**Ammonia Synthesis**

**1 Introduction**

Ammonia is an attractive option as an energy storage vector. This is because ammonia is easy to handle, and has a relatively low energy cost of storage as compared to alternatives such as hydrogen. Although several methods of ammonia synthesis, including electrochemical methods were explored, the Haber Bosch process waschosen due to the availability of well-established design practices, and lower cost of production compared to electrochemical methods. In this section, we will explore the constraints of the ammonia synthesis reactor, and then decide on the design parameters of the reactor.

To find the minimum volume of the ammonia reactor that would minimise cost, **V\_L\_A\_3D.m** from “RateVersion3.2(V\_L\_A\_3D)” is run to give a plot of the Volume vs Length vs cross-sectional-area of the pipe-shaped reactor. Reactor characteristics can be changed via **BuildReactor.m**

**1.1 Design Objectives**

The aim of this project is to calculate the design parameters of the reactor that would produce the minimum flow rate required downstream of the plant at the ammonia storage subsystem. These design parameters are operating temperature, pressure, input material flow rates, concentrations, and dimensions of reactor beds. The said design parameters will determine the resulting performance of the entire ammonia synthesis subsystem, which will be compared to the design goals as seen in Table 1 below.

|  |  |
| --- | --- |
| **Measures of ammonia subsystem performance** | **Benchmark** |
| Output Ammonia Flow Rate | 4 00 kmol/h |
| Ammonia Output Purity | ≥ 99 % |
| Single Pass Conversion | ≥ 50 % Equilibrium Conversion, Xeq |
| Overall Conversion | ≥ 95 % |

**Table 1 –** Table showing benchmark design objective of the overall ammonia reactor subsystem.

**1.2 Design Approach**

A bottom-up approach was taken, starting from catalyst design**.** MATLAB was then used to model the reactor beds (PFR) with catalysts. After that, ASPEN was used to integrate three reactor beds with recycle loops to increase the overall ammonia yield. Finally, inter-stage cooling was introduced to further increase the overall efficiency of the reactor system.

**2 Catalyst**

The three most commonly used catalyst in the Haber Bosch ammonia synthesis process are fused iron, ruthenium, and Cobalt-Molybdenum-Nitridecatalysts:

**2.1 Fused Iron (Fe 111)**

Fused iron has traditionally been the chosen catalyst for the Haber-Bosch process. This is because of iron’s high activity, robustness, and low cost. Fused iron catalysts are commonly formed by precursors such as K2O, CaO, SiO2, and Al2O3. Although the degradation of iron catalysts is as long as 14-20 years (Appl., 2012), they generally require high temperatures and pressures in order to be activated.

**2.2 Ruthenium catalyst**

Ruthenium is a relatively new catalyst that has been proven experimentally to yield activities that can reach up to 20 times that of its iron counterparts. Despite this advantage, Ruthenium is costly and susceptible to H2 poisoning (Kitano et al., 2012).  Hence, when estimating the overall cost of using Ru as a catalyst, the savings in operational cost over the lifetime of the plant must outweigh the extra capital costs associated with choosing Ru over other cheaper alternatives.

**2.3 Cobalt-Molybdenum-Nitride catalyst**

The cobalt-molybdenum nitride catalyst is the latest type of catalyst present in ammonia synthesis research, proposed by Nörskov et al. The Co-Mo-N catalyst was discovered to have higher activity than that of Ru and Os. However, the Co-Mo-N catalyst is a very new technology, and there is speculation about its susceptibility to deactivation by ammonia at high concentrations.

Based on the abovementioned considerations, multi-criteria analysis was used to choose the most suitable catalyst for our model.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Catalyst** | **Weight** | **Fe (111)** | **Ruthenium** | **Co-Mo-N** |
| Cost | x 5 | 9/10 | 5/10 | 3/10 |
| Activity | x 3 | 6/10 | 7/10 | 8/10 |
| Susceptibility to deactivation | x 2 | 7/10 | 4/10 | 5/10 |
| **TOTAL** |  | **77/100** | 54/100 | 49/100 |

**Table 2 -** Multi-criteria Analysis used to determine the most suitable catalyst for the Haber-Bosch process.

Based on Table 1, Iron scored the highest, and was hence the preferred catalyst of choice. Iron also has higher tolerance towards catalyst poisoning compared to Ru. Higher activity is achieved by using specifically, Fe (111) due to its surface crystal structure that promotes high catalytic activity. (Spencer, 1982).

**3 Rate Equation**

**3.1 Literature Review of the Temkin-Pyzhev Rate Equation**

The Temkin-Pyzhev equation (Dasthi et al) is a well-established rate equation used to calculate the rate of ammonia production per volume of catalyst used. This equation has been verified empirically through many published papers, and is the expression used to find the rate of ammonia produced per volume of catalyst used.

N2 + 3 H2 2 NH3 (H = -92.4 kJ / mol) **(1)**

**(2**

where = rate of ammonia produced in kmol/h/m3 catalyst

= partial pressure of species *j* in bar

= rate constant for forward reaction

= rate constant for backward reaction

α = constant between 0.5 to 0.75 (α = 0.5 for this model)

The expressions for the pre-exponential factors, and are obtained from the Arrhenius Equation

**(3)**

**(4)**

where = pre-exponential factors

= activation energy

= Boltzmann constant

T = temperature in Kelvin

The rate equation is formed by summing the forward and backward reactions. The rate of ammonia production increases with the concentration of N2 and H2. This agrees with Le Chatelier’s Principle, i.e. the reaction equilibrium shifts to the right hand side as the concentration of the reactants is increased. Additionally, the rate of ammonia production decreases as the concentration of ammonia increases as well. This however, is due to catalyst degradation by ammonia poisoning. The values for the pre-exponential factors and activation energy are taken from Dashti et al.

**3.2 Effect of Temperature and Pressure on Rate of Reaction**

When considering temperature, a high operating temperature increases the initial rate of ammonia production. This is because as temperature increases, the average kinetic energy of the molecules increases. The probability of the molecules colliding with each other to form products increases. Thus, a suitably high temperature of operation is favoured. However, Equation 1 shows that the forward reaction is exothermic. This means that as temperature increases, the reaction equilibrium will shift to the backward reaction. This in turn lowers the equilibrium conversion, which is undesirable. Ultimately, a suitable compromise between a high rate of reaction and a favourable reaction equilibrium has to be made.

Additionally, a high operating pressure also increases the initial rate of ammonia production. According to Le Chatelier’s Principle, the equilibrium reaction shifts to the right-hand-side of the equilibrium equation as seen in Equation 1, thus producing more ammonia. Hence, a high operating pressure is also desired.

**4 MATLAB Model of Reactor Beds (PFR)**

The reactor beds are modeled as an adiabatic Plug Flow Reactor (PFR) as shown in the diagram.

|  |
| --- |
| **N2 + 3 H2**    **2 NH3** |
| **Figure 1 –** Diagram showing a model of a reactor bed sliced into discs. |

The PFR is treated as a summation of many batch reactors in series. Each disc represents a batch reactor, where the production of ammonia is calculated using the Temkin-Pyzhev equation. The output of the batch reactor is the input of the next adjacent batch reactor as shown below:

|  |
| --- |
| **NH3**  **N2 + H2** |
| **N2 + H2**  **. . . .**  **NH3** |
| **Figure 2 –** Diagram showing the PFR reactor bed modelled as a summation of many batch reactors. |

Looking at a single batch reactor, the accumulation of ammonia can be expressed by the mass-balance equation:

**(5)**

where = ammonia accumulated in moles

= ammonia flow rate

= volume of reactor bed

Since we are assuming steady state, with constant density of chemical mixture along the PFR, the accumulation term, yielding the simplified equation:

and hence,

**(6)**

We now have the main equation used to find the total amount of produced per unit time, for a specific set of operating conditions. The next design step is to obtain the ideal operating conditions systematically. The design procedure of obtaining the operating conditions is described in the next section.

**5 Reactor Bed Operating Conditions**

**5.1 Investigating the Effect of Operating Conditions on Theoretical Reaction Rate**

The entire ammonia synthesis subsystem requires a minimum output flow rate of 45 kmol/h to the ammonia storage subsystem downstream. The first, second, and third reactor beds have been estimated to produce an equal amount of about 33.3% of the total required flow rate each. Hence, in theory, we can make an initial assumption that each reactor bed produces approximately 15 kmol/h/ m3 catalyst of ammonia. To determine the set of suitable operating pressures and temperatures of the PFR, a 3-dimensional plot of P and T vs. rate of NH3 reaction rate was produced in Figure 3.

Figure 3 represents a snapshot of the reaction rate at the inlet of the PFR. This is the upper bound of the reaction rate at a specific set of operating conditions. If we consider the reaction rate along the PFR, the rate will decrease as we progress through the length of the PFR. This is because the concentrations of the reactants, N2 and H2 decreases along the length. Based on Le Chatelier’s principle, a lower concentration of reactants will cause the equilibrium to shift to the left-hand-side of Equation 1, hence resulting in a lower production rate.

|  |
| --- |
|  |
| **Figure 3 –** Plot showing the desired NH3 reaction rate with corresponding pressure and temperature values. |

**5.2 Choosing Optimum Inlet Pressure and Temperature**

Figure 3 is useful for determining the range of pressures and temperatures in which the rate of reaction is not either too high or too low for the downstream ammonia storage to cope with. With this in mind, as seen in Figure 3, a temperature range of 600-690 Kelvin and a pressure range of 150-400 bar is the feasible region. This is operating region of the reactor bed that yields a reaction rate that is larger than zero and yet less than 120 kmol/h/m3 catalyst, the decided upper bound of the ammonia production rate.

The minimum required reactor ammonia output flow rate is 15 kmol/h/ m3 Based on Figure 3, this corresponds to P = 200 bar and T = 405 ºC. Thus, these values have been chosen as the minimal inlet operating conditions of the PFRs. Note that the PFR is modelled as an adiabatic, isobaric reactor. Hence, temperature of the mixture increases along the length of the PFR, but the same is not true for pressure. Pressure drop across the PFR can be modelled using the Ergun Equation. However, since the length of the PFR in this model is relatively small, the change in pressure along the PFR is assumed to be insignificant.

It is also noted that the individual PFR reactor beds in the final reactor subsystem is unlikely to output 15 kmol/h of ammonia flow rate. This is because the entire reactor subsystem is later modelled using ASPEN, which takes into account catalyst effects, inter-stage cooling, recycle loops etc. However, this value serves as a benchmark value with the correct order of magnitude for a feasible set of operating conditions based on the downstream flow requirements. The value of this ammonia flow rate was later verified to agree with that of the final ASPEN model with an approximate 10% error, hence, is an acceptable initial estimate for the design parameters of the individual PFRs.

In order to improve the overall accuracy of the required output flow rate of the ammonia subsystem, sensitivity analysis on ASPEN was done by varying the purge ratio, recycle ratio, split ratio, and also the temperature drops across each reactor bed. This will be described in more detail in Section 5.6.

**5. 3 Validation of MATLAB Model**

In order to ensure that the reactor bed/PFR is behaving as expected to theory, a plot of the concentration of the chemical species is produced:

|  |
| --- |
| **NH3 output mole fraction = 0.08** |
| **Figure 4 –** Plot showing variation of ammonia, nitrogen, and hydrogen concentrations along the length of the reactor bed (PFRs). |

This result agrees with that of theory, i.e. exponential curves for both the reactants, N2, H2, and the product, NH3. Note that the output mole fraction of ammonia is about 0.08. In a 92 kmol/h total output flow, this corresponds to about 7.4 kmol/h of ammonia produced in a single pass for a single PFR. As discussed in Section 5.2, this value falls short of the previous theoretical design objective of 15 kmol/h for a single PFR. This is expected, as the previous theoretical reaction rate does not take into account the actual dimensions of the reactor bed, the varying concentrations of the chemical species along the length of the PFR, and also the changing operating conditions along the PFR due to the adiabatic nature of the reaction.

Hence, there is a need to further increase the output ammonia production flow rate. This is later achieved by having three PFRs connected in series, and implementing a recycle loop. This will significantly increase the overall conversion, and thus produce the required flow rate of ammonia downstream to the ammonia storage.

In order to assess the performance of the PFR, the conversion of N2 was plotted along the length of the PFR:

|  |
| --- |
|  |
| **Figure 5 –** Plot showing the conversion of nitrogen along the length of the reactor bed. |

The conversion of N2 tapers off at X = 0.1432 at the end of the PFR. This means that 14% of the input N2 participates in the reaction to form NH3. The theoretical maximum conversion of N2 is known as the Equilibrium Conversion, Xeq. The Xeq for the same operating conditions was determined in order to compare with the MATLAB Model as shown in Figure 6 below:

|  |
| --- |
| Inlet Op. Temp |
| **Figure 6 –** Plot of nitrogen equilibrium conversion (theoretical limit) with respect to temperature. |

At P = 200 bar, T = 405 ºC, Xeq = 0.2467. Hence, the MATLAB model has achieved ~42%, the theoretical maximum N2 conversion, a satisfactory result.

Although it is possible to alter reactor inlet operating conditions to produce conversions that are as close to 90% of the equilibrium conversion, the extra capital and operating costs of maintaining such conditions were taken into account. At last, a compromise between reaction rate and economic feasibility was reached.

**5.4 Sizing the Reactor Beds**

The PFR was modelled as a cylindrical tube. Hence, the parameters to be determined are the cross-sectional area, CSA and the length, L of the PFR.

A method of trial and error was carried out to determine the set of CSA and L values that would produce an ammonia production rate of 7.4 kmol/h. The minimum CSA and L values were obtained in order to minimise the amount of material required for the construction of the PFR. The final result obtained is CSA = 0.5, L = 0.4m.

**5.5 Summary of Reactor Bed (PFR) Design**

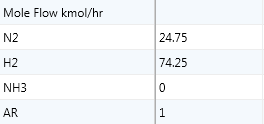
|  |  |
| --- | --- |
|  | |
| Operating Pressure | 200 bar |
| Inlet operating Temperature | 405 ºC |
| PFR Volume | 0.2 m3 |
| PFR Length | 0.4 m |
| PFR CSA | 0.5 m2 |
| Single Stage Conversion, X1 | 0.14 |
| Catalyst | Fe (111) |

**Table 3 –** Summary of the design parameters of the reactor bed.

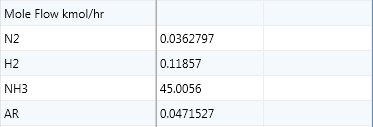
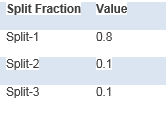
**6 ASPEN Model of Overall Reactor Subsystem**

Having the required design parameters of the individual reactor beds, the reactor beds were then incorporated into the larger multi-stage ammonia synthesis subsystem as seen in Figure 7. The aim was to further increase the overall efficiency of the reactor system. It was decided that three PFRs connected in series, horizontally, was the ideal configuration.

|  |
| --- |
| Input streams  Compressor and heater  Recycle, purge, and condenser unit  Ammonia synthesis unit  One Reactor Bed (PFR)  **Split-3**  **Split-2**  **Split-1**  **To Storage** |
| **Figure 7 -** ASPEN Process Flow Diagram of entire reactor subsystem. |



**Input**



To Storage

**6.1 Recycle Loops**

As discussed in previous sections, a recycle loop is required to compensate for the relatively low single pass conversion of the individual PFRs. Results show that the overall conversion of N2 achieved was 99%, thus fulfilling the >95% benchmark design objective in Section 1.1.

**6.2 Heaters and Compressors**

Heaters and compressors were used to heat and compress the raw feeds from the Electrolyser and the PSA components. By varying the temperature and pressure, a production output of 8% flexibility was achieved. Hence, the turn-down ratio is about **1.08**.

**6.3 Inter-stage Cooling**

Since the reaction is exothermic in nature, the temperature of the mixture increases dramatically after each reaction stage. If the temperature is too high, the equilibrium will favour the backward reaction, lowering NH3 yield. In order to shift the equilibrium to the forward reaction, heat exchangers (modelled as simple coolers here), are introduced after each stage to lower the temperature of the mixture before it passes through the next reaction stage. The high-grade heat (513 ºC) removed from each stage is used to heat the pre-cracker.

|  |
| --- |
| Heat exchangers  Heat-Ex  Direct-quench cooling |
| **Figure 8 -** ASPEN diagram highlighting the use of inter-stage cooling to increase overall efficiency. |

In addition to heat exchangers, direct-quench cooling of the mixture between stages were also implemented using splitters. Using this method, the input feed into the first stage is cooled by a fraction of the input feed prior to the second stage.

By varying the temperature drop between the stages, the overall ammonia production rate can be varied, depending on the required loads upstream and downstream. This adds robustness and flexibility to the overall ammonia subsystem.

|  |
| --- |
| (Mean)  **505**  Bed 1  Bed 2  Bed 3 |
| **Figure 9 –** Temperature profile along length of reactor beds. |

The aim of interstage-cooling is to have Bed 1 operate adiabatically, and for Bed 2 and Bed 3 to be as isothermal as possible. This can be seen in the Figure 9 shown above as the operating temperature was maintained at a mean of 505 ºC, which is within the range of the industrial norm.

**6.3 Summary of Overall Reactor Subsystem**

The final performance of the overall ammonia synthesis subsystem was compared to the benchmark design objectives discussed in Section 1.1 as in tabulated in Table 4.

|  |  |  |  |
| --- | --- | --- | --- |
| **Parameters** | **Final Results** | **Benchmark** | **Error** |
| Ammonia output | 45.01 kmol/h | 45.00 kmol/h | +0.01% |
| Ammonia output purity | 99.6% | ≥ 99% | 0% |
| Single Pass N2 Conversion | 42% Xeq | ≥ 50% Xeq | -16% |
| Overall N2 Conversion | 99% | ≥ 95% | 0% |
| Operating Pressure | 200 bar | - | - |
| Inlet Temperature | 405 ºC | - | - |
| N2 Feed (from PSA) | 24.75 kmol/h | - | - |
| H2 Feed (from Electrolyser) | 74.25 kmol/h | - | - |
| Ar Feed | 1.00 kmol/h | - | - |
| Catalyst | Fe (111) | - | - |

**Table 4 –** Table showing summary of the design parameters of the overall ammonia reactor subsystem

**5.7 Sizing and Materials**

**7.1 Size of Reactor Bed Shell**

Previously, we have designed for the dimensions of the individual reactor beds. However, the volume obtained from Table 3 (Section 5.5) for the PFR only accounts for the volume of the catalyst itself in the reactor beds. To determine the size of the pressure vessel/ shell encapsulating the reactor beds, a few assumptions were considered.

A rough estimate of the PFR volume was obtained by considering the following assumptions:

1. Iron catalyst was used without catalyst supports. This is because iron is rigid enough to withstand the range temperatures without yielding significantly under thermal stresses.
2. The iron catalysts are porous and robust enough to have a high surface area for reaction.
3. The PFR was modelled as a cylinder, and a safety factor of 1.5 was multiplied to the catalyst volume in order to estimate the size of the encasement to allow space for thermal expansion of the catalysts.

Calculating the radius of the reactor bed (PFR) encasement, R to give the size of an encasement:

*Volume of catalyst,* **(7)**

*CSA of catalyst,* **(8)**

*Radius of PFR encasement,* **(9)**

**7.2 Material of Reactor Bed Shell**

Special considerations have been taken into account when choosing the material used for the PFR shell. In order to ensure that the reactor bed encasement can withstand the high operating temperatures and pressures, coupled with high concentrations of corrosive chemicals, the reactor bed encasement has been designed to operate, at full capacity, under harsh conditions for a period of 20 years.

**Corrosion by Nitridation:**

Nitridation is the phenomenon in which nitrogen reacts with iron to form a hard, brittle Fe-N compound. When cyclic thermal stresses are applied, the nitride layer forms micro-cracks that grow and propagate. In time, macro-cracks form, causing leaks of the pressure vessel.

Industry standards for corrosion-resistant materials include the 300-Series stainless steels, Monel, and Inconel alloys. (R. K. Sinnott, 2009). In the design of the PFR inner lining, type 304 Stainless Steel was chosen due to its particularly high resistance towards nitridation attack, ease of working, and low cost, compared to Monel and Inconel alloys.

**7.3 Thickness of Reactor Bed Shell**

The PFR shell was modelled as a thin-walled cylindrical tube made of type 304 Stainless Steel. We use the following equation to find the minimum thickness of the PFR shell:

**(10)**

where = minimum design thickness of PFR wall

= operating pressure of PFR

= outer radius of PFR shell

= yield stress (hoop) of type 304 Stainless Steel

= corrosion allowance for nitridation

The nitridation rate of type 304 Stainless Steel was found to be 250µm/year (George Y. Lai et al). For a designed plant lifetime of 20 years, . Substitution of the previously obtained parameters of , , (quotation by AK Steel) yields the minimum wall thickness to be:

**(11)**

Note: Since , the thin-wall assumption is valid.

**8 Cost Analysis**

**8.1 Capital Expenditure (CAPEX)**

Capital Expenditure was estimated using the module factor method developed by Guthrie:

**(12)**

where = base cost of equipment module

= reference cost for the same equipment type

= capacity of equipment module

= reference capacity for the same equipment type

= fixed power coefficient

After obtaining a value of the Base Cost of the module, labor costs, piping instruments and accessories are then taken into account by multiplying the Base Cost by a coefficient, called the Module Factor (MF). Due to the special operational needs of the reactor, such as high temperature and pressure, special materials are required to construct for such high performance equipment. Hence, the use of special material in equipment was taken into account by the Materials and Pressure Correction Factor (MPF). The total installed Cost was calculated using the following formula:

**(13)**

where = total installation cost of equipment module

= base cost of equipment module

= Materials and Pressure Correction Factor (high temperature/pressure materials)

= Module Factor (labor, piping, accessories etc.)

We can obtain the values for MF based on the type of equipment concerned from a standardized table. MPF, however, is not only a function of the equipment type, but also the material, pressure, temperature, and configuration of the equipment, expressed by coefficients , , and . The following table of the said coefficients, obtained from (Biegler et al, 1997) and (Seider et al, 2010) shows the calculation of MPF based on our required specifications of 200 atm, 678 ºC, using Type 304 Stainless Steel material:

|  |  |  |  |
| --- | --- | --- | --- |
| **Equipment** | **MF (based on equipment type)** | **Data (based on specifications required)** | **MPF** |
| Pressure Vessels | 4.06 |  |  |
| Heat Exchangers | 1.83 |  |  |
| Coolers | 1.42 |  |  |
| Compressors | 2.93 |  |  |

**Table 5 –** Table showing Module Factor (MF) and the Materials and Pressure Correction Factor (MPF) values.

Finally, we can then calculate the total module cost by adjusting the values for MF and MPF to its current value compared to the time the MPF values were tabulated by Guthrie:

**(14)**

where = total installation cost of equipment module

=

U accounts for inflation from mid-1968. The values from the table for MF and MPF were obtained from Guthrie (year 1968). The Base Cost Index of 1968 was **115**. The current

estimated Present Cost Index for 2017 is **558.5**. Hence, U = **4.86**, as shown above.

The total CAPEX for the ammonia synthesis subsystem is summed up in the following table:

|  |  |  |  |
| --- | --- | --- | --- |
| **Equipment** | **Capacity Units** | **Base Cost per unit, B / $** | **Total Module Cost/ $** |
| Pressure Vessels | m3 | 733 | 80,455 |
| Heat Exchangers | m2 | 4,468 | 170,248 |
| Heaters and refrigerators | kW | 24,856 | 671,116 |
| Compressor | kW | 11,547 | 164,427 |
| Catalyst | m3 | 5,252 | 15,755 |
| Auxiliary equipment and contingencies | ~50% of B | 551,000 | 551,000 |
| Total CAPEX, $ |  |  | 1,653,000 $ |
| **Total CAPEX, £ (x 0.8)** |  |  | **1,322,400 £** |

**Table 6 –** Table of overall CAPEX estimation of the ammonia synthesis subsystem.

**8.2 Operational Expenditure (OPEX)**

Based on Turton et al, the Operational Expenditure can be broken down into the following:

**(15)**

Fixed Capital Investment, a.k.a Grass Roots Cost is related to the depreciation of the equipment, taxes and insurance. The utilities cost of the ammonia synthesis subsystem was expected to be minimal. This is because the plant is grid-independent, and hence all electrical power is obtained from the wind farm, or from burning stored ammonia. Full utilisation of heat exchangers also minimise the need for separate heaters and refrigerators.

The main component in the OPEX would be labour costs, calculated using:

**(16)**

where = number of processing steps that includes solid material handling

= number of non-particulate processing equipment. E.g. compressors, heat- exchangers, reactors etc.

Since there are 3 heat exchangers, 1 compressor, 1 reactor, and 2 refrigerators in the entire subsystem, then .

Assuming the ammonia subsystem runs at full capacity 24 hours a day, all year round, and that there are 3 shifts/day, then there are 1095 shifts/year. If operators work for 5 shifts/week, 50 weeks/year, then each operator works 250 shifts/year. 1095 shifts/year divide by 250 shifts/year/operator = 4.4 shifts.

**(17)**

**(18)**

The above result is the upper bound of the required labour. When an overall economic analysis of the entire plant was performed, it was found that the total number of required labour in the ammonia synthesis subsystem is slightly lower than this initial estimate. This is because the operators can maintain multiple plant subsystems in shifts instead of being confined to one.

The final OPEX breakdown is shown in the table below, assuming that each operator’s mean wage is 30,000 £ /year, and that maintenance cost is approximately 4% of the total CAPEX (Khalid et al.):

|  |  |
| --- | --- |
| **OPEX** | **£ /year** |
| Catalyst replacement (once every 3 years) | 4,201 |
| Labour | 370,920 |
| Maintenance | 52,896 |
| **TOTAL, £ /year** | **428,017 £ /year** |
| **Cost/ ton Ammonia** | **100 £ /ton** |

**Table 7 –** Table of overall OPEX estimation of the ammonia synthesis subsystem.

**9 Safety**

Extra care has to be taken into account when operating the ammonia synthesis subsystem. Ammonia is a toxic chemical, and can cause fatal injuries in high concentrations. Furthermore, ammonia can also potentially form explosive mixtures with air above a certain concentration of approximately 14%. Thus, it is of utmost importance that care is taken into account in operating the plant. A safety assessment for the subsystem is carried out as follows:

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Parameter** | **Deviation** | **Causes** | **Possible Consequences** | **Actions/ Precautions** |
| Pressure | MORE | -Control system malfunction | -Vessel rupture  -High pressure explosion | -Install pressure sensors  -Install emergency pressure release valves |
| LESS | -Compressor failure  -Leakage of pressure vessel | -Reduced efficiency | -Use parallel configuration of power supply to minimize breakdown |
| NONE | -Complete blockage of pipe | -Pressure build-up upstream, explosion | -Emergency shutdown of plant to investigate |
| Temperature | MORE | -Heater failure  -Material flow rate too low | -Reactor vessel may yield  -Power wastage | -Install thermal sensors  -Ensure positive feedback loops are not present |
| LESS | -Control system failure | -Increased deactivation rate of catalyst  -Reduced efficiency | -Emergency heaters/ heat-exchangers |
| NONE | -Supply power cut | -Low production yield | - Emergency heaters/ heat-exchangers |
| Ammonia production | MORE | -Temperature is too high | -Ammonia leakage  -Downstream storage capacity is overloaded  -Increased corrosion of vessels and piping | -Emergency shut down of reactor  -Ammonia concentration detection system  -Emergency flow release outlets |
| LESS | -Temperature is too low  -Catalyst deactivation | -Demand downstream is not supplied | -Monitor operating conditions  -Use control actuators with optimal response time |
| NONE | -Complete catalyst deactivation  -Pipe blockage or leakage | -Material wastage  -Possible buildup of pressure and temperature | -Ensure catalyst are changed every 3 years  -Install flow sensors in piping |

**Table 8 –** HAZOP table for the ammonia synthesis subsystem.

**10 Conclusion**

Overall, the ammonia synthesis subsystem has been designed to provide the required ammonia production rate downstream of the plant at minimum cost. Therefore, effort has been put into optimizing the operating conditions and to reduce material and power wastage. Initial cost estimates suggest that the price per ton of ammonia produced via this subsystem is about **100 £ /ton ammonia.** Depending on various factors, such as fossil fuel and urea price, transportation costs, labour etc., the current market price of ammonia ranges from 200-400 $/ton, which is about 160-320 £/ ton ammonia.

This ammonia subsystem is able to achieve lower production costs because the subsystem does not incur significant raw material cost as it utilises water and air as its raw material. By fully taking advantage of heat integration and grid-independency, utility costs were also minimised. This result however is likely to be higher if commercialisation costs are taken into account as well.

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