COFE Simulator.

V. ENERGY OPTIMIZATION

When modelled PFRs were incorporated in the referred topography and simulated, the Heat Exchanger duties were as follows:

H-501 = 8 MW 
H-583 = 45.56 MW

An energy optimization was carried out in the flow sheet. Pinch temperature analysis was done considering the necessary hot and cold streams that participated in the heat exchange. The feed composition was altered to ensure the maximum output of Argon (inert) in stream number 25.

This led to the H-501 heat exchanger duty to rise to 18 MW producing a high quality 22000 kg/h of steam at 40.5°C superheat and at a high pressure of 35 bars.

The H-583 heat exchanger duty reduced to 26.4 MW which led to the requirement of the cooling water to go down to 600000 kg/h (which was initially 700000kg/h)

This was done for different values of flow rates of the feed. The figures depicting the energy optimized flowsheet and the corresponding stream data is shown below:

![Fig. 1: A part of the code in Scilab unit operation](image_url)

![Fig. 2: Scilab Unit Operation – GUI Model](image_url)
The pressure drop across each bed was assumed to be 1 bar, this assumption was made on the basis of the referred paper (Araújo & Skogestad, 2008)

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### Table 3(i): Stream Report (Fig 2)

<table>
<thead>
<tr>
<th>Stream</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<td>206.957</td>
<td>206.957</td>
<td>206.957</td>
<td>206.957</td>
<td>206.957</td>
<td>206.957</td>
<td>206.957</td>
</tr>
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<td>275.036</td>
<td>438.776</td>
<td>275.036</td>
<td>275.036</td>
<td>275.036</td>
<td>275.036</td>
<td>275.036</td>
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<td>1480.17</td>
<td>1480.17</td>
<td>740.03</td>
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<td>46.1294</td>
<td>270.729</td>
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<td>0.611973</td>
<td>0.611973</td>
<td>0.611973</td>
<td>0.611973</td>
<td>0.611973</td>
<td>0.611973</td>
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<td>0.2774</td>
<td>0.2774</td>
<td>0.2774</td>
<td>0.2774</td>
<td>0.2774</td>
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<td>0.2774</td>
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<tr>
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<td>0.00368112</td>
<td>0.00368112</td>
<td>0.00368112</td>
<td>0.00368112</td>
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<td>0.00368112</td>
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<td>0.09229201</td>
<td>0.09229201</td>
<td>0.09229201</td>
<td>0.09229201</td>
<td>0.09229201</td>
<td>0.09229201</td>
<td>0.09229201</td>
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### Table 3(ii): Stream Report (Fig 2)

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<th>Material properties</th>
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<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
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<th>Information Stream 2 - 3</th>
<th>Unit</th>
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<tr>
<td>Pressure</td>
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<td>206.957</td>
<td>206.957</td>
<td>206.957</td>
<td>206.957</td>
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<td>206.957</td>
<td>206.957</td>
<td>206.957</td>
<td>206.957</td>
<td>bar</td>
</tr>
<tr>
<td>Temperature</td>
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</tr>
<tr>
<td>Flow rate</td>
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<td>194146</td>
<td>2222025</td>
<td>2222025</td>
<td>296804</td>
<td>296804</td>
<td>296804</td>
<td>0.061973</td>
<td>0.061973</td>
<td>kg / h</td>
</tr>
<tr>
<td>Mole frac Hydrogen</td>
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<td>0.611973</td>
<td>0.564131</td>
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<td>0.498656</td>
<td>0.532233</td>
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<td>0.465011</td>
<td>0.2774</td>
<td>0.2774</td>
<td>-</td>
</tr>
<tr>
<td>Mole frac Nitrogen</td>
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<td>0.2032</td>
<td>0.265015</td>
<td>0.246791</td>
<td>0.25268</td>
<td>0.238203</td>
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<td>0.238203</td>
<td>0.00602568</td>
<td>0.00602568</td>
<td>-</td>
</tr>
<tr>
<td>Mole frac Methane</td>
<td>0.00602568</td>
<td>0.00602568</td>
<td>0.00602568</td>
<td>0.00602568</td>
<td>0.00602568</td>
<td>0.00602568</td>
<td>0.00602568</td>
<td>0.00602568</td>
<td>0.00602568</td>
<td>0.00602568</td>
<td>-</td>
</tr>
<tr>
<td>Mole frac Argon</td>
<td>0.00368112</td>
<td>0.00368112</td>
<td>0.00368112</td>
<td>0.00368112</td>
<td>0.00368112</td>
<td>0.00368112</td>
<td>0.00368112</td>
<td>0.00368112</td>
<td>0.00368112</td>
<td>0.00368112</td>
<td>-</td>
</tr>
<tr>
<td>Mole frac Ammonia</td>
<td>0.09229201</td>
<td>0.09229201</td>
<td>0.09229201</td>
<td>0.09229201</td>
<td>0.09229201</td>
<td>0.09229201</td>
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<td>0.09229201</td>
<td>0.09229201</td>
<td>0.09229201</td>
<td>-</td>
</tr>
</tbody>
</table>

---

The pressure drop across each bed was assumed to be 1 bar, this assumption was made on the basis of the referred paper (Araújo & Skogestad, 2008)

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**Fig 3: Energy Optimized Flow Sheet**
VI. PROFIT ANALYSIS

The results that were achieved by the analysis of change in parameters with respective changes in the inlet flow rates were used to calculate the net operational profit for all the inlet flow rates. This helped us to analyse how the flow rates affect the earnings by the process. The parameters taken into consideration are:

1) Net ammonia flow at the outlet of the flash distillation unit.
2) Amount of feed at the inlet.
3) Amount of purge.
4) The total duty required by the 2 compressors.
5) Utilities that include:
   a) Steam produced – positive utility.
   b) Amount of cooling water required – negative utility.

The Operational Profit is calculated by the formula: (Araújo & Skogestad, 2008)

\[ P = S_{prod} (x_{NH3} F_{prod}) + S_{purge} F_{purge} + S_{steam} F_{steam} - S_{gas} F_{gas} - S_{WS} (W_{K-401} + W_{K-402}) - S_{CW} F_{CW} \]  

(19)

Where \( x_{NH3} \) is the product purity, \( F_{steam} \) is the steam generation in kg/h and \( F_{CW} \) is the amount of cooling water required in m³/h.

Note that \( P \) is the operational profit and does not include other fixed costs or capital costs.

The prices are

\[ S_{prod} = 0.200\$/kg, \]
\[ S_{purge} = 0.010\$/kg, \]
\[ S_{steam} = 0.017\$/kg, \]
\[ S_{gas} = 0.080\$/kg, \]
\[ S_{WS} = 0.040\$/unit and, \]
\[ S_{CW} = 0.137366/m^3. \]  (Ulrich & Vasudevan, 2006)

The above formula gives us the profit in \$/h.

VII. RESULTS AND DISCUSSIONS

After optimising the flow sheet for various flow rates, the following results were observed:

1) There is a fixed pattern in the temperatures of the respective beds for different flow rates. It is quite evident from the temperature profile along the beds shown below. (Fig 4)
Here, on the x-axis, the scale indicates:

1 – Bed 1 inlet
2 – Bed 1 outlet
3 – Bed 2 inlet
4 – Bed 2 outlet
5 – Bed 3 inlet
6 – Bed 3 outlet

From the plot, it is observed that the temperature profile for the feed flow rate of 70000 kg/h behaves a bit differently from the other flow rates across the bed. The temperature at the outlet of bed 2 for the feed flow rate of 68000 kg/h goes beyond 500°C, which is generally the upper limit for a reactor temperature in an ammonia synthesis process. This is because the inlet temperature of the reactor is very high.

2) It is also observed that the ammonia production increases as we increase the feed flow rates.

3) The Operational Profit (P), on an overall basis, increases as we increase the feed flow rate. The plot of P vs Flow Rates is shown below:  (Fig 5)
4) It can be noticed that the Profit sees an almost-stagnant zone between the flow rates of 69000 kg/h to 70000 kg/h. The major reason for this anomaly is the unusual behaviour of the temperature along the bed 1 for the 70000 kg/h flow rate. This unexpected drop in the temperatures results in the reduction of the overall conversion of the process, which, in turn, produces lesser ammonia than expected hence, limiting the profit.

Another conclusion that can be made from this information is that, the profit from the process majorly depends upon the total production of ammonia in the process.

(NOTE: We can see that the amount of steam generated and the cooling water required remain constant throughout. This is because we have taken constant duties across the respective heat exchangers and kept the flow rates constant too in order to obtain more relatable results for the varying flow rates of feed at the inlet. (Table 5)

5) We can also see that the conversions in each and every subsequent case increase slightly. This is basically due to relative composition of ammonia entering the reactor inlet in each case. We experience these changes because we change the conditions of the flash distillation units in each and every case to balance out the inerts entering the process via the feed in order to avoid accumulation (refer Table). This is because, the accumulation of inerts in the process would keep on reducing the overall conversion of the process over time and this would result in reduced profits because of lesser ammonia at the outlet. (Table 6).

Because more amount of ammonia is removed in each and every case, lesser ammonia goes into recycle and hence the molar composition of ammonia at the reactor inlet drops.

Since the molar composition of ammonia in the inlet drops, it forces the equilibrium to shift forward, giving us a larger conversion in return.

Table 5: Heat Exchanger Duties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-501</td>
<td>18</td>
<td>MW</td>
</tr>
<tr>
<td>H-583</td>
<td>26.3912</td>
<td>MW</td>
</tr>
</tbody>
</table>

Table 6: Conversion with Different Flowrates

<table>
<thead>
<tr>
<th>Flow rate (kg/h)</th>
<th>Mole Fraction Of Ammonia Entering The Reactor</th>
<th>Flash Conditions</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature (°C)</td>
<td>Pressure (bar)</td>
</tr>
<tr>
<td>68000</td>
<td>0.096</td>
<td>20.25</td>
<td>199</td>
</tr>
<tr>
<td>69000</td>
<td>0.0957</td>
<td>21</td>
<td>200.284</td>
</tr>
<tr>
<td>70000</td>
<td>0.094</td>
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<tr>
<td>71000</td>
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<td>72000</td>
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<td>73000</td>
<td>0.0878</td>
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<td>203.284</td>
</tr>
</tbody>
</table>

Table 1: Coefficient for specific heat capacity of gas mixture (Ukpaka & Izonowei, 2017)

<table>
<thead>
<tr>
<th>Constants</th>
<th>Component</th>
<th>H₂</th>
<th>N₂</th>
<th>CH₄</th>
<th>Ar</th>
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<tbody>
<tr>
<td>a</td>
<td></td>
<td>6.952</td>
<td>6.903</td>
<td>4.75</td>
<td>4.9675</td>
</tr>
<tr>
<td>b x 10⁵</td>
<td></td>
<td>-0.04567</td>
<td>-0.03753</td>
<td>1.2</td>
<td>-</td>
</tr>
<tr>
<td>c x 10⁵</td>
<td></td>
<td>0.095663</td>
<td>0.193</td>
<td>0.303</td>
<td>-</td>
</tr>
<tr>
<td>d x 10⁵</td>
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<td>-0.2079</td>
<td>-0.6861</td>
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Table 2: coefficients of effectiveness factor

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>b⁰</th>
<th>b¹</th>
<th>b²</th>
<th>b³</th>
<th>b⁴</th>
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REFERENCES