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Simulation of ammonia synthesis

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Abstract: Ammonia is prodeuced to give a final product named urea which is a very important fertilizer for higher nitrogen content.Several processes has been invented for optimum production of ammonia. Now-a-days, Ammonia production is mainly done by Haber process in which nitrogen andhydrogen react in the presence of an iron catalyst to form ammonia. The hydrogen is formedby reacting natural gas and steam at high temperatures and the nitrogen is supplied from theair. Other gases (such as water and carbon dioxide) are removed from the gas stream andthe nitrogen and hydrogen passed over an iron catalyst at high temperature and pressure toform the ammonia. In our work, simulation of ammonia synthesis process is done on Aspen Hysys 7.1. By using 1.07e+005kmole/hr methane, 2.8e+005kmole/hr hydrogen, 1.02e+005kmole/hr nitrogen, we haveproduced4.6e+004 kmole/hr ammonia.It has also been found that ammonia production increases with the rise of pressure of fresh feed.

Keywords: Ammonia, Simulation, Heber, Fertilizer, Reformer

1. Introduction

Ammonia is a compound of nitrogen and hydrogen with the formula NH_3. It is a colorless gas with acharacteristic pungent smell. Ammonia [1] contributes significantly to the nutritional needs of terrestrial organisms byserving as a precursor to food andfertilizers [5]industry [8]. Ammonia, both directly or indirectly, is also a building-block for thesynthesis of many pharmaceuticals and is used in many commercial cleaning products. Although in wide use,ammonia is both caustic and hazardous. Theglobal production of ammonia for 2012 is anticipated to be 198 milliontons, a 35% increase over the estimated 2006 global output of 146.5 million tones.

Ammonia, as used commercially, is often called anhydrous [2] ammonia. This term emphasizes the absence of water inthe material. Because NH_3 boils at −33.34 °C (−28.012 °F) at a pressure of 1 atmosphere, the liquid must be storedunder high pressure [3] or at low temperature. "Household ammonia" or "ammonium hydroxide" is a solution of NH_3 inwater. The concentration of such solutions is measured in units of the Baumészale (density), with 26 degreesBaumé (about 30% w/w ammonia at 15.5 °C) being the typical high-concentration commercial product. Householdammonia ranges in concentration from 5 to 10 weight percent ammonia.

In this experiment a detailed study is performed about the process by means of simulation in Aspen Hysysv7.1 [11].Since Haber process is widely used for maximum production of ammonia, we have simulated the process that is based on Haber [10] process. Though simulation does not give the real world performance or the real life production environment but if the basic process is known and related data are available, it surely is the best way by which an individual can get ideas of an industrial process without conducting any experiment.

2. Methodology

The process of producing ammonia is simulated in Simulation software Aspen Hysys7.1. Aspen HYSYS process simulator is a core element of AspenTech'sAspenONE®engineering applications. It provides quite accurate results which makes it an efficient simulator. It provides comprehensive thermodynamics basis for accurate determination of physical properties, transport properties, and phase behavior. Aspen HYSYS can be used to determine outlet process conditions if the inlet conditions like temperature, pressure, and composition are specified. In this simulation we used Peng-Robinson model fits best to equilibrium process.

2.1. Process Description

The simplified block diagram ofammonia synthesis is given below.

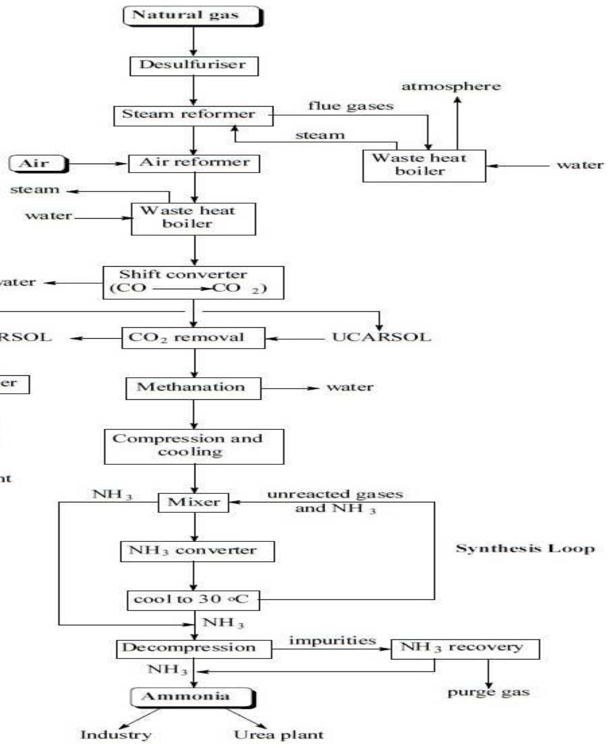


Figure 01. *block diagram of ammonia synthesis.*

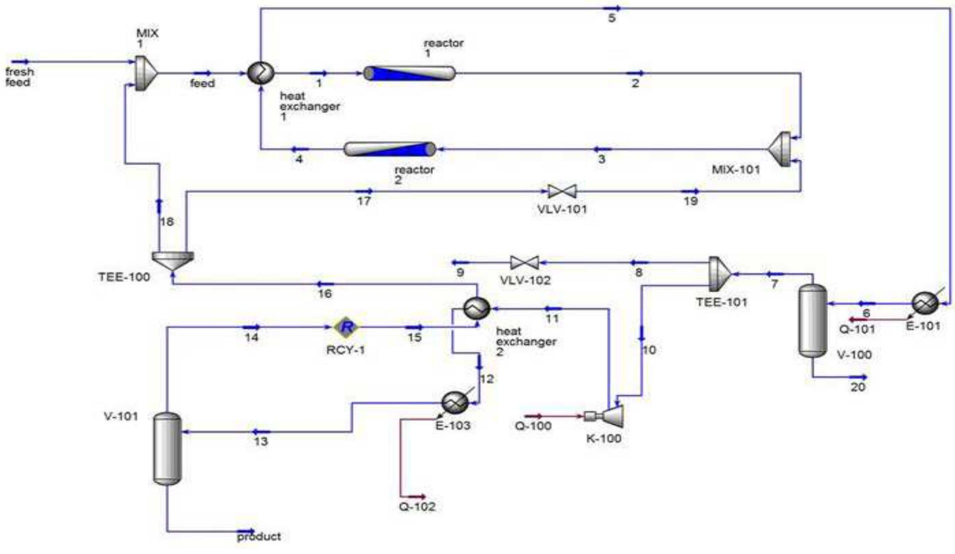


Figure 02. *Hysys Process flow diagram of ammonia synthesis.*

2.1. Reaction Involved

In hydrogen production step, four reactions are involved.Which are-

$$ZnO + H_2S = ZnS + H_2O$$

this reaction is done to carried out all sulpher compounds from natural gas.

Following reactions occur in reformer-

$$CH_4 + H_2O = 3H_2 + CO$$

$$CH_4 + 2H_2O = 4H_2 + CO_2$$

$$CO + H_2O = H_2 + CO_2$$

This gaseous mixture is known as synthesis gas.

In nitrogen addition step, synthesis gases are mixed with air in the secondary reformer. The reactions are-

$$CO + H_2O = CO_2 + H_2$$

$$O_2 + 2CH_4 = 2CO + 4H_2$$

$$O_2 + CH_4 = CO_2 + 2H_2$$

$$2O_2 + CH_4 = 2H_2O + CO_2$$

In carbon monoxide removal step, carbon monoxide is removed by water gas shift reaction.

$$CO + H_2O = CO_2 + H_2$$

In Removal of carbon oxides step, all carbon oxides are converted to methane by following reactions-

$$CO + 3H_2 = CH_4 + H_2O$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

In ammonia synthesis step, fowlloing reaction provides final product ammonia-

$$N_2 + 3H_2 = 2NH_3$$

2.1.1. Hydrogen Production

Hydrogen is produced by the reaction of methane with water. However, before this can becarried out, all sulfurous compounds must be removed from the natural gas to preventcatalyst[4] poisoning. These are removed by heating the gas to 400 ^oC and reacting it with zincoxide. Following this, the gas is sent to the primary reformer for steam reforming, where super-heated steam is fed into the reformer with the methane. The gas mixture heated with naturalgas and purge gas to 770^oC in the presence of nickel catalyst. At this, methane converts to hydrogen,carbon dioxide and small quantities of carbon monoxide.

2.1.2. Nitrogen Addition

The synthesis gas is cooled slightly to 735^0C. It then flows to the secondary reformer whereit is mixed with a calculated amount of air. The highly exothermic reaction between oxygenand methane produces more hydrogen. In addition, the necessary nitrogen[6] is added in the secondary reformer.As the catalyst that is used to form the ammonia is pure iron, water, carbon dioxide andcarbon monoxide must be removed from the gas stream to prevent oxidation of the iron. Thisis carried out in the next three steps.

2.1.3 Removal of Carbon Monoxide

Here the carbon monoxide is converted to carbon dioxide (which is used later in the synthesisof urea) in a reaction known as the water gas shift reaction.This is achieved in two steps. Firstly, the gas stream is passed over a Cr/Fe_3O_4catalyst [9] at360^0C and then over a Cu/ZnO/Cr catalyst at 210^0C. The same reaction occurs in both steps,but using the two steps maximizes conversion.

2.1.4. Water Removal

The gas mixture is further cooled to 40^0C, at which temperature the water condenses out andis removed.

2.1.5. Removal of Carbon Oxides

The gases are then pumped up through a counter-current of UCARSOL solution (aMDEA solution). Carbon dioxide is highly soluble in UCARSOL, and more than 99.9% of the CO_2in the mixture dissolves in it. The remaining CO_2 (as well as any CO thatwas not converted to CO_2 in Step 3) is converted to methane (methanation) using a Ni/Al_2O_3catalyst at 325^0C. The water which is produced in these reactions is removed by condensation at 40^0C as above.The carbon dioxide is stripped from the UCARSOL and used in urea manufacture. TheUCARSOL is cooled and reused for carbon dioxide removal.

2.1.6. Synthesis of Ammonia

The gas mixture is now cooled, compressed and fed into the ammonia synthesis loop. A mixture of ammonia and unreacted gases which have already been around theloop are mixed with the incoming gas stream and cooled to 5^0C. The ammonia present isremoved and the unreacted gases heated to 400^0C at a pressure of 330barg and passed overan iron catalyst. Under these conditions 26% of the hydrogen and nitrogen are converted toammonia. The outlet gas from the ammonia converter is cooled from 220^0C to 30^0C. Thiscooling process condenses more the half of the ammonia, which is then separated out.The remaining gas is mixed with more cooled, compressed incoming gas. The reactionoccurs in the ammonia converter.The ammonia is rapidly decompressed to 24barg. At this pressure, impurities such asmethane and hydrogen become gases. The gas mixture above the liquid ammonia (whichalso contains significant levels of ammonia) is removed and sent to the ammonia recoveryunit. This is an absorber-stripper system using water as solvent. The remaining gas (purgegas) is used as fuel for the heating of the primary reformer. The pure ammonia remaining ismixed with the pure ammonia from the initial condensation above and is ready for use in ureaproduction, for storage or for direct sale.

3. Results and Discussions

By using 1.07e+005kmole/hr methane, 2.8e+005kmole/hr hydrogen, 1.02e+005kmole/hr nitrogen we have produced4.6e+004kmole/hr ammonia. From graph we can see that ammonia production increases with the rise of pressure of fresh feed.

From figure-03, it has been seen that with increase of pressure of resh feed tube side delta T decreases gradually to -46.45^0C at 1.200e+004 kPa. After reaching this value delta T increases at high rate.

From figure -04, in the case of tube side delta T(^0C),delta T increases to -242.5 ^0C in a linear fashion with positive slope with respect to fresh feed temperature. On the other hand, in the case of shell side delta T(^0C),delta T decreases in a linear fashion with negative slope.

From figure-05, product flow rate increasses quickly with the increase of fresh feed pressure to 4.000e-004 at 1.750e+004 kPa. After reaching this point product flow rate slows down and tends to become constant.

In figure-06, product molar flow increases with the increase of fresh feed molar flow in linear pattern.

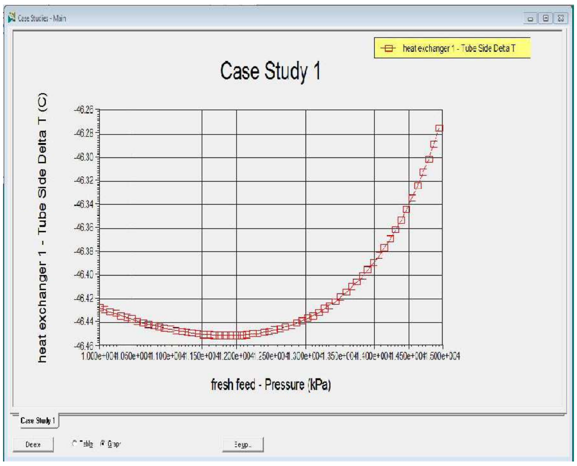


Figure 03. *Case Dtrdy1 – effect of fresh feed-pressure (kPa) on heat exchanger 1 – Tube Side Delta T (^{0}C).*

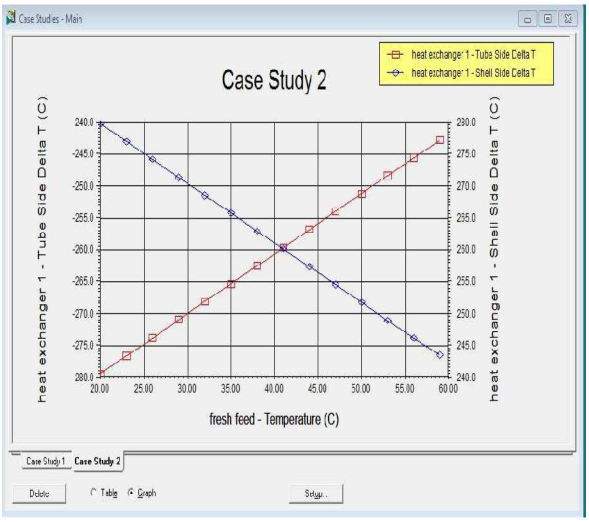


Figure 04. *Case Study2 – effect of fresh feed- temperature (^{0}C) on heat exchanger 1 – Tube Side Delta T (^{0}C) and Shell Side Delta T (^{0}C).*

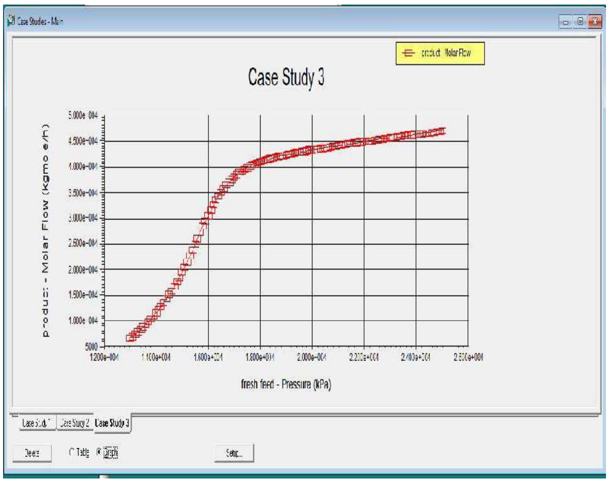


Figure 05. *Case Study1 – effect of fresh feed- pressure (kPa) on product-molar flow (kgmole/hr).*

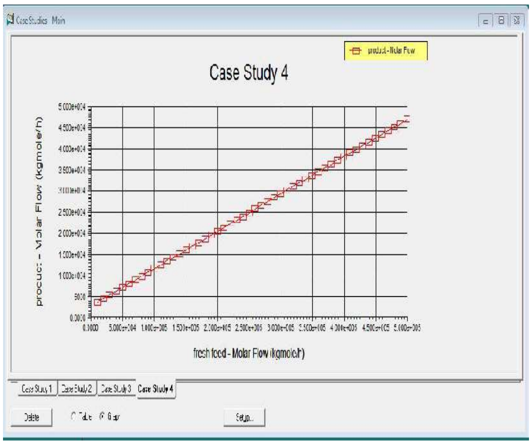


Figure 06. *Case Study4 – effect of fresh feed- molar flow (kgmole/hr) on product-molar flow (kgmole/hr).*

There are several boiling point curve associated with the simulation which are included below-

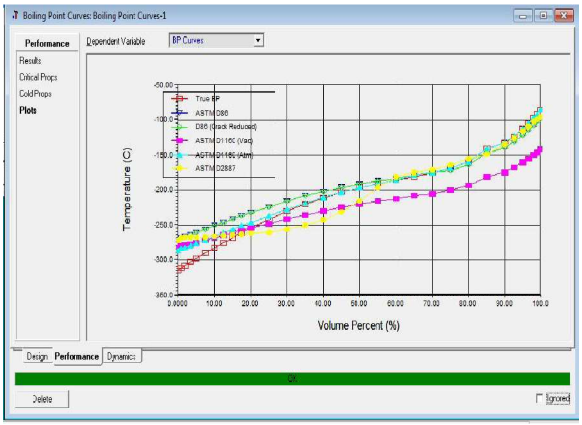
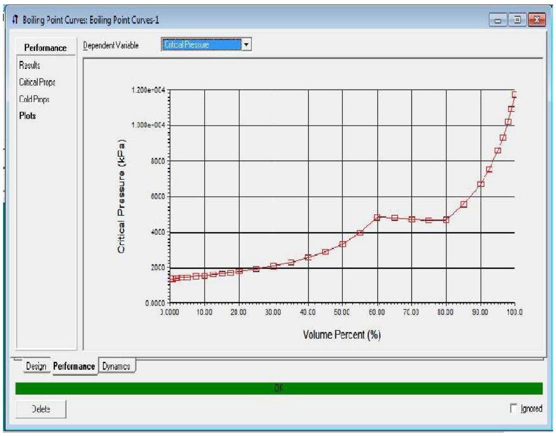


Figure 07. *Case Temperature (^{0}C) vs volume percent(%) plot.*

Figure 08. *Critical Temperature (^{0}C) vs volume percent(%) plot.*

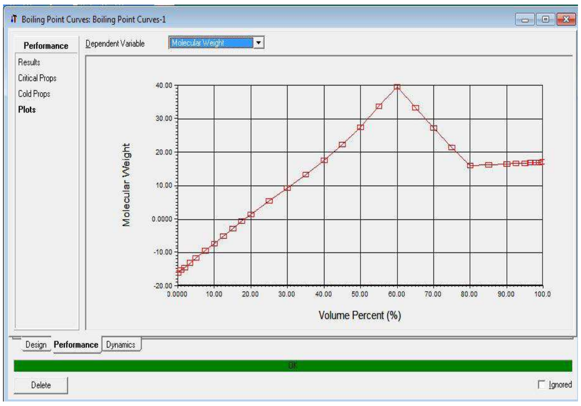
From figure-07, we can see that at 0% volume percent boiling point is -325^{0}C and at 100% it becomes -80^{0}C with gradual increase from 0-100%.

From figure-08, critical temperature starts from -290^{0}C and increases in linear fashion upto -100^{0}C at 70% volume percent. Than it becomes constant upto 75% at the same temperarure. It again increases in linear fashion with greater slope than previous one.



Dependent Variable: Critical Pressure

__Figure 09.__ Critical Pressure (kPa) vs volume percent(%) plot.



Dependent Variable: Molecular Weight

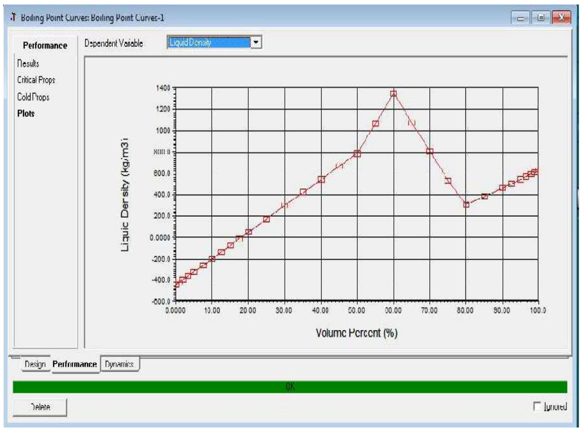
__Figure 10.__ Molecular Weight vs volume percent (%) plot.

From figure-09, critical pressure increases at slower rate starting from 1500 kPa upto 5000 kPa at 60 volume percent. It then remains almost constant at the same pressure to 80% and then increases it rapidly.

From figure-10, molecular weight increases from -5.00 to 40 at 60% in almost straight line pattern.It then decreases in linear fashion to 16 at 80% and remains constant for remaing volume percent.

Dependent Variable: Acentric Factor

__Figure 11.__ Acentric Factor vs volume percent (%) plot.



Dependent Variable: Liquid Density

__Figure 12.__ Liquid Density (kg/m^3) vs volume percent(%) plot.

From figure-11, acentric factor increases quite rapidly from -0.5000 to -0.2800 at 1% volume percent. It than increases slowly with slope smaller than previous increase upto 0.0300 at 50%. It then decreases and remain constant upto 80% and then starts to increase.

From figure-12, liquid density increases linearly from -475.0 kg/m^3 to 1390 kg/m^3 at 60% It is then decreases linearly upto 300.0kg/m^3 at 80% and increases for the remaining volume percent upto 600 kg/m^3.

4. Conclusions

Ammonia is a very important product. It is used in various purposes. Ammonia production depends on plentiful supplies of natural gas, a finite resource, to provide the hydrogen. Due to ammonia's critical role in intensive agriculture and other processes, sustainable production is desirable. Hysys helped us a lot to understand and to designammonia production. The work discussed in this project was focused on the development using different kind ofreactors which can be processed to produce ammonia. Different units have been specified according to the desired requirement of the product. Product flow rate was increased by increasing fresh feed flow rate. Other than fresh feed flow rate, product flow rate can also be increased by increasing fresh feed pressure. It was quite similar to the real plant operation. So we can predict quite accurately about the process by simulating it in Hysys.

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