MINI PROJECT:

ABSORPTION UNIT IN DILUTE NITRIC ACID PRODUCTION

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Introduction

Process Background
Nitric acid (HNO₃) is a highly corrosive, strong inorganic acid and one of the industry’s main feedstock. Their importance can be seen through its usage in many industries ranging from small daily household items such as fertilizer and drugs to dangerous and massive engineering marvels like rocket fuels and explosives. Normally, the nitric acid used in the fertilizer industry is a diluted acid with concentrations of 50-70%. Meanwhile in other industries, especially in rocket fuel production, they use concentrations of up to 90-100%, mainly for nitration processes. (Lefers, 1980)

Since the 1920’s, the production of nitric acid through the Oswald’s process became more popular than ever with the implementation of Haber process in the industry. There are 3 popular methods of producing nitric acid which are:

1. Chile Saltpetre method
2. Birkeland and Eyde Method
3. Oswald’s Method

Chile Saltpetre method
Chile Saltpetre method is based on a laboratory scale reaction. It was once popular in the 1920’s. Chile saltpeter, a material which contains sodium nitrate NaNO₃ with percentage around 35-60%, and remaining percentage compounds with KNO₃ and NaCl. Refined Chile Saltpetre and concentrated sulfuric acid are mixed in the following chemical reaction to produce the desired nitric acid in vapor form. The vapor is then condensed into liquid nitric acid.

\[ \text{NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HNO}_3 \]

Birkeland and Eyde method
Birkeland and Eyde method utilizes the nitrogen gas and oxygen in air to form nitrogen dioxide which is then reacted with water to produce nitric acid. The reaction of nitrogen and oxygen in air takes place in a Birkeland Eyde reactor, specifically, near the electric arc produced inside the reactor, whereby the temperature which exceeds 3000°C causes the nitrogen and oxygen reacted in the following reaction:

\[ \text{N}_2 + \text{O}_2 \rightarrow 2 \text{NO} \]
\[ 2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 \]
\[ 3 \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 + \text{NO} \]

Although this process seemed cost wise, but to operate a Birkeland Eyde reactor on a large scale production uses so much energy making this method inefficient as far as energy consumption is concerned. Therefore this method was gradually replaced in the 1920s by the Oswald’s method.

Oswald’s method
Oswald’s method of producing nitric acid makes use of ammonia from the recent industrially introduced (1913) Haber process. Ammonia is oxidized in an oxidation chamber to form nitrogen monoxide in an equilibrium reaction:
4 NH₃ + 5 O₂ ↔ 4 NO + 6 H₂O \ldots [1]
2 NO + O₂ ↔ 2 NO₂ \ldots [2]

The nitrogen monoxide is then oxidized again with oxygen to form nitrogen dioxide. Please take note that both of these oxidation processes were catalyzed by Platinum–Rhodium catalyst. The nitrogen dioxide is then passed through an absorption column with water being the liquid input.

3 NO₂ + H₂O → 2 HNO₃ + NO \ldots [3]

The produced nitric acid produced from this reaction is very dilute. To concentrate it, it is passed through concentrated sulfuric acid in a dehydration reaction which removes water from the nitric acid solution producing a concentrated one.

Remark: For the purpose of this project, the researchers decided to put emphasis on the Oswald process focusing on the absorption unit. A big picture of this process can be seen through the process flow diagram. (figure 1)

**Project aim**
The aim of this project is to:
1. Describe how does the Oswald process is being implemented in the industry.
2. Discuss how nitrogen dioxide is being processed in a liquid gas absorber
3. Do a material balance calculation for the absorber process unit

A Detailed look into the Oswald’s Process

The process started out with dry ammonia and dry air as its main feed to the plant. The ammonia is either produced on-site exploiting the Haber process or bought from other vendors depending on the cost effectiveness. The dry air used is filtered appropriately based on the condition of the local pollution level. Sometimes, gas scrubbers are used (Keleti, 1985) to remove unwanted pollutants that might react with ammonia and produce other sub-compound. According to Lefers (1980), in a mono pressure system, the feed ratio is 10% ammonia and 90% air.

Ammonia mixed with air enters a converter (B) in which the gas mixture is passed over a platinum gauze catalyst at a temperature of 850-920°C. This reaction occurs according to equation 1. The converter can be operated either at high pressure (7-10 bar), medium pressure (3-5 bar), or even at atmospheric pressure (1.01 bar). The hot gases leaving the converter are cooled in a waste heat boiler to generate steam. The temperature is further reduced to 20°-40°C in a cooler-condenser (D), and at the same time the NO formed is oxidized to NO₂ (refer equation 2).

The water formed condenses in the cooler-condenser and some weak acid is produced. The gas mixture, containing about **10 volume % NOₓ**, enters the acid absorber (E) where it reacts with water in the liquid phase at ambient temperature and at the respective operating pressure in the converter. This reaction follows equation 3.
60% nitric acid containing some dissolved nitrogen oxides leaves the absorber from the bottom and is stripped with air in a bleaching column (F). The tail gas, containing 200-2000ppm of NOx is heated and the energy produced by the gas expansion is used to run a turbine (G). However, international environmental laws requires a maximum 200ppm of NOx released from new plants and 500ppm for old ones. (Keleti, 1985)

Fig. 1 The D.S.M. nitric acid process (mono-pressure system).
1: air, 2: NH₃, 3: 10% NH₃ in air, 4: NO, 5: NO₂, 6: weak acid, 7: tail gas containing 200-2000 ppm NOx, 8: unbleached 60% nitric acid, 9: NO₂, 10: bleached 60% nitric acid, 11: air, 12: water.

Lefers added that, other than a single pressure system, a dual pressure system is used; whereby the conversion (equation 1 and 2) takes place at a lower pressure then the absorption (equation 3). For this, a nitrous gas compressor is needed. The advantage of a dual pressure system is a lower loss of ammonia and platinum catalyst. However, investments on such system are higher compared to the mono pressure system.
The Absorption unit

According to Felder and Rouseau (2005), absorption is defined as, “a process in which a gas mixture contacts a liquid solvent and a component (or several components) of the gas dissolves in the liquid.” The process unit is called absorption column or absorption tower or just simply an absorber. It is a continuous process unit. The purpose of the absorption tower is to dissolve one or more components of the gas into the liquid. It uses the basic principle of gravity and density. The liquid flows down in the direction of gravity while the gas flows upwards due to its lower density compared to air. The two components meet and react and continue to flow in their respective way. The solvent enters from the top, in this case water and the gas (in this case NO₂) is fed from the bottom. The gas that emerged from the top is the top product (tail gas) while the bottom product is liquid the required nitric acid (figure). The contact point of the gas and the liquid is called packing (figure 3). It is designed and shaped specifically to provide maximum contact area within the volume of the absorber and contact time of the two phases. The packing is made from inert materials such as ceramics so that it would not react with the feed.

Usually, an absorption tower is accompanied by several other absorption towers depending on the design and pressure of the systems. For the sole purpose of this paper, the authors exclusively focus on a single tower design with atmospheric pressure and ambient temperature as its operating condition.
A MEB is calculated for the absorption tower manually and through software called Aspen HYSYS. Both results are then compared and analyzed. The objective of this is to prove that mass and energy is conserved for this process unit.

The basic information for the absorber is as follows:
- 10% mole fraction NO₂ and the excess is air
- 100% distilled, demineralised water input feed
- 60% of HNO₃ is formed
- Pressure of system is 1 atm
- Temperature of system is 25°C
- Unknowns: efficiency of column/ extent of reaction and molar flowrate.
- Basis of calculation: 100 mol/hour of feed for NO₂ stream

Assumptions:
1. Efficiency is assumed to be 60% for this system (Keleti, 1985)
2. Air does not dissolve in water and is inert to other reactants to make calculations simpler
3. Reaction model is assumed to be single reaction. (in reality, it is a complex, multiphase reaction)

**Table 1: Table of selected chemical properties**

<table>
<thead>
<tr>
<th>Compound</th>
<th>NO₂ (g)</th>
<th>H₂O (l)</th>
<th>HNO₃ (aq)</th>
<th>NO (g)</th>
<th>Air (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M (kg/kg-mol)</td>
<td>46</td>
<td>18</td>
<td>63</td>
<td>30</td>
<td>29</td>
</tr>
<tr>
<td>ΔHᵣ (kJ/mol)</td>
<td>+33.2</td>
<td>-285.8</td>
<td>-207</td>
<td>90.29</td>
<td>-</td>
</tr>
<tr>
<td>ΔH (std)</td>
<td>0.914</td>
<td>1.885</td>
<td>2.75</td>
<td>0.74</td>
<td>0.7248</td>
</tr>
<tr>
<td>Cₚ,25°C (kJ/mol.°C)</td>
<td>0.037</td>
<td>0.0754</td>
<td>0.0297</td>
<td>110</td>
<td>0.0290</td>
</tr>
</tbody>
</table>

Reaction:

\[
3 \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 + \text{NO}, \quad \Delta H = -117 \text{kJ/mol}
\]

The simple process flow sheet for the absorber is as follows:
The summary for the mass balance calculation

<table>
<thead>
<tr>
<th></th>
<th>molar mass</th>
<th>mole in</th>
<th>mass in</th>
<th>mole out</th>
<th>mass out</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO2</td>
<td>46</td>
<td>10</td>
<td>460</td>
<td>4</td>
<td>184</td>
</tr>
<tr>
<td>H2O</td>
<td>18</td>
<td>4.75</td>
<td>85.5</td>
<td>2.75</td>
<td>49.5</td>
</tr>
<tr>
<td>HNO3</td>
<td>63</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>252</td>
</tr>
<tr>
<td>NO</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>air</td>
<td>29</td>
<td>90</td>
<td>2610</td>
<td>90</td>
<td>2610</td>
</tr>
<tr>
<td>SUM</td>
<td></td>
<td></td>
<td>3155.5</td>
<td></td>
<td>3155.5</td>
</tr>
</tbody>
</table>

Hence, mass is balanced for this process unit.

From the above table, data for the streams can be deduced as below

<table>
<thead>
<tr>
<th>Stream</th>
<th>Bottom in (kg/hour)</th>
<th>Top in</th>
<th>Top out</th>
<th>Bottom out</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass flow rate</td>
<td>3070</td>
<td>85.5</td>
<td>2854</td>
<td>301.5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure (atm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition (mole %)</td>
<td>NO2: 10% Air: 90%</td>
<td>H2O: 100%</td>
<td>NO: 2.17% Air: 97.83%</td>
<td>HNO3: 59% ≃ 60% H2O: 41%</td>
</tr>
</tbody>
</table>

Conclusion

In the absorption unit of Ostwald Process, the efficiency of the overall reaction is only about 60% from the targeted amount reacted. Therefore, to ensure the reaction to be almost 100% efficiency, a method where the unreacted reaction will be entering another absorber to go through another reaction so that more amount of product can be produce. The overall reaction in the unit is:

\[
3 \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 + \text{NO}, \quad \Delta H = -117 \text{kJ/mol}
\]

The reaction is an exothermic reaction whereas the system is maintained at 1atm and 25°C throughout the absorption unit.
References


