

SIMULATION OF PRODUCTION OF NITRIC ACID

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Abstract: Nitric acid is a highly corrosive mineral acid and is commonly used as a strong oxidizing agent. The main industrial use of nitric acid is for the production of fertilizers. Nitric acid is produced industrially through a multistep reaction process known as Ostwald process. The purpose of this simulation was to observe the thermodynamic properties of the process. In design and optimization of nitric acid process, it is essential to understand the rate controlling step for ammonia oxidation process, strategy to be adopted for heat exchanger network design, rates of mass transfer and chemical reaction for nitrogen oxide absorption and the combined effects of several equilibria. In simulation, compressed air of 10atm and compressed ammonia of 10atm was introduced in three different reactors and the product was cooled and separated. Nitric acid was cooled from 700°C to 300°C before flash separation to get main product liquid nitric acid. By performing simulation, 29.0% aqueous HNO₃ was obtained for 2.0 kgmole/hr air and 0.50 kgmole/hr ammonia inlets. The major contributing process parameters have been analyzed for the purpose of optimization of nitric acid plant and their relation with one another were shown through several graphical representations. After analyzing the process variables, the profit was optimized using HYSYS optimizer.

Keywords: Ostwald, Simulation, Nitric acid, Oxidizing agent, Fertilizer

1. INTRODUCTION

Nitric acid is one of the basic industrial chemicals with annual world production of about 50 million metric ton/year (100% basis). Around 80% of nitric acid is produced as “weak acid” (50-69%) and is used in fertilizers production. The major products of nitric acid-based fertilizers industry are ammonium nitrate (AN), calcium-ammonium nitrate (CAN), urea-ammonium nitrate solutions (UAN) and some kinds of complex NP and NPK fertilizers (nitro-phosphates). The weak nitric acid production is based on three main chemical processes: catalytic oxidation of ammonia in air to nitric oxide, homogeneous oxidation of NO to NO₂ and absorption of NO₂ in water. Due to the specificity of these chemical reactions, two main features exist in nitric acid plants: environmental problems, ensuing from N₂O and NO_x presence in the waste gas (referred as “tail gas”) and high energy recovery, making nitric acid production process a very interesting subject of Second-Law-based analysis and optimization investigations [1].

Nitric acid production is one of the large-scale processes in chemical industry. The process involves the catalytic oxidation of ammonia by air (oxygen) yielding nitrogen oxide then oxidized into nitrogen dioxide and absorbed in water. The desired product yield essentially depends on the catalyst selectivity and of course on the operating conditions [2]. Ammonia usually comprises ca. 90% of the nitric acid production cost. Therefore, the ammonia oxidation efficiency is a key factor for the nitric

acid production [3]. In the first industrial process of nitric acid production by ammonia oxidation designed by Ostwald at the beginning of the 19th century, pure platinum gauzes served as the catalyst. Later pure platinum was displaced by platinum–rhodium alloys, in which the rhodium content varied from 5 to 10% [4].

Nitric acid production represents the largest source of N₂O in the chemical industry, with a global annual emission of 400 kt N₂O. The high impact of N₂O on the environment as greenhouse gas and stratospheric ozone depletor, and the ongoing agreements and prospective regulations calls for the development of efficient and economical systems for N₂O mitigation, but no mature commercial technology is yet available[5]. The reaction of nitric acid oxidation unavoidably generates nitrous oxide. Either the isothermal reactor or the adiabatic reactor is believed appropriate to use as the decomposition reactor in catalytic decomposition of N₂O [6]. Converting the nitrogen oxides into concentrated nitric acid requires an extensive equipment and is a considerable item in the cost of manufacture [7].

Although every individual stage of the overall process is relatively simple, there exists a number of variables in each to make possible a wide range of combinations of operating conditions. Specific combinations of these have led to the development of a range of proprietary nitric acid processes that are now offered to the chemical industry under license, mainly through chemical plant contractors. Prospective plant operators thus have to evaluate the economic and technical features of the

available competing processes against the background of their individual local operating conditions. Since the final selection of a particular process is inevitably based on economic considerations, the complex interdependence of the numerous process operating variables, and the plant capital investment and operating costs makes this task a formidable one [8]. The reaction is highly exothermic and in many modern high pressure plants the heat energy from the tail-gas is recovered as it passes through a turbine, thus contributing to the power required to compress the process gas. For a long time the desirability of obtaining this energy as electricity, rather than as heat, has been appreciated [9].

Greater awareness of environmental effects has led to a demand for the control of emissions, in particular the colored nitrous plumes, from nitric acid plants. The platinum group metals again feature prominently and are used almost exclusively as the catalyst in emission treatment on account of their high intrinsic activity, durability and resistance to poisoning. The Honeycat system, in which the catalyst is supported on a ceramic honeycomb, is now a well-established technology and can effectively and economically reduce emissions to a low level [10]. Accumulation of chlorides in nitric acid, resulting from inadequate removal facilities, causes rapid acceleration of the corrosion rate of the stainless steel concentrator [11].

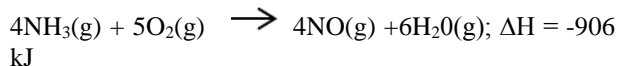
2. METHODOLOGY

The process of synthesis of nitric acid from ammonia by Ostwald's process is simulated in simulation software Aspen HYSYS 6.0. Aspen HYSYS is a widely used process simulator which provides quite accurate results compared to the real life result. It provides comprehensive thermodynamics basis for accurate determination of physical properties, transport properties, and phase behavior. Aspen HYSYS can be used to determine the outlet process conditions if inlet conditions are specified. For simulation Peng Robinson has been chosen as fluid package. Components for this simulation are Ammonia (NH₃), Nitrogen (N₂), Oxygen (O₂), Water (H₂O), Nitric-oxide (NO), Nitrogen di-oxide (NO₂), Nitric acid (HNO₃).

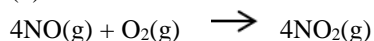
2.1 Reactions Involved

The three main reactions involved are-

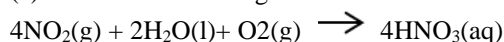
(a) Oxidization of ammonia to form nitric oxide



(b) Oxidization of nitric oxide to form nitrogen di-oxide



(c) Conversion of nitrogen di-oxide into nitric acid



2.2 Process Description

Once ammonia has been produced by the Haber process, it can be converted into nitric acid through a multi-step procedure known as the Ostwald process. Figure 2.1 shows the simplified block diagram of of

Ostwald process for nitric acid production.

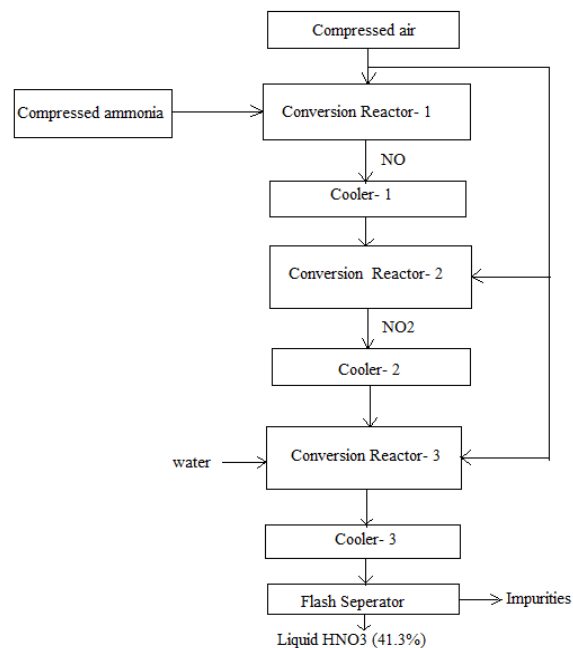


Fig.1: Simplified block diagram of Ostwald process for nitric acid production.

Following figure shows the HYSYS flow diagram of this process.

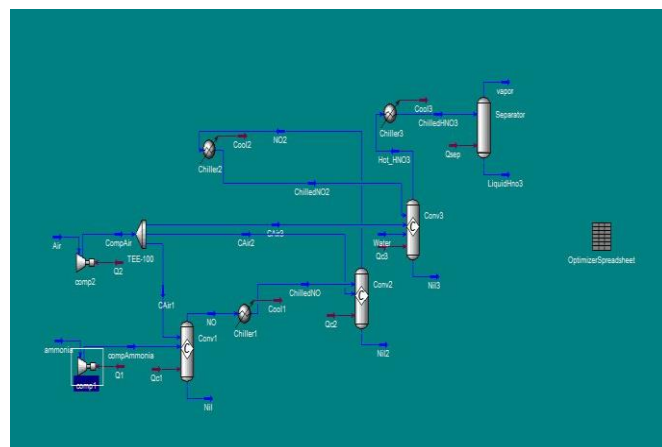


Fig.2: HYSYS process flow diagram of Ostwald process for nitric acid production.

2.2.1 Primary Oxidation

Oxidation of ammonia is carried out in a reactor in which whole part of ammonia and nearly one third part of oxygen by mass or mole are introduced. The temperature of chamber is about 900°C. From the basis of Ostwald's principle, the reaction is catalytic and contains a platinum gauze which serves as catalyst. Primary Oxidization of ammonia is reversible and exothermic process. Therefore according to Le- chatelier's principle, a decrease in temperature favors reaction in forward direction. In primary oxidization 22.4% of ammonia is converted into nitric oxide (NO).

2.2.2 Secondary Oxidation

Nitric oxide gas is obtained by the oxidation of ammonia which is very hot. In order to reduce its temperature, it is passed through a cooler where the temperature of nitric oxide is reduced from 900°C to 250°C. After cooling, Nitric oxide is transferred to another oxidizing tower where at about 200°C it is oxidized to NO₂.

2.2.3 Nitric Acid Production (Absorption Process)

The produced NO₂(g) reacts with water (H₂O) and oxygen(O₂) to produce nitric acid (HNO₃). In reference to Le Chatelier's principle, since the reaction is exothermic, conditions that would favor the forward reaction and shift the equilibrium to the right by decreasing the temperature and increasing the concentration, pressure and volume [7]. To ensure favorable conditions, a cooler is used to decrease the temperature to 300°C and constant addition of water and oxygen for this process as reactants to increase the concentration. The catalyst that is used for this reaction is platinum gauze. It would be heated and sometimes in substitute a copper wire or rod can be served as a proper catalyst for this process. After further cooling and flash separator 29.0% liquid nitric acid is obtained as final desired product.

2.2.4 Optimization

Here the parameter that was optimized was the hourly profit. The optimization function of profit can be defined as

$$P = S - TC \quad (1)$$

i.e. Profit = Total Selling Cost - Total Operating Cost; where selling cost included the cost of sale of Nitric acid and operating cost included the Ammonia consumption and operating cost related to Cooler, Compressor, Converter & Separator. The primary variables used for optimization were water pressure, water molar flow, ammonia molar flow, air molar flow, chilled HNO₃ temperature.

3. RESULTS AND DISCUSSIONS

In the simulation, 29.0% HNO₃ was found in the final product. We can change the amount of HNO₃ by varying different parameters. Some of the data and graphs are shown.

3.1. Effect of Input Ammonia Flow On % of HNO₃ in Final Product.

From figure 3, it is clearly seen that composition of HNO₃ in final product increases with increase in ammonia flow rate up to a certain range. Then it decreases with increasing ammonia flow rate.

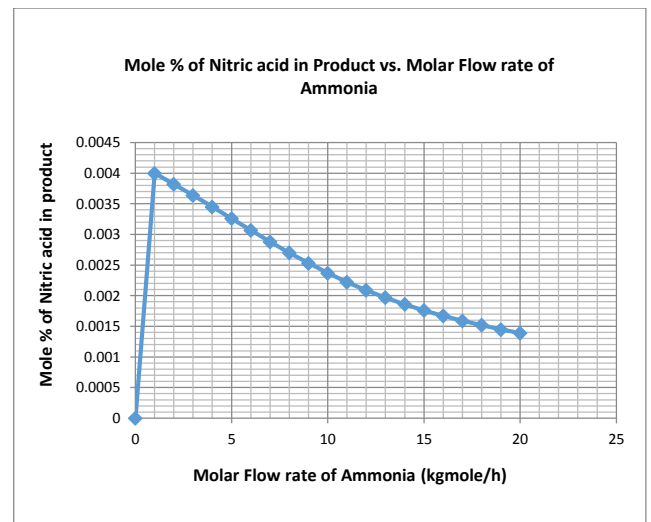


Fig.3: Effect of input ammonia flow on % of HNO₃ in final product.

3.2. Effect of Air Flow Rate On % of HNO₃ in Final Product.

From figure 4, it is seen that composition of HNO₃ in final product increases with increase in air flow rate up to a certain range.

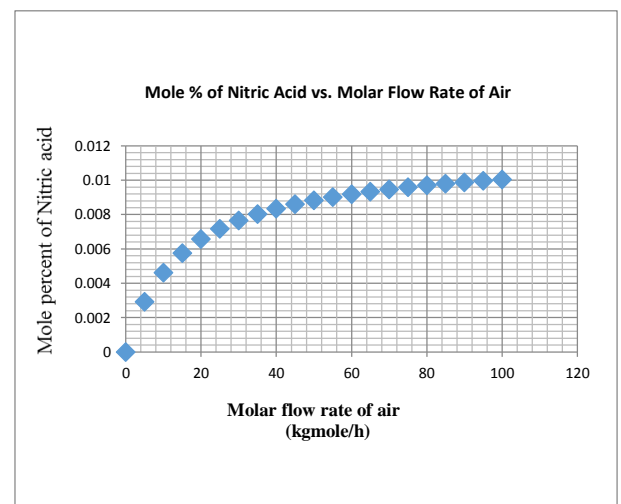


Fig.4: Effect of air flow rate on % of HNO₃ in final product.

3.3. Effect of Molar Flow Rate of Water On % of HNO₃ in Final Product.

From figure 5, it can be seen that composition of HNO₃ in final product decreases with increase in water flow rate.

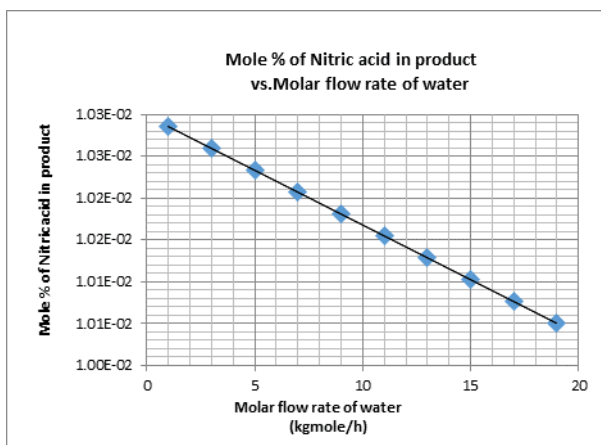


Fig.5: Effect of molar flow rate of water on % of HNO_3 in final product.

3.4. Effect of Input Temperature of Chilled NO on % of HNO_3 in Final Product.

From figure 6, it can be seen that composition of HNO_3 in final product remains constant with changes in temperature of chilled NO .

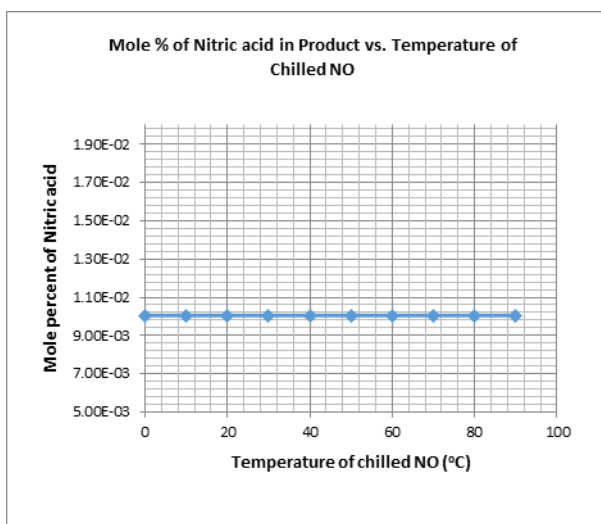


Fig.6: Effect of input Temperature of chilled NO on % of HNO_3 in final product.

3.5. Effect of Temperature of Chilled NO_2 on % of HNO_3 in Final Product.

From figure 7, it can be seen that composition of HNO_3 in final product remains constant with changes in temperature of chilled NO_2 .

3.6. Effect of Cooling Temperature Before Entering Separator on % of HNO_3 in Final Product.

From figure 8, it is seen that composition of HNO_3 in final product remains constant with changes in cooling temperature before entering separator.

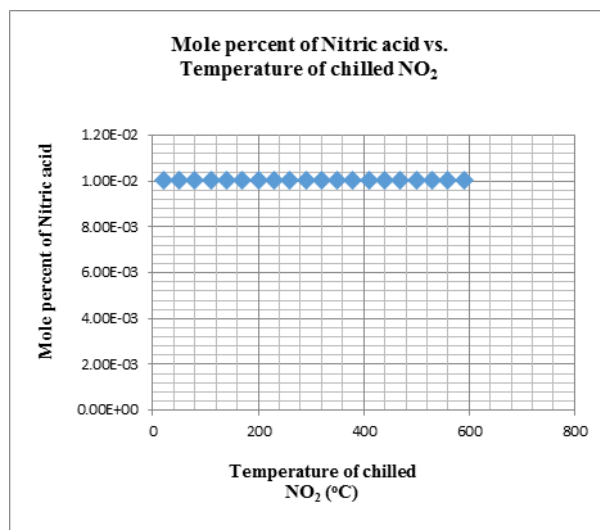


Fig.7: Effect of temperature of chilled NO_2 on % of HNO_3 in final product.

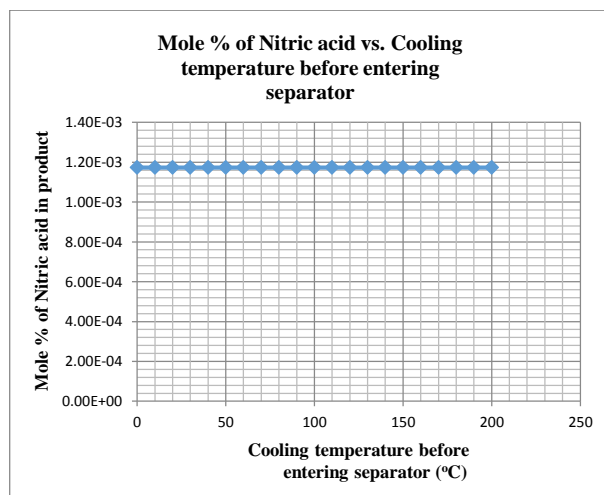


Fig.8: Effect of cooling temperature before entering separator on % of HNO_3 in final product.

4. CONCLUSIONS

Nitric acid (HNO_3) is a colorless liquid that is used in the manufacture of inorganic and organic nitrates and nitro compounds for fertilizers, dye intermediates, explosives, and many different organic chemicals. Continued exposure to vapor may cause chronic bronchitis; chemical pneumonitis may occur [12]. Nitric acid is not combustible [13]. Nitric acid is formed in the troposphere by gas-phase chemistry [14]. Nitric acid is very rich in oxygen and contains 76% by weight of oxygen and is a very convenient oxidizing agent [15].

Nitric acid production is an important chemical process. In this paper, data have been generated based on the simulation performed in HYSYS. These data can help to understand the process in different situations in industrial practice. This project can be used to conduct economic assessment. This developed simulation model can also be used as a guide for understanding the whole process of producing nitric acid and it can also be a

starting point for more sophisticated models, for process equipment selection and plant design.

5. REFERENCES

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6. NOMENCLATURE

Symbol	Meaning	Unit
P	Profit	\$/hour
S	Total Selling Cost	\$/hour
TC	Total Operating Cost	\$/hour