DESIGN AND FEASIBLITY OF SINGLE STAGE ISOTHERMAL CO SHIFT REACTOR(S)

By

Mohammad Hamza

Hamza Farooq

Danish Kaleem

School of Chemical and Materials Engineering
National University of Sciences and Technology
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By

Leader - 00000214806 Mohammad Hamza
Member 1 - 00000219775 Hamza Farooq
Member 2 - 00000225398 Danish Kaleem

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CERTIFICATE

This is to certify that work in this thesis has been completed by Mr. Mohammad Hamza, Mr. Hamza Farooq and Mr. Danish Kaleem under the supervision of Lec. Ayesha Raza and Dr. Taqi Mehran at School of Chemical and Materials Engineering (SCME), National University of Sciences and Technology, H-12, Islamabad, Pakistan.

Advisor:

Lec. Ayesha Raza

Department of Chemical Engineering
School of Chemical and Materials Engineering

National University of Sciences and Technology

Co - Advisor:

Dr. Taqi Mehran

Department of Chemical Engineering
School of Chemical and Materials Engineering

National University of Sciences and Technology

Submitted Through:

HOD **Dr. Erum Pervaiz**

Department of Chemical Engineering
School of Chemical and Materials Engineering

National University of Sciences and Technology

Principal/Dean **Dr. Amir Azam Khan**
School of Chemical and Materials Engineering

National University of Sciences and Technology

DEDICATION

TO OUR PARENTS

Without whom none of this would have been possible and for their support throughout our lives.

AND TEACHERS

For inspiring us and supporting us throughout the entirety of this project.

ACKNOWLEDGEMENTS

First of all, we would like to express our utmost gratitude to **Almighty Allah**. Without His mercy, we would never been able to complete our project.

We would like to thank our parents for their support for motivating and praying for us.

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ABSTRACT

Water gas shift reaction is a heterogeneous catalytic reaction. The reactions' equilibrium Does not allow it to complete in one stage. For maximum conversions, a two-stage reactor system with interstage cooling is conventionally used in industry. However, huge catalyst volumes are required for achieving maximum conversion. This project aims to propose three cases in which carbon monoxide desired conversions are achieved in single stage isothermally. Reduced catalyst volumes were required if selective hydrogen separation is carried out with the help of Palladium membranes prior to the reaction or is carried out simultaneously with the reaction in membrane reactors. The proposed solutions gave realistically reduced catalyst volumes, hence, reduced the operating cost of the process. Design of high temperature shift reactors, membranes and membrane reactor was done with the aid of Polymath 6.0. The behavior of membranes and membrane reactor was modelled mathematically on Polymath 6.0. The calculated results correlated with the results of the simulation achieved using Aspen HYSYS. The economical and HAZOP analysis was also done for all the cases.

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CHAPTER 1

INTRODUCTION

1.1 Scope of The Project:

Fauji Fertilizer Bin Qasim Limited (FFBL) is a joint venture of Fauji Fertilizer Company and Fauji Foundation along with other shareholders. FFBL is the only producer of Diammonium phosphate (DAP) and granular urea in Pakistan [1]. The raw material for the production of both the products of FFBL is natural gas. MarI Gas provides natural gas to FFBL. The production capacity off FFBL's plant is as following:

Plant Name	**Plant Location**	**DAP Production (MT/Day)**	**Urea Production (MT/Day)**
FFBL	Karachi	2523	1920

Table 1 FFBL DAP and Urea Production Data

Ammonia is the raw material to produce both DAP and Urea. Ammonia is synthesized by reforming of methane which is present in the natural gas feed. There are several steps required first for the purification of the natural gas and then for the conversion of methane to carbon dioxide and hydrogen. However, in the steam methane reforming reactions, the complete conversion of methane to carbon dioxide does not occur. Instead carbon monoxide is evolved during steam methane reforming in large amounts. This carbon monoxide needs to be converted to carbon dioxide so that it does not poison the catalyst of ammonia synthesis reactor and does not burden the methanation reactor. This also needs to be done for increasing the yield of hydrogennce hydrogen and nitrogen are required in three ratios one in the ammonia synthesis reactor. It has been determined experimentally by FFBL that even a very minute slippage off carbon monoxide from shift reactors causes are huge loss of yield in the ammonia synthesis reactors. That conventional water gas shift (WGS) reaction occurs in two stages namely High Temperature Shift (HTS) reaction at 400^{o}C - 450^{o}C and Low Temperature Shift (LTS) reaction at 300^{o}C - 350^{o}C [2]. The goal of HTS and LTS in series is eliminate CO present in the gas which is going towards the ammonia synthesis reactors. however, the HTS and LTS require huge amounts of catalyst to undergo the desired reaction. Following is the water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_r = -41.5 \text{ kJ/mol}$$

This project entails a detailed study of design and feasibility of a single stage isothermal CO shift reactor design in which the desired conversions are achieved with less catalyst weight and low operation costs. The focus of this study is to design a synthesis gas production plant in which water gas shift reaction occurs in single stage at isothermal conditions. To achieve the desired goals mathematical design, simulation, economics analysis and HAZOP analysis is done to develop a convenient solution for reducing catalyst weights in HTS and LTS by eliminating the low temperature stage. By utilizing newly emerging and advanced Palladium membranes and Palladium (Pd) membrane reactors single stage water gas shift reaction can occur with surprisingly low catalyst weights and low operating costs with the production of pure stream of hydrogen which can be used as a fuel for various applications and can be sent to the ammonia synthesis reactor as well. Hydrogen is a fuel which is going to replace the petroleum fuels in the near future as the hydrogen powered cars and engines are already being developed [2].

1.2 Introduction to Ammonia:

Ammonia as a chemical compound having no colour with a piquant odour and alkaline in nature. Naturally, ammonia is very scarce and is produced as a result of degradation of organic molecules like proteins present in plants and animal wastes. Ammonia is consistently and constantly is being produced in soil based on the rate of microbial activity and conditions of the soil [3]. Artificially ammonia is produced majorly using the Haber's process. Ammonia is the among the top ten large scale commercially produced chemicals and around 130 million tonnes of ammonia are produced annually [4]. Majorly ammonia is used to produce fertilizers as it is too volatile to be directly introduced to plants as a nitrogen substitute.

1.2.1 Chemical and Physical Properties of Ammonia:

Ammonia is a polar covalent compound which has hydrogen bonding among its molecules [4]. Ammonia is a good organic solvent due to its lower dielectric constant. Following are the chemical and physical properties of ammonia:

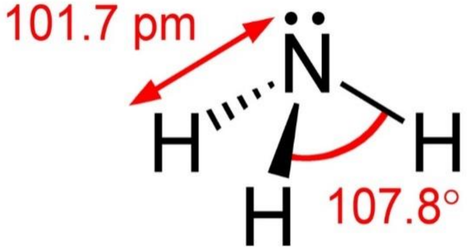
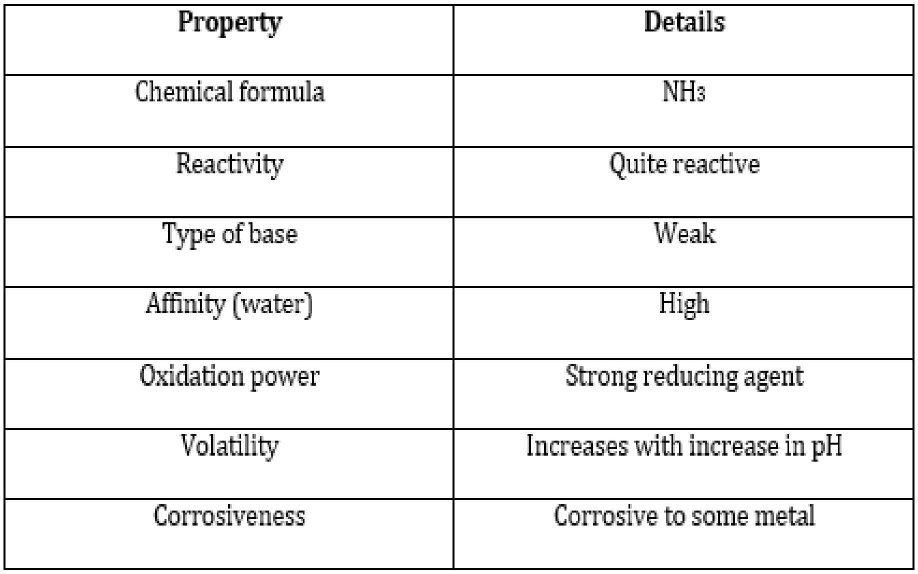
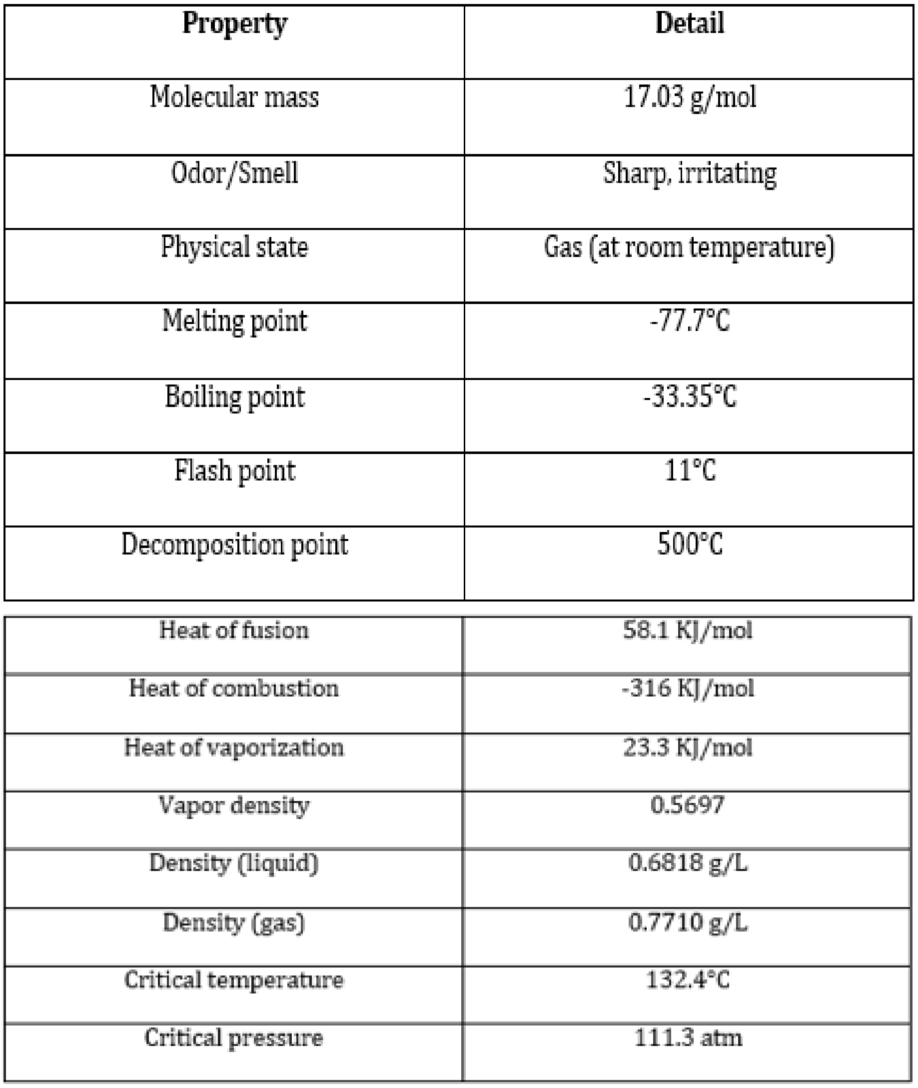


Figure 1 Structure of Ammonia



Property	Details
Chemical formula	NH_3
Reactivity	Quite reactive
Type of base	Weak
Affinity (water)	High
Oxidation power	Strong reducing agent
Volatility	Increases with increase in pH
Corrosiveness	Corrosive to some metal

Table 2 Chemical Properties of Ammonia



Property	Detail
Molecular mass	17.03 g/mol
Odor/Smell	Sharp, irritating
Physical state	Gas (at room temperature)
Melting point	-77.7°C
Boiling point	-33.35°C
Flash point	11°C
Decomposition point	500°C
Heat of fusion	58.1 KJ/mol
Heat of combustion	-316 KJ/mol
Heat of vaporization	23.3 KJ/mol
Vapor density	0.5697
Density (liquid)	0.6818 g/L
Density (gas)	0.7710 g/L
Critical temperature	132.4°C
Critical pressure	111.3 atm

Table 3 Physical Properties of Ammonia

1.2.2 Chemical Reactivity of Ammonia:

1.2.2.1 Combustion:

Combustion of Ammonia is difficult as it requires a lot of energy to produce N_2 gas and water.

$$4NH_3 + 3O_2 + \text{heat} \rightarrow 2N_2 + 6H_2O$$

However, in the presence of catalyst NOx's are produced.

1.2.2.2 Reaction with water:

Ammonia on its own dissolve in water with release of heat.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

NH_4OH is basically aqueous solution of ammonia and is basic in nature. In equilibrium molar solution of 1.0 of NH3 produces 4.2 milli moles of hydroxide ion.

1.2.2.3 Self-dissociation Reaction:

Ammonia undergoes auto ionization like water to its acid and base conjugate.

$$2NH_3 \text{ (aq)} \rightleftharpoons NH_4^+ \text{ (aq)} + NH_2^- \text{ (aq)}$$

NH_3 is a weak base.

1.2.3 Applications and Uses of Ammonia:

Following are the major applications of ammonia:

1.2.3.1 Fertilizer Production:

Mainly ammonia is used in the manufacturing and production of fertilizers. It serves as a best nitrogen based nutrient supply for the soil which helps in production of food crops. Ammonia cannot be directly introduced to the soil due to its volatility but is used in synthesis of Urea which is consumed by plants.

1.2.3.2 Water Purification:

Ammonia is used in purification of water supplies. It is used to produce mono-chloro-amine which is used as a disinfectant and helps in purifying water thus reducing the risk of water borne diseases.

1.2.3.3 Cleaner purposes:

Ammonia is used as cleaning purposes in household which is usually ammonium hydroxide. It is mostly used in cleaning of stainless steel, ovens, and soaking things. The ammonia used in household usually consist of 5 to 10 % of ammonia.

1.2.3.4 Fermentation process:

In fermentation industry the solution of ammonia (having 16% to 24% ammonia) is used in industry of fermentation. They are the source of N_2 for microorganism and vary pH level during fermentation process,

1.2.3.5 Refrigeration:

It is used as a refrigerant gas and used in ACs because it can adsorb huge amount of heat from outside refrigerator.

1.2.3.6 Textile:

Ammonia can also be used in the making of synthetic fibre such rayon and nylon fabric. It can be used in dyeing and scouring of silk, cotton, and wool.

1.2.3.7 Other Industrial Uses:

Many products are made of ammonia which includes plastics, explosives, fabrics, dyes, and pesticides. It is used as stabilizer to carry out several functions. It is used in the manufacturing of compounds like nitric acid, Hydrogen cyanide, Ammonium carbonate and many other compounds.

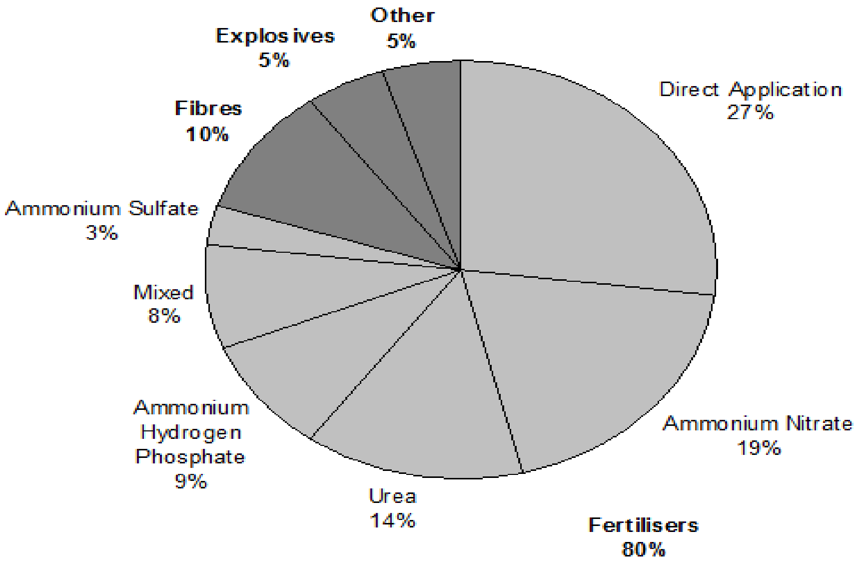


Figure 2 Applications of Ammonia

1.2.3.8 Ammonia as Energy Transporter:

Ammonia due to its flexible nature and being carbon free carrier offers good energy density as compared to compressed air. These properties of ammonia suggest that it can be useful in the future for the transportation purposed and power houses.

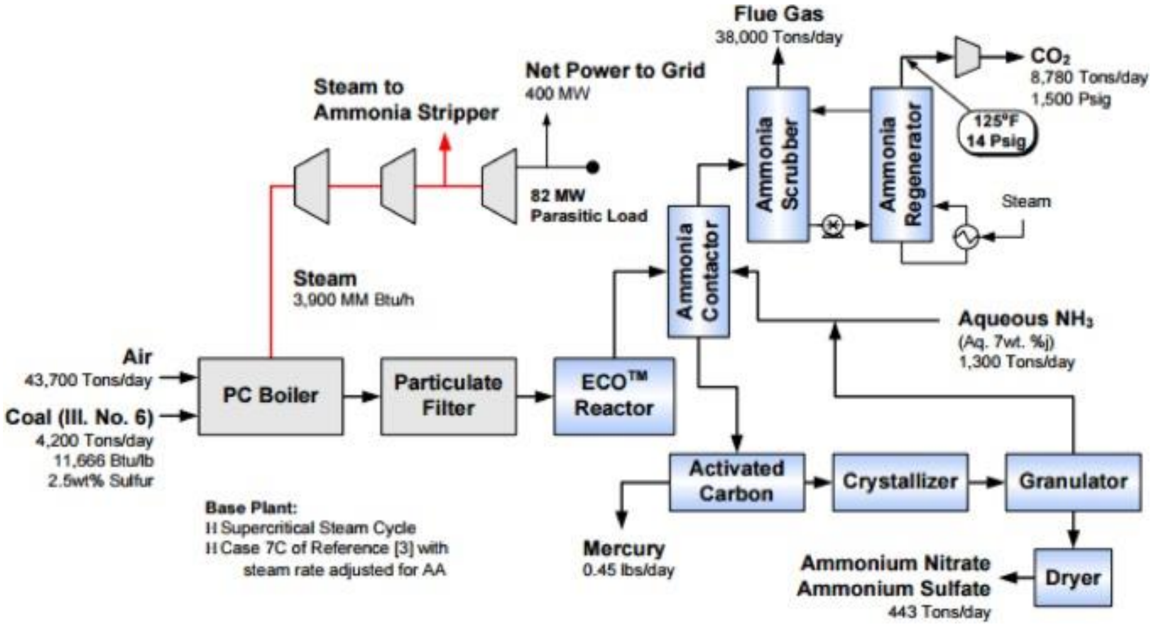


Figure 3 Power plant using ammonia as energy carrier

CHAPTER 2

LITERATURE REVIEW

Ammonia is made of two elements nitrogen and hydrogen, formed from a gas phase mixture of the aforementioned in a ratio of almost 1 to 3, with the formula NH_3. It is a stationary binary hydride, and the most simplistic pnictogen hydride, Ammonia has no colour of its gas and a pungent odour. Either advertently or indirectly, ammonia considered as the basic component material for the integration of many pharmaceutical goods.

Before the Haber-Bosch Process, NH_3 was accumulated from the process of dry distillation of nitrogen compound vegetable. Reduction of nitrous acid is done by distillation or nitrites with hydrogen. It was also obtained when coal was distilled or when ammonium salts were decomposed by alkaline hydroxides.

2.1 Haber Bosch Process:

Following are some of the typical processes used in the manufacture of NH_3 by Haber Bosch process; steam reforming in primary reformer, air in secondary reformer, Water gas shift, removal of carbon oxides, syntheses of Ammonia and finally discarding of un-necessary gases. This process is even more cheap, in terms of consumption of energy when excess air in the secondary reforming is rescued and when the reforming gas is treated with different hydrogen rich steam and returns that steam to the synthesis gas. After carbon monoxide is removed, the reformer product gas is then compressed by, at the least, 50 per cent, if no more. The same process consequently can also occur at a plant which has a gas circulator, even if the plant does not have an air compressor. The synthesis gas is kept at a pressure of about 40 to 80 bar abs. The temperature of about range 350 to 430 C is usually provided or maintained at the outlet, in a presence of catalyst consisting of cobalt, iron and other reaction promoting compounds. From other stream of the reformer product gas, the hydrogen-rich stream is recovered.

2.2 Ammonia Production Using Naphtha:

Ammonia is produced in plants, which can be used as feed for Naphtha acts as a production of hydrogen, while the required amount of N_2 is extracted from the air. Naphtha feed, which tends to have a higher carbon to hydrogen ratio (CHR), when is worked with, the generated CO_2 tends to be excessive. In a R-LNG the CO_2, that is generated, is quite less, Naphtha has higher CRH then ammonia. The ammonia production is a process which can be divided into 2 sections: Syngas Production (preparation of feedstock) and Synthesis of ammonia.

2.2.1 Syngas Production:

This part of the process includes desulphurisation, steam reforming, which is done in primary reformer, air reforming (secondary reforming), methanation, water gas shift reactions of carbon monoxide, and removal of carbon dioxide.

The process of desulphurisation is then further divided into 2 parts: pre-desulphurisation, or PDS, and final desulphurization, or FDS. In Pre-desulphurisation, sulphur compounds, which are organic removal is done by converting them to hydrogen sulphides, with the use of a catalyst. This then is separated from the inlet by distillation.

2.2.2 Ammonia Synthesis:

In this process the nitrogen and hydrogen react in a ratio of 1 and 3 to form ammonia, referred to as synthesis gas or syngas. For that, the reaction of reformation is split into 2 sections: primary reformer and secondary reformer.

In primary reforming, where there is steam, hydrocarbon reforming takes place. This is a controlled reaction, in order to maintain a percentage of 10.5% of the gas, which is present in product stream, that is actually needed to perform overall air reforming which is done in secondary reformer. But when using natural gas, the gas now sulphur free, is fed to steam and endothermic reaction in nature takes place and metallic nickel is used as a catalyst in the primary reformer [7].

In secondary reformer, the nitrogen, by air reforming, is obtained for ammonia synthesis. By combustion of molecules of the mixture of gases in air, heat is supplied here. The gas being burnt then provides the heat which is then used for the reforming process or what is left of it. Whereas after the reforming section is done, the product stream consists of H_2, N_2, CO, CO_2, and 0.3 mol% of unreacted hydrocarbons. And Since only pure nitrogen and pure hydrogen gases are needed for ammonia synthesis, any carbon oxide is removed, as it is also necessary, from the raw Syngas. For the secondary reformer using natural gas, the processed gas exits the primary reformer and then enters a secondary reformer. Compressed and processed air from the atmosphere is then heated in the convection zone. An air gas reaction then occurs at the uP|per available space of the secondary reformer. The reformer output stream may contain carbon monoxide and some varying amounts of carbon Dioxide, but that amount is dependent upon the process technology and feedstock. Carbon oxides are removed from the equation using shift converters and Carbon Dioxide absorbers.

In a Water gas shift converter, the CO is the reducing agent for water to produce hydrogen and carbon dioxide gases. The carbon Monoxide is thus converted promptly into removable carbon dioxide. The carbon Dioxide is then removed by absorbing in 0.31 mol % MDEA (methyl di-ethanolamine.) Even after a shift reaction and the removal of carbon dioxide from the stream, the output stream still consists of some traces of carbon monoxide and carbon dioxide. Whereas, when it comes to using natural gas, the gases that are exiting the secondary reformer after the reaction are extremely hot. The heat that is obtained from these gases is then utilised to produce a high-pressure stream. This high-pressure stream then is used to run a high-pressure turbine. Here the process of the shift converter can be divided further into 2 parts: High temperature shift converter and low temperature shift converter.

In a high temperature shift converter, the gases from the secondary reformer are cooled down by passing them through a waste heat reboiler. The reformed gas from the secondary converter now contains some carbon monoxide. The carbon monoxide is then converted into carbon dioxide by oxidising it by reacting carbon monoxide with steam. Iron oxide is already present in the gas and is used as a catalyst here to speed and help the oxidation reaction. On the other hand, in a low temperature shift converter, the gas is cooled down by passing it through a waste heat re-boiler. The gas, which has now been cooled, is fed to an LTS and here it reacts with steam. Copper (II) Oxide is used as a catalyst and passing the gas through the LTS helps to dilute the concentration of carbon monoxide in the gas. The gas still contains carbon dioxide and carbon monoxide. Carbon dioxide is removed from the gas with a process known as "Benfield System." During this process, Carbon dioxide is absorbed by the Benfield solution, which consists of hot potassium carbonate K_2CO_3, potassium bicarbonate $KHCO_3$, diethanolamine (DEA) as a promoter and potassium metavanadate KVO_3 as a corrosion inhibitor. Packed bed absorbers containing Pall Rings absorb carbon dioxide. The gas injected from the bottom is then sprayed with the Benfield solution from the top. The solution then flows down and absorbs carbon dioxide from the gas and is then called Rich carbon dioxide solution. This solution is then passed onto the stripping tower from an outlet at the bottom and is regenerated into Benfield solution again. Of all the processes involved that tend to remove carbon oxides from the stream, methanation might be the simplest one, but that still does not mean it is easy. This method is used to lower the carbon dioxide concentration in the output stream to below 10 ppm. The stream outputting after methanation has a composition of nitrogen gas to hydrogen gas of 1 to 3 and is referred to as syngas. Even for the methanation of the stream, natural gas is required as that stream too has carbon monoxide and carbon dioxide. Here carbon Monoxide and carbon Dioxide are converted into methane gas. This is a reverse process to hydrogenation reaction and methane is not a catalyst poisoning agent.

2.3 Alternatives to Haber-Bosch Process:

Ammonia has a great importance in production of hydrogen in future as it is a good source of hydrogen. Even though ammonia, for a large percentage of global production, is used for the production of fertilisers, it has also been used as a fuel for space heating and in transport vehicles. Ammonia is produced through Haber-Bosch process, a well-known and a very energy and capital taking process at the present, and is considered to be an good energy storage source, moreover, the infrastructure for its transport is readily available and its distribution is also readily available in many countries throughout the world.

There are many new processes which are under way, in order to search for the more efficient and cheap processes of excellent ammonia production growth forecast. The electrochemical tracks, among these methods, have the potential to extensively decrease the energy feed. It also has the potential to easy operate the reactor plans and to decrease the difficulty and expenses of the balance of plants as contrasted to the traditional ammonia generation techniques.

2.3.1 R-LNG (as compared to other fuels):

Process of Naphtha reforming in presence of steam and usage of Naphtha as a fuel, the ammonia plant was designed. Whereas another type of plant of ammonia is being designed for natural gas as the fuel. The plant allows the usage of R-LNG feed, Naphtha feed or mixed feed. The R-LNG can also be used as a fuel for the feed re-heaters or the primary reformer. Although, in order for the R-LNG to be used, new and additional equipment is needed to be incorporated. Some alterations or modifications are also required to some of the processes or process parameters in order to accommodate the overall changes in the whole process and overall reforming process and reaction. The industry is looking to make a switch from Naphtha or natural gas to R-LNG when it comes to the ammonia production. This is a plausible effort by the industry folks to utilise cleaner and cheaper feed stocks or fuel. This helps the industry to achieve a reduction in consumption of energy in the syngas unit verily. Using a Life Cycle Assessment or an LCA, different methods for the production of ammonia can be compared and evaluated. The first ammonia production system consists of an electrolyser for the production of hydrogen gas and a Haber-Bosch plant for the process of ammonia synthesis. Many resources can be utilised to fulfil the energy requirements of the system, hydropower sector, nuclear power, biomass, or waste of municipal. The LCA, or the check the cycle of life, methodology is utilised to identify the quality of environmental effects in increasing earth temperature potential, abiotic depletion, or toxicity of human. Each type of category is assessed during the LCA for each method. Whilst the unfamiliar production of ammonia options is carried competitively in terms of environmental effects, and energy and energy efficiency, both are treated as important criteria for practical application of ammonia production. It can be inferred from the check the life cycle, or the LCA results that municipal waste incineration plants, or the hydropower-based ammonia production methods have the least environmental impact as compared to other considered methods. The greenhouse gas emission which prediction is done already, or the GHG, is calculated for carbon dioxide emission per production of kg of ammonia. The index of sustainability values is also calculated according to the comparatively evaluated energy and energy efficiencies of the system, which also serves as an indicator of any potential improvement.

Using glucose as a substrate, the production of bio-hydrogen was investigated for the ammonia inhibition-I batch and continuous flow reactors. The rate of production of bio-hydrogen was highly dependent on the pH and the concentration of ammonia. In batch tests, the yield of hydrogen remained relatively constant, but in continuous flow tests, yields of hydrogen and rate of production of hydrogen, both were adversely affected by ammonia.

There has been a proposal of using hydrogen as a source of fuel cells thanks to the catalytic decomposition of ammonia. However, the catalyst required is ruthenium, which is quite costly. Even though there are many connections for the catalyst activity that imply that there are many potential and useful alternatives, but the particular candidate differs.

Changes to Traditional Plant to Accommodate the Usage of R-LNG.

2.3.1.1 LNG Preheater:

In order to preheat the natural gas a heater is required. Cylindrical draft type heaters are being used by using fuel which is natural gas.

2.3.1.2 New Sulphur Absorbers:

The PDS, or pre-desulphurisation, is eliminated from the overall process as the sulphur content in the feed stream is low. Only the FDS, or the final desulphurisation, section remains a part of the process in the flow line. In a single sulphur absorber, the accessible volume of sulphur absorption catalyst is not enough to give a consistent catalyst continuance. A new sulphur absorber is placed upstream, as it is necessary, and as such the existing comes at the downstream position. Here, the absorber tends to act as a backup absorber in a case when the new absorber is removed or is not in service for catalyst replacement, or if sulphur breakthroughs from the new absorber. Now, desulphurisation is referred to as hydro-desulfurization and now consists of 2 processes; first, the organic contents of sulphur are being converted into hydrogen sulphide in a hydrogenator and then the hydrogen sulphide is removed by absorbing it in the sulphur absorbers. Each has its own catalyst bed consisting of a high-density zinc oxide as the catalyst. The benefit of uniquely tailored fluid units, its robustness and dependability are the working temperature.

2.3.1.3 Modification & Rerouting of Piping around HDS:

After the new reactor is installed, some alterations or modifications are required. An additional upstream inlet is required for water for the existing hydrogenation reactor, as R-LNG is being used as feedstock, for suppression of all reactions taking place in reactor that involves hydrocracking. It is because there is no moisture in R-LNG.

2.3.1.4 Reformer Burners:

The traditional ammonia production plants use primary reformers designed for the vaporised Naphtha combustion along with off gasses that ae present in nozzle, but volumetric flow of the fuel is increased when the feedstock is switched to R-LNG from commonly used Naphtha, and there is need to install new burners that have dual nozzle. Moreover, fuel headers size is not sufficient for the massive volumetric flow in case of R-LNG feedstock. If the current fuel headers are to be used, this can result in maldistribution of the fuel present in burner as there will be a great drop in the pressure. A fuel header is needed, suitable or compatible with the usage for R-LNG and the fuel headers can be used for off gas combustion as well as for Naphtha.

2.3.1.5 Fuel Preheater for LNG:

Normally supply of re - gasified Natural Gas is at a battery limit, the depressurisation of the pressure of fuel gas will result in a notable decrease in temperature. There is will be suitable to install a new fuel preheater.

2.3.1.6 Mixing Point of Feed Stream:

As plant has capacity to continues its operation both for LNG as well as Naphtha, it is mandatory to have an accurate method for measuring amount of carbon present in feed so control of steam to carbon ratio will become easy. A vortex flow meter is installed for this very purpose along with flow orifice already present in the bypass over the existing feed control valve. On basis of large range of flows measurements, determination of feed’s molecular weight has become easy and straightforward.

2.4 Carbon Deposition in Steam Reforming and Methanation:

2.4.1 Structure of Carbon & Coke:

Carbon is an outlet of carbon monoxide incongruity while coking is manufactured from breakdown or reduction of feed on metals. Actually the coke forms, nevertheless, varies from high molecular weight hydrocarbons to carbon, depends upon the condition under which the coking started and forged or carbon or coke species are seen in reforming with steam; whisker like carbon formed at higher temperatures and including hydrocarbon films made by polymerization or pyrolytic carbon from cracking of hydrocarbons. Recent studies of the a very good nickel having a bonding and structure of carbon on it and covers by diffraction (LEED) and Auger electron spectroscopy (AES) confirm the presence of "dispersed" or atomic carbon stable and polymerized carbon stable.

2.4.2 Removal:

One of the major and severe problems in conventional steam reforming using R-LNG is the formation of coke. The usual molar ratio of steam to methane that is done in steam reformer or the initial composition, with or feed is with oxygen and it is well distributed in the tubes of primary reformer reactor. It is quite clear that adding the oxygen will help move the system far from the boundary because O_2 aids to prevent the formation of the coke deposits inside the tubes of primary reformer, as its importantly know all the process take place under catalyst. Extracting hydrogen gas leads to the travel of the reactant side operation point along a line directed away. Extraction of hydrogen might very well, by permeation, not lead any greater chances of deposition of carbon may actually reduce the formation of the coke. This is a very crucial search with practical demonstration, and it is also notable that there have not been any idea of for formation of coke in the FDMR reactor, as usually hydrogen removal, like decreasing the amount of water will also increase the formation of carbon on tubes of reformer. Although it can reasonably be inferred that there is still a great need for confirmation that if it will be this way for the longer duration of the processes or operations that the approximated hours of the experimentation.

2.5 Palladium Membranes:

2.5.1 Role of Hydrogen:

Palladium membranes are used especially for hydrogen separation worldwide. Because hydrogen is used as an important energy source all over the world. By using palladium membrane, we can separate hydrogen because these membranes are very selective for hydrogen [7]. Hydrogen has variety of applications including fuel cells, hydrocracking to treat petroleum products, to remove contaminants like Sulphur products.

2.5.2 Use of Pd/Alloy Membrane:

Palladium based membrane is usually very selective for hydrogen separation. The efficiency of hydrogen separation in these membrane separators is very high. The use of these separators in water gas shift reaction in ammonia is very effective to enhance the conversion of CO [14].

2.5.3 Solution Diffusion Model:

Hydrogen separated through these membranes via solution diffusion model. According to which hydrogen gas is adsorbed on the surface of membrane then hydrogen molecule breaks into atoms and then atoms move through the palladium lattice while electrons are interacting with metal lattice and then on the permeate side hydrogen atoms recombine and desorbed. These membranes are also helpful for capturing of CO_2. The solubility of H_2 is defined as the ratio of hydrogen atoms absorbed per hydrogen atom and is the function of partial pressure of hydrogen and temperature. Pd and metallic hydrogen form alloy after diffusion of H_2 in Pd. These are called Pd hydrides. Pd and H_2 form a solution as the atomic radius of both are very close to each other. In addition, atomic H is small enough to fit into interstitial positions of Pd, so that the Pd hydride is recognized as a kind of interstitial solid solution. Generally, there are two phases called alpha phase consist of Pd hydride having less hydrogen and smaller lattice parameter and the second one is beta phase consisting of Pd hydrides having more hydrogen and larger lattice parameter. The structure of both phases is FCC.

2.5.4 Sieverts law:

When the diffusion of H_2 through membrane becomes rate limiting we use Sieverts law. It describes the solubility of a diatomic gas in metals which is proportional to the square root of the partial pressure of the gas in a thermodynamic equilibrium [14, 15]. According to this law the flux of hydrogen through membrane is proportional to the square root of differences of partial pressure on the permeate side and retentate side. Eq for the flux is given below:

$$J_{H_2} = K_d \, . \, (\theta^2 - K_a) \, . \, (P_{H_2} . (1-\theta^2))$$

J_{H_2} represents the hydrogen flux.

P_{H_2} is the partial pressure of hydrogen.

θ is the surface that hydrogen covers.

K_a and K_d are the rate constants for adsorption and desorption.

Another way of expressing Sievert's Law is as following:

$$J_{H2} = \text{Ø}_{H_sS}\,\text{poisoning} \,.\, \text{Ø}_{\text{Au alloying}} \; \frac{Q\,.(\sqrt{P_H(renteta)}\ -\sqrt{P_H(permeate)}}{\delta}$$

Where,

$$Q = Q_0 \,.\, \exp(\frac{-E_Q}{\mathrm{RT}})$$

Ø_{HsS} poisoning is the permeance declined coefficient due to exposure to 2 ppm H_2S at 400 ^{0}C.

$\text{Ø}_{\text{Au alloying}}$ is the permeance declined coefficient due to alloying of 12 wt% Au.

δ is the Pd/Au membrane thickness in µm.

Q is the H_2 permeability of pure Pd foils in m^3- µm/(m^2-h-$bar^{0.5}$).

Q_0 is the H_2 permeability constant in m^3-µm/(m^2-h-$bar^{0.5}$).

E_Q represents the activation energy for H_2 permeation in Kj/gmol.

R is the gas constant in J/(gmol-k).

T is the operating temperature in kelvin.

P_H(retenteate) and P_H(permeate) represents the H_2 partial pressure (bar) in the retentate side and permeate side respectively.

2.5.5 Module of Membrane/Membrane Reactor:

A dense tubular Pd based membrane reactor is generally used for hydrogen separation. It consists of two concentric tubes; the catalysts pellets are packed in the membrane zone (reaction zone) while the annulus constitutes the permeate side (shell zone) [8,15].

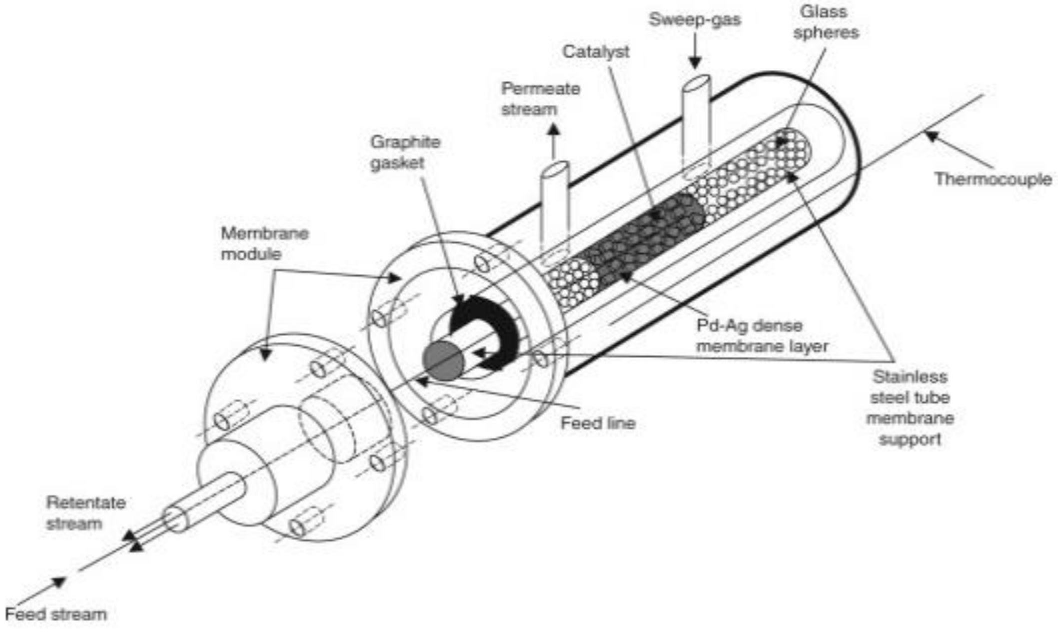


Figure 4 Membrane/Membrane Reactor Module

2.5.6 Advantage of Pd based membrane over porous membrane:

Pd based membrane has several advantages over porous membrane which include their high selectivity for hydrogen gas and also high solubility of hydrogen in pd based membrane. Also, by using pd based membrane we gain better conversion of CO because the reaction is shifted towards the product side even at low temperatures. A smaller amount of methane would be burnt which reduces the amount of CO_2 produced.

2.5.7 Membrane Reactors:

Instrument used to convert reactants into products along with the separation of products. We can use membrane for different purposes:

2.5.7.1 Operations:

Different operations can be performed with the membrane reactor:

- Selective separation of material.
- Control of catalyst.
- Support of catalyst.

There are two operations performing in the membrane reactor i.e., membrane separation along with chemical reaction. The selective separation results in the enhancement of conversion of product.

2.5.7.2 Types of Membrane Reactors:

There are usually numerous types of reactors. Details of which are given below:

1. **Catalytic membrane reactor:**

In this type usually a catalyst is introduced inside the membrane reactor that is why it is called catalytic membrane reactor. In CMR the membrane is made up of material that contains catalysts.in this reactor membrane itself take part in the reaction. Some of the reactants pass through the membrane and exit the reactor on permeate side.

2. **Packed bed membrane reactor:**

If there is a catalyst fixed inside the membrane reactor the reactor is called packed bed membrane reactor. It is in contact with the permselective membrane. In most packed bed membrane reactor tubular module is used. There are number of advantages of packed bed membrane reactor over other reactors including optimal gas contact, proper management of heat, reduce bed to membrane mass transfer limitations.

3. **Fluidized bed membrane reactor:**

If the size of particle is small and the speed of gas is high so that fluidization of bed occurs, then the reactor is called fluidized bed membrane reactor. There are number of advantages of fluidized bed membrane reactor over other reactors including optimal gas contact, proper management of heat, reduce bed to membrane mass transfer limitations.

2.5.7.3 Applications of Membrane Reactors:

There are numerous applications of membrane reactors. Some of which are:

1. **Hydrogen Separation:**

   Hydrogen is used as a fuel in all over the world. So, it is necessary to separate pure hydrogen after the reaction. For this we usually use Pd based membrane reactor in water gas shift reaction because this membrane is selective for hydrogen separation. It has high solubility of hydrogen gas into it.

2. **Hydrogen from Coal:**

   Hydrogen producing technique also include coal gasification. So, to separate out the hydrogen we use Pd based membrane reactor which were used in water gas shift reaction due to their high selectivity for hydrogen gas.

3. **Wastewater Treatment:**

   For wastewater treatment process filtration-based membrane reactors are used.

4. **Electrochemical based Membrane Reactors:**

   These reactors are used in the electrolysis process for the production of chlorine and caustic soda in the industry.

5. **Enzyme Membrane Reactors:**

   The use of these reactors is for the separation of enzyme molecules having different sizes mainly used for the production of amino acids.

2.6 Kinetics of Water Gas Shift Reaction:

In ammonia plant, there is a need of WGSR to convert CO into CO_2 basically for the enhancement of hydrogen to carbon monoxide ratio. Water gas shift reaction is moderately exothermic reaction. High temperature is required for the large conversion. But as the temperature is high it would increase the reaction rate but decreases `the equilibrium conversion of CO. so there are two different reactors for WGSR.

2.6.1 High Temperature Shift Reaction:

In this reaction, the catalyst used is Fe based and contains Cr_2O_3 as a promotor. The mechanisms used to describe the catalytic behavior are based on two different models namely associative and regenerative model.

2.6.2 Langmuir-Hinshelwood Mechanism:

Rate equations on the basis of this mechanism are for the steady state data of WGS. But the rate expression on the transient time are very different than the steady state because the hydrogen separate out slower than that of CO_2 formation and catalyst pretreatment also affect the formation of hydrogen[9]. That is why associative and regenerative based model's mechanism is considered important to explain the reaction rates in the transient period. Empirical power law rate equation is considered more appropriate to explain the reaction kinetics of the HTS reaction. But is valid for specific catalyst and conditions.

2.6.3 Low Temperature shift reactions:

Cu based ZnO_2 catalyst is used in low temperature shift reaction usually at a temperature of 180 to 215 ^{0}C. The catalytic activity of Cu based catalyst depend upon the catalyst composition. To maximize the rate constant the Cu/Zn atomic ratio would be 0.4. The dispersion of Cu and surface area is also linked with catalyst activity. The high concentration of Cu does not necessarily enhance the reaction rate. The reaction rate would be lower due to the sintering of Cu particles. To maintain a balance between lower impact of sintering and higher impact of active site, the concentration of Cu would be 29 mol% [11].

2.6.4 Mechanisms:

There are generally two mechanism for LTS namely “Redox mechanism” and “carboxyl mechanism”.

1. **Redox mechanism:**

The adsorption of CO on surface of Cu then it will be oxidized by atomic oxygen. The atomic O is obtained by the dissociation of OH.

2. **Carboxyl Mechanism:**

In this mechanism the CO is oxidized by OH* instead of O and produce COOH* which is the oxidized to produce CO_2 and H_2

Empirical power rate equation is better to explain the reaction rates of the WGS

2.7 Power Rate Equation for WGS:

Following is the experimentally determined kinetic rate equation for WGS [15]:

Rate of Reaction =

$$R_{WGS} = (1-\mathcal{E}) \,.\, d_{cat} \,.\, (1-\theta) \,.\, 1000.\, 10^{2.845} \,.\, \exp(\frac{-111000}{RT}) \,.\, P_{CO2} \,.\, P_{CO2}{}^{-0.36} \,.\, P_{H2}{}^{-0.05} \,.$$

$$(1- \frac{P_{CO2}\ .\ P_{H2}\ .}{K_{eq}\ .\ P_{CO2}\ .\ P_{H2O}})$$

Where Ɛ is the bed voidage, ɵ is the catalyst voidage. dcat is the catalyst density, R is the ideal gas constant and T is the absolute temperature while P_i is the partial pressure of each component.

Equilibrium Constant =

$$K_{eq} = \exp(\frac{4577.8}{T} - 4.33)$$

Component Reaction Rate =

$$r_{CO} = (-1).\, R_{WGS}$$

$$r_{H2O} = (-1).\ \mathrm{R_{WGS}}$$

$$r_{H2} = (1)\ .\ R_{WGS}$$

$$r_{CO2} = (1).\ \mathrm{R_{WGS}}$$

The reactor design is based on the above stated equations.

CHAPTER 3

CONVENTIONAL PROCESS AT FFBL AND PROPOSED SOLUTIONS

In Pakistan, Ammonia preparation plants extract H_2 from a hydrocarbon in the form of natural gas. And as with all Ammonia preparation plants, N_2 is distilled from atmospheric air. Some of the processes of utmost importance, when it comes to preparation of Ammonia, are mentioned below:

Hydrogen (H_2) and Nitrogen (N_2) are mixed, the resultant compound is called Ammonia. The H_2 to N_2 ratio is 3 to 1, respectively. The mixture might also contain, to a limited degree, some inert gases, i.e. Argon or Methane.

In the desulphurization section, the process gas is utterly desulphurized.

The Hydrocarbon, now desulphurized, is now converted to raw synthesis gas, collectively with steam and air. This gas contains Hydrogen, Nitrogen, Carbon Dioxide, and Carbon Monoxide. This reformation happens at approx. 30 Kg/cm^2.

During Gas Purification, Carbon Monoxide is converted into Carbon Dioxide and Hydrogen, and then Carbon Dioxide is removed by absorbing it into The Benfield Solution.

In Ammonia Synthesis, using a catalytic reaction, the purified synthesis gas is then converted into Ammonia, after being compressed to a pressure of 260 Kg/cm^2.

3.1.A Desulphurization:

The natural gas that is supplied to the plant, is kept at a pressure between 38-45 Kg/cm^2, as a pressure of approx. 40 Kg/cm^2 is required for the process. The natural gas is then heated in a preheater and passed through a de-sulphizer, where the sulphur in the natural gas is removed. But it is normally bypassed since no sulphur is present in current feed.

3.2.A Primary Steam Reforming:

After then the feed which is sulphur-free gas with steam. The following is the resultant reaction of Methane and Steam.

Steam reforming reactions:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CO + H_2O \rightarrow CO2 + H_2$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

This highly endothermic reaction contains metallic Nickel as the catalyst in the primary reformer.

3.3.A Secondary Reformer:

Processed gas, from the primary reformer, now enters a secondary reformer. In the convection zone, compressed, processed air from the atmosphere is heated.

In the upper, available space of secondary reformer, an air gas reaction occurs. There is a high gas temperature at the bottom and front of the catalyst bed, because of the combustion of air. 950 ^{o}C is the approx. exit temperature, whereas the reaction, in contact with the catalyst, will occur at approx. 1100-1200 ^{o}C.

3.4.A Shift Conversion:

The gases, exiting secondary reformer, are extremely hot and tend to have a temperature of more than 1000 ^{o}C. The heat from these gases is then utilized in the production of high-pressure steam, which tends to be of approx. 34 Kg/cm^2 pressure. This high-pressure steam is then used to run a high-pressure turbine.

The process of shift conversion is divided into two steps.

3.4.1.A High-Temperature Shift Converter:

Hot gases, from the secondary reformer, are then cooled down to a temperature of 336 ^{o}C, after passing them through a waste heat re-boiler. The now reformed gas, from the secondary reformer, contains about 11.9% CO. This CO is oxidized into CO_2 by reaction with steam, using Iron Oxide as the catalyst, that is already present in the gas.

$$CO + H_2O \rightarrow CO_2 + H_2$$

3.4.2.A Low-Temperature Shift Converter:

The gas, with the temperature of up to 430 ^{o}C, is cooled to a temperature of 203 ^{o}C by passing it through waste heat re-boiler. Now cooled gas is fed to LTS, where it again reacts with steam and CuO is used as the catalyst. After passing through LTS, CO's concentration is lessened to approx. 0.18%.

$CO + H_2O \rightarrow CO_2 + H_2$

3.5.A Carbon Dioxide Removal:

The gas now contains 18.5% CO_2 and 0.18% CO. The CO_2 is removed from the gas by a process called "Benfield System."

During this process, CO_2 is absorbed by the Benfield Solution, that is the Pot. Carbonate Solution.

Packed bed absorbers, containing Pall Rings, absorb CO_2. Gas injected from the bottom is sprayed with The Benfield Solution, from the top. The solution flows down and is called Rich CO_2 solution.

The gas, consisting of 0.1% CO_2, is released from the top, and the CO_2 Rich solution is passed on to the stripping tower, from the bottom, where it is regenerated into Benfield Solution again.

3.5.1.A Regeneration of the Benfield Solution:

Regeneration of The Benfield Solution occurs in the stripper, in which, CO_2 is divested from the Rich CO_2 Benfield Solution.

The operation conditions for stripper are:

1. High temperature.
2. Low pressure.

The solution enters from the top of the stripper and passes through many plates and sieves. The stripper operates at a low and high temperature. The CO_2-free solution is then sent back to the absorber from the bottom. LS provides the heat in the stripper. The excess CO_2 is then transported to a Urea Preparation Plant.

3.6.A Methanator:

The gas still consisting of CO and CO_2. CO and CO_2 are then converted into Methane. The process is an inverse of a reforming process and is an exothermic hydrogenation reaction. Methane is not a catalyst poisoning agent.

3.7.A Ammonia Synthesis & Refrigeration:

The synthesised gas, after being compressed to a pressure of approx. 250 Kg/cm_2, is passed to an axial radial flow converter at a temperature of about 380-520 ^oC. The gas is passed over Iron which acts as a catalyst, and about 33% of the gas is converted into Ammonia. The reaction effluent is cooled Ammonia, which liquified and separated. The un-reacted gas is recycled.

Main steps involved are:

1. Synthesis gas compression and recycle of unreacted gas.
2. Separation of ammonia and refrigeration.
3. Ammonia storage.

3.8.A Compression of Synthesized Gas & Recycling of Unreacted Gas:

Synthesized gas is compressed from a pressure of 26 Kg/cm^2 to a pressure of 250 Kg/cm^2, with a 4-case centrifugal compressor. The last casing contains a re-circulator, with an impeller and adjustable inlet guide vanes, and re-circulator raises the pressure of the recycled gas, to the extent of pressure drop in the synthesis loop. A set of 2 turbines runs the compressor, extracting and condensing the steam. These turbines are provided with 100 Kg/cm^2 steam, produced in The Ammonia Plant. Steam is extracted at approx. 37 Kg/cm^2 and is used for the turbines.

3.9.A Synthesis Loop Cooling & Purging:

A synthesis loop consists of an axial radial converter. The gas flows through 3 catalyst beds, in the inward direction.

The gas is inserted in the loop, after compression, in between 2 Ammonia chillers. This removes the minute traces of CO_2 and H_2O vapours in the methanator. Failure to remove these can result in the formation of Carbamate, which is corrosive to the catalyst. In exchanger, the mixture is chilled, and Ammonia is liquified and extracted in an Ammonia Separator. The gas, from the separator, is heated in the exchanger. The gas's pressure is raised by passing it through re-circulator. The gas is further heated in an exchanger tube side and admitted to the converter.

3.10.A Separation & Refrigeration of Ammonia:

Converter effluent, consisting of Synthesized Ammonia, unreacted gas (after cooling), is purged and mixed with make-up synthesis gas and is further cooled in the II chiller. Liquid Ammonia is separated in a separator. Liquid Ammonia is then inserted, from a separator, in a down Vessel, and its pressure is reduced to approx. 25 Kg/cm^2. Ammonia is then supplied to a Urea Plant directly from this vessel. The excessive liquid Ammonia, from Knock-out drums, is depressurized to 3.5 Kg/cm^2 and is sent to Ammonia Storage. Some Ammonia from that storage is recycled for refrigeration loop that consists of a compressor, condensers, and a Knock-out vessel.

3.1.B Proposed Solutions:

After the study of WGSR and the catalytic adsorption and desorption equations with the help of power law or the power rate equation we have understood that the maximum conversion for WGS can we achieved when there is no or less amount of product of forward reaction are present. This can be understood by considering the case of equilibrium reactions where, if the concentration of the products start increasing then the reverse reaction starts and the rate of this reaction keeps on increasing so that an equilibrium is achieved when there is no change in the reaction mixture and the concentration stops varying. This means that there is always going to be a limiting amount of product concentration which will suppress the forward water gas shift reaction. The temperature also has a major role to play in the WGS reaction because at high temperatures the equilibrium values are such that the kinetics of the reactions are very fast but the equilibrium does not allow conversions do a maximum level, hence, there is a need to decrease the temperature as currently being done in conventional WGS reaction. However, with the emerging technologies where we can shift the equilibrium of the gaseous mixture by selectively separating out a small gaseous molecule such as hydrogen helps us in developing a strategy for causing single stage WGS reaction.

Thus, we have proposed three solutions for achieving maximum conversion with respect to CO in high temperature shift reactors by employing Palladium membranes for selective hydrogen separation prior to the reaction. One of the unique cases of simultaneous hydrogen separation and WGS reaction is also considered in a membrane reactor to optimize the CO Shift.

3.2.B Case – 1:

In Case - 1 we have tried to achieve maximum CO conversion in a single HTS reactor operating at 450^{o}C in isothermal conditions. But for achieving our goal we have employed empty Palladium membrane modules without catalyst prior to the HTS reactor so that maximum hydrogen is recovered before the reaction and the equilibrium shifts toward the forward water gas shift reaction. For this specific case the plant was designed which will be discussed ahead. Following is the Process Flow Diagram (PFD) of Case – 1:

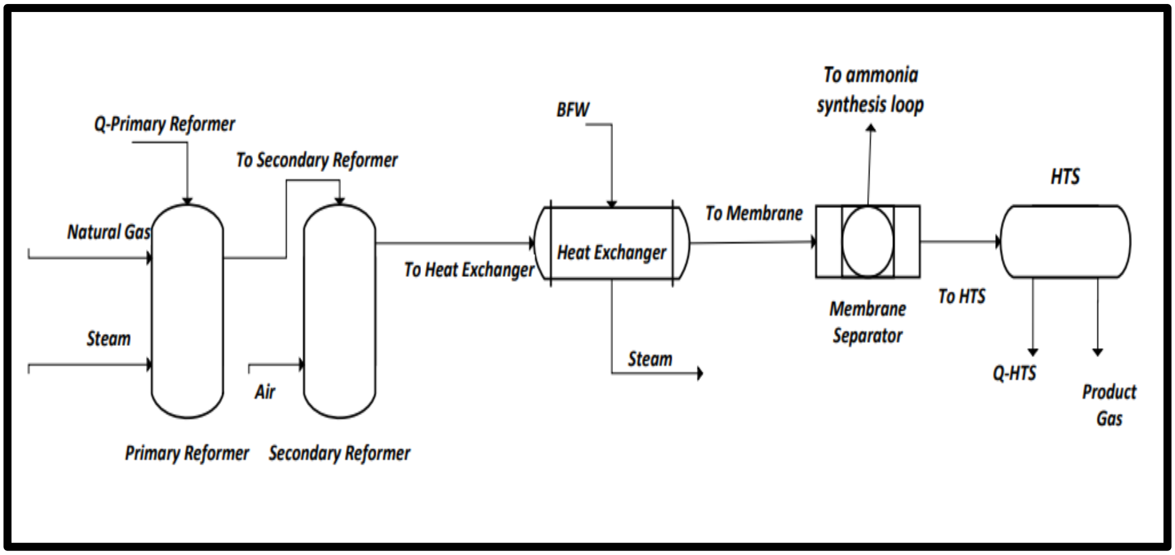


Figure 5 Case – 1 Process Flow Diagram

3.3.B Case – 2:

In Case – 2, considering that desired conversion was not achieved in case one we have employed another membrane separation unit after HTS reactor as in Case - 1 and after the membrane separation we have installed another HTS reactor. The membranes installed in both the cases are tubular metallic Palladium membrane modules. In this case the HTS reactors are operating at the same temperatures and pressures as in Case – 1. Only the account of pressure drop through the membrane after HTS – 1 as shown in PFD below is accounted hypothetically for the reactor design. The aim of both the cases is to conduct WGS in minimum catalyst weights. Following is the PFD of Case – 2:

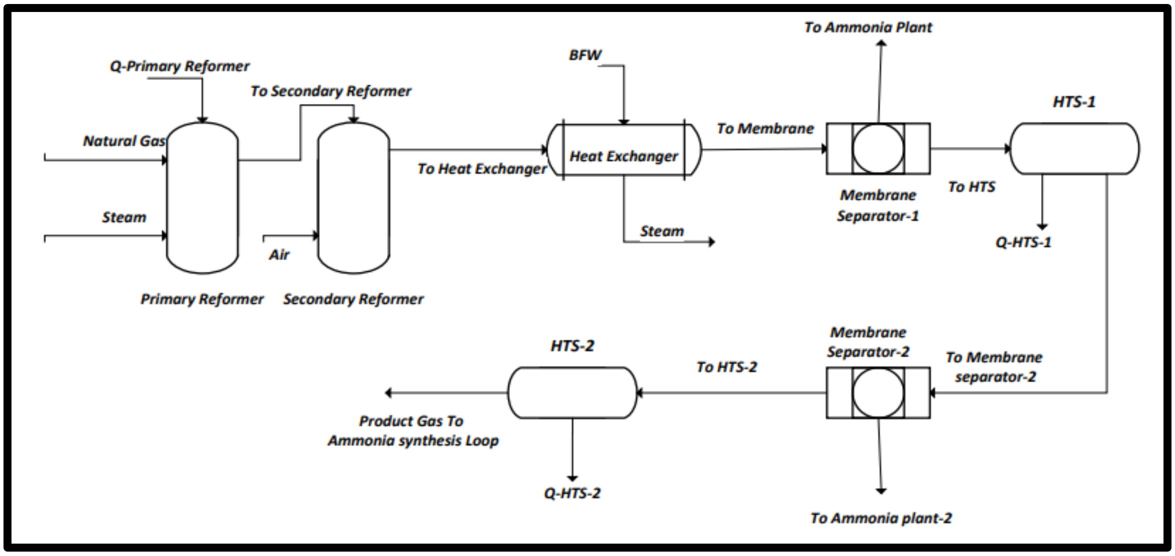


Figure 6 Case – 2 Process Flow Diagram

3.4.B Case – 3:

In this case instead of membrane separation unit in series with HTS has not been considered like Case – 1 but a membrane reactor is considered where selective hydrogen separation and WGS reaction are taking place simultaneously. Just like all the other reactors in all three cases, the membrane reactor is also operating at isothermal conditions at 400°C. Following is the PFD of Case - 3:

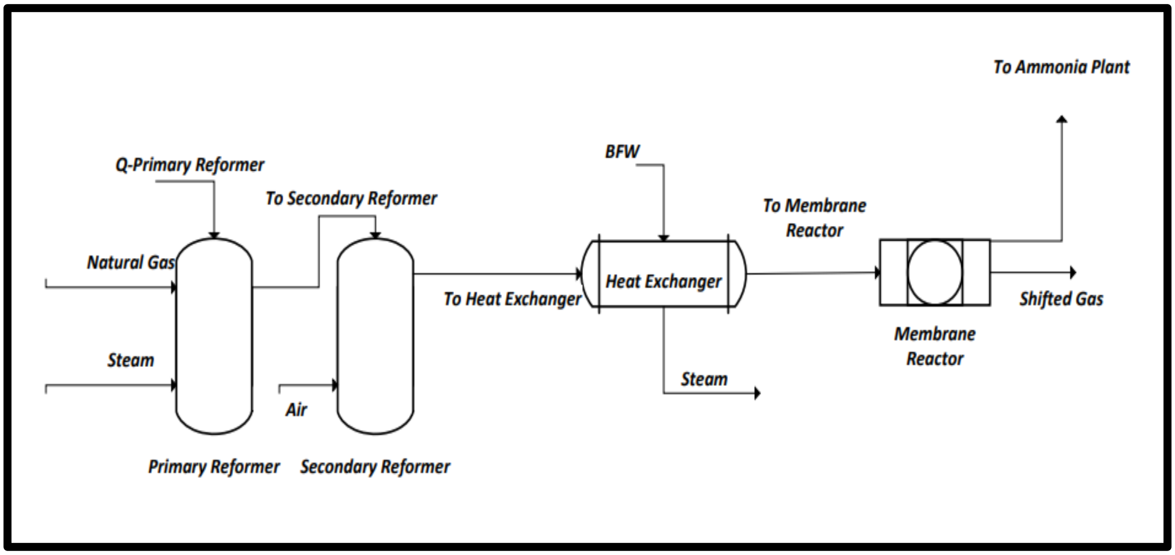


Figure 7 Case – 3 Process Flow Diagram

The three cases will be studied in detail to find out the best case and the most feasible solution for single stage isothermal CO shift reaction.

CHAPTER 4

MATERIAL BALANCE

In this chapter, we did material balance to find out the impact of new feed on the plant. The manual calculations were done by hand and also on excel sheet for further improvements. Material balance on reactors and separation columns and Benfield section was applied as they are the main units installed.

1 hour was taken as the basis of the material balance and the plant was assumed to be at steady state, implying there is no accumulation. Process flow diagrams are also been added for reference and to understand process. Furthermore, equations and formulas are given where required and tables are been formed to show input and output streams of raw materials and products.

Material Balance is important because it tells us about flow rates and how the equipment is handling and doing the required job. Usually we apply law of conservation of mass for material balance that says that mass can neither be created nor destroyed.

4.1 Material balance on Equipment:

To apply material balance on the reactors following steps were followed:

1. The material balance was applied on basis of one hour.
2. Steady state process was assumed meaning no accumulation.

General Material Balance Equation:

$$In - out = Generation - Consumption + Accumulation$$

Sievert's Law:

$$Flux = \frac{Area}{Length} \times Permeability \times (\sqrt{(Partial\ Pressure\ in\ Feed} - \sqrt{Partial\ Pressure\ in\ Retentate})$$

Applying steady state process condition (Accumulation = 0)

$$In - out = Generation - Consumption$$

3. All the units were converted into kg mol
4. Conversions of each reactor occurring in the reactor were calculated

   Conversion (%) = $\frac{\text{Moles in feed stream} - \text{Moles in product stream}}{\text{Moles in feed stream}} \times 100$
5. These conversions were then used to find the moles of reactant of each reaction.

4.1.2 Primary Reformer Case – 1,2,3:

Following reactions occur inside Primary Reformer:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \text{ ... Conversion = 40 \%}$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \text{ ... Conversion = 30 \%}$$

Following is the material balance:

Primary Reformer		
Component	**Moles In**	**Moles Out**
Methane	848.068	254.4204
Water	2350	1501.932
Carbon monoxide	0	339.2272
Carbon dioxide	27.066	281.4864
Hydrogen	9.022	2044.309497
Nitrogen	18.044	18.044
Total Moles	**3252.2**	**4439.419497**
Total Mass	**57655.77781**	**57656.08312**

Table 4 Primary Reformer Material Balance

4.1.2 Secondary Reformer Case – 1,2,3:

Following reactions occur inside Secondary Reformer:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$ ... Conversion = 40 %

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$ ... Conversion = 30 %

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$ ... Conversion = 100 %

$$CO_2 + H_2 \rightarrow CO + H_2O$$ ... Conversion = 9.89 %

Following is the material balance:

Secondary Reformer		
Component	**Moles In**	**Moles Out**
Methane	254.4204	0
Water	2675.727312	2800.094457
Carbon monoxide	339.2272	485.4982075
Carbon dioxide	281.4864	389.635794
Hydrogen	2044.309497	2428.77775
Nitrogen	933.9110748	933.9110748
Oxygen	1159.325411	2.43458E-06
Total Moles	**7688.407295**	**7037.917285**
Total Mass	**112248.9752**	**112249.0472**

Table 5 Secondary Reformer Material Balance

4.1.3 Heat Exchanger Case – 1,2,3:

There are no reactions taking place in heat exchanger. Following is the material balance:

Heat Exchanger		
Shell Side		
Component	**Moles In**	**Moles Out**
Water	101	101
Tube Side		
Component	**Moles In**	**Moles Out**
Water	2800.094457	2800.094457
Carbon monoxide	485.4982075	485.4982075
Carbon dioxide	389.635794	389.635794
Hydrogen	2428.77775	2428.77775
Nitrogen	933.9110748	933.9110748
Total Moles	**7037.917283**	**7037.917283**
Total Mass	**112249.0472**	**112249.0472**

Table 6 Heat Exchanger Material Balance

4.1.4 Membrane Case – 1:

Following is the material balance:

Membrane, Case - 1		
Permeate Side		
Component	**Moles In**	**Moles Out**
Hydrogen	0	960
Retentate Side		
Component	**Moles In**	**Moles Out**
Water	2800.094457	2800.094457
Carbon monoxide	485.4982075	485.4982075
Carbon dioxide	389.635794	389.635794
Hydrogen	2428.77775	1468.77775
Nitrogen	933.9110748	933.9110748
Total Moles	**7037.917283**	**7037.917283**
Total Mass	**112249.0472**	**112249.0472**

Table 7 Membrane Case - 1 Material Balance

4.1.5 HTS Case – 1:

Following reactions occur inside HTS Case - 1:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \text{ ... Conversion = 83 \%}$$

Following is the material balance:

HTS, Case – 1		
Component	**Moles In**	**Moles Out**
Water	2800.094457	2398.661183
Carbon monoxide	485.4982075	84.06532725
Carbon dioxide	389.635794	791.0694846
Hydrogen	1468.77775	1870.211175
Nitrogen	933.9110748	933.9110748
Total Moles	**6077.917283**	**6077.918244**
Total Mass	**110313.5963**	**110313.5963**

Table 8 HTS Case - 1 Material Balance

4.1.6 Membrane – 1, Case – 2:

Following is the material balance:

Membrane - 1, Case – 2		
Permeate Side		
Component	**Moles In**	**Moles Out**
Hydrogen	0	720
Retentate Side		
Component	**Moles In**	**Moles Out**
Water	3501.619675	3501.62
Carbon monoxide	401.1521827	401.1522
Carbon dioxide	473.9818173	473.9818
Hydrogen	2518.410141	1798.41
Nitrogen	923.9672071	923.9672
Total Moles	**7819.131023**	**7099.131**
Total Mass	**126138.6709**	**126138.7**

Table 9 Membrane - 1, Case - 2 Material Balance

4.1.7 HTS – 1, Case – 2:

Following reactions occur inside HTS – 1, Case - 2:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \text{ ... Conversion = 82 \%}$$

Following is the material balance:

HTS - 1, Case – 2		
Component	**Moles In**	**Moles Out**
Water	3501.619675	3173.694579
Carbon monoxide	401.1521827	73.2269954
Carbon dioxide	473.9818173	801.907103
Hydrogen	1798.410141	2126.3353
Nitrogen	923.9672071	923.9672071
Total Moles	**7099.131023**	**7099.131184**
Total Mass	**124687.0584**	**124687.0584**

Table 10 HTS – 1, Case - 2 Material Balance

4.1.8 Membrane – 2, Case – 2:

Following is the material balance:

Membrane - 2, Case - 2		
Permeate Side		
Component	**Moles In**	**Moles Out**
Hydrogen	0	850
Retentate Side		
Component	**Moles In**	**Moles Out**
Water	3173.694579	3173.694579
Carbon monoxide	73.2269954	73.2269954
Carbon dioxide	801.907103	801.907103
Hydrogen	2126.3353	1276.3353
Nitrogen	923.9672071	923.9672071
Total Moles	**7099.131184**	**6249.131184**
Total Mass	**124687.0584**	**124687.0584**

Table 11 Membrane - 2, Case - 2 Material Balance

4.1.9 HTS – 2, Case – 2:

Following reactions occur inside HTS – 2, Case - 2:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \ldots \text{Conversion} = 36\ \%$$

Following is the material balance:

HTS - 2, Case - 2		
Component	**Moles In**	**Moles Out**
Water	3173.694579	3147.206312
Carbon monoxide	73.2269954	46.73892844
Carbon dioxide	801.907103	828.3955846
Hydrogen	1276.3353	1302.823711
Nitrogen	923.9672071	923.9672071
Total Moles	**6249.131184**	**6249.131743**
Total Mass	**122973.4658**	**122973.4658**

Table 12 HTS – 2, Case - 2 Material Balance

4.1.10 Membrane Reactor, Case – 3:

Following reactions occur inside Membrane Reactor, Case - 3:

$CO + H_2O \leftrightarrow CO_2 + H_2$ … Conversion = 87 %

Following is the material balance:

Membrane Reactor, Case - 3		
Permeate Side		
Component	**Moles In**	**Moles Out**
Hydrogen	0	495.6762081
Retentate Side		
Component	**Moles In**	**Moles Out**
Water	2800.094457	2735.862
Carbon monoxide	485.4982075	63.938
Carbon dioxide	389.635794	810.72
Hydrogen	1468.77775	1037.81
Nitrogen	933.9110748	933.9110748
Total Moles	**6077.917283**	**6077.917283**
Total Mass	**112249.0472**	**112249.0472**

Table 13 Membrane Reactor, Case - 3 Material Balance

CHAPTER 5

ENERGY BALANCE

In this chapter, energy balance of on the ammonia plant using mixed feed of LNG and Mari gas was applied. The manual calculations were done by hand and also on excel sheet for further improvements. Energy balance on furnace, reactor, compressors, and multiple heat exchangers was applied as they are the main units impacted by the changed feed.

The main equation used in this balance was the law of conservation of energy i.e. energy of input streams will be equal to outlet streams if there is no accumulation or generation of energy. Equations and formulas are given where required and tables are been formed to show input and output streams of raw materials and products. Energy balance is very important because it provides information about heat input, output, accumulation, and temperatures of streams etc.

Values of different factors such as specific heats were either taken from Perry's chemical engineering or by using Aspen HYSYS (As it gives values of C_p, C_v, average temperatures etc.). Temperatures of different streams were taken from the literature review or from different research papers.

5.1 Assumptions and formulas used in energy balance:

Following assumptions were made for the energy balance of the plant:

1. The process is considered as steady state process which implies:

$$\Delta U + \Delta E_k + \Delta E_p = Q - W_s + W_{fl}$$

$$\Delta E_k = \Delta E_p = 0$$

$$\Delta H = Q + W_{fl}$$

2. For energy balance of a component of a plant involving a reaction following equation is used:

$$\Delta H_{r,t} = \Delta H_P - \Delta H_R + \Delta H_{reaction} \text{ (kJ/hr)}$$

3. Enthalpy of each stream was calculated using following formula:

$$H_T = \int_{Td}^{T} Cp * dT \qquad \text{(kJ /hr)}$$

4. To calculate C_p of a mixed stream, containing more than one chemical species following formula was used:

$$Cp\ (\text{mixture}) = x_a\, C_pa + x_b\, C_pb + x_c\, C_pc + \ldots\ldots\ldots$$

5.1.1 Primary Reformer, Case – 1,2,3:

Following is the energy balance data:

Primary Reformer		
Parameters	**In**	**Out**
Temperature (C)	371.1111	926.6667
Pressure (kPa)	3447.38	3447.38
Molar Flow (kg mol)	3252.278	4439.419
Cp (Kj/Kg mol/C)	-50.0718	-93.982
Enthalpy (kJ)	-6E+07	-3.9E+08
Heat of Reaction (kJ)	552305016.5	
Q (kj)	**226110549.6**	
Q (kW)	**610498.4838**	

Table 14 Primary Reformer Energy Balance

5.1.2 Secondary Reformer, Case – 1,2,3:

Following is the energy balance data:

Secondary Reformer		
Parameters	**In**	**Out**
Temperature (C)	926.6667	1131.707
Pressure (kPa)	3447.38	3447.38
Molar Flow (kg mol)	7688.407	7037.917
Cp (Kj/Kg mol/C)	-93.0784	-83.2575
Enthalpy (kJ)	-6.6E+08	-6.6E+08
Heat of Reaction (kJ)	-10940.65347	
Q (kj)	**0**	
Q (kW)	**0**	

Table 15 Secondary Reformer Energy Balance

5.1.3 Heat Exchanger, Case – 1,2,3:

Following is the energy balance data:

Heat Exchanger		
Shell Side		
Parameters	**In**	**Out**
Temperature (C)	25	99.86959
Pressure (kPa)	101	101
Molar Flow (kg mol)	7023	7023
Cp (Kj/Kg mol/C)	-11416.3	-2683.37
Enthalpy (kJ)	-2E+09	-1.9E+09
Q (kj)	**341122848.3**	
Q (kW)	**921031.6905**	
Tube Side		
Parameters	**In**	**Out**
Temperature (C)	926.7072	450
Pressure (kPa)	3447.38	3447.38
Molar Flow (kg mol)	7037.917	7037.917
Cp (Kj/Kg mol/C)	-101.675	-248.014
Enthalpy (kJ)	-6.6E+08	-7.9E+08
Q (kj)	**341122848.3**	
Q (kW)	**921031.6905**	

Table 16 Heat Exchanger Energy Balance

5.1.4 Membrane, Case – 1:

Following is the energy balance data:

Membrane, Case - 1		
Permeate Side		
Parameters	**In**	**Out**
Temperature (C)	0	450
Pressure (kPa)	0	1200
Molar Flow (kg mol)	0	960
Cp (Kj/Kg mol/C)	0	27.63322
Enthalpy (kJ)	0	11937549
Retentate Side		
Parameters	**In**	**Out**
Temperature (C)	450	450.3202
Pressure (kPa)	3447.38	3200
Molar Flow (kg mol)	7037.917	6077.917
Cp (Kj/Kg mol/C)	-248.014	-291.344
Enthalpy (kJ)	-7.9E+08	-8E+08
Q (kj)	**0**	
Q (kW)	**0**	

Table 17 Membrane Case - 1 Energy Balance

5.1.5 HTS, Case – 1:

Following is the energy balance data:

HTS, Case - 1		
Parameters	**In**	**Out**
Temperature (C)	450.3202	450
Pressure (kPa)	3200	3200
Molar Flow (kg mol)	6077.917	6077.918
Cp (Kj/Kg mol/C)	-291.344	-297.191
Enthalpy (kJ)	-8E+08	-8.1E+08
Heat of Reaction (kJ)	-15424444.53	
Q (kj)	**-15423444.53**	
Q (kW)	**-41643.30023**	

Table 18 HTS, Case – 1 Energy Balance

5.1.6 Membrane - 1, Case – 2:

Following is the energy balance data:

Membrane - 1, Case - 2		
Permeate Side		
Parameters	**In**	**Out**
Temperature (C)	0	450
Pressure (kPa)	0	1200
Molar Flow (kg mol)	0	720
Cp (Kj/Kg mol/C)	0	27.63322
Enthalpy (kJ)	0	8953162
Retentate Side		
Parameters	**In**	**Out**
Temperature (C)	450	450.05
Pressure (kPa)	3447.38	3200
Molar Flow (kg mol)	7819.131	7099.131
Cp (Kj/Kg mol/C)	-35.8666	-305.405
Enthalpy (kJ)	-9.7E+08	-9.80E+08
Q (kj)	**0**	
Q (kW)	**0**	

Table 19 Membrane = 1, Case – 2 Energy Balance

5.1.7 HTS - 1, Case – 2:

Following is the energy balance data:

HTS - 1, Case - 2		
Parameters	**In**	**Out**
Temperature (C)	450.05	450
Pressure (kPa)	3200	3200
Molar Flow (kg mol)	7099.131	7099.131
Cp (Kj/Kg mol/C)	0.002222	-309.364
Enthalpy (kJ)	-9.8E+08	-9.9E+08
Heat of Reaction (kJ)	-1032354.326	
Q (kj)	**-12541807.16**	
Q (kW)	**-33862.87933**	

Table 20 HTS – 1, Case – 2 Energy Balance

5.1.8 Membrane - 2, Case – 2:

Following is the energy balance data:

Membrane - 2, Case - 2		
Permeate Side		
Parameters	**In**	**Out**
Temperature (C)	0	452.7481082
Pressure (kPa)	0	1200
Molar Flow (kg mol)	0	850
Cp (Kj/Kg mol/C)	0	27.64427427
Enthalpy (kJ)	0	10638508.95
Retentate Side		
Parameters	**In**	**Out**
Temperature (C)	450	450
Pressure (kPa)	3200	3000
Molar Flow (kg mol)	7099.131	6249.131187
Cp (Kj/Kg mol/C)	-309.364	-355.226894
Enthalpy (kJ)	-9.9E+08	-998936758
Q (kj)		**0**
Q (kW)		**0**

Table 21 Membrane – 2, Case – 2 Energy Balance

5.1.9 HTS - 2, Case – 2:

Following is the energy balance data:

HTS - 2, Case - 2		
Parameters	**In**	**Out**
Temperature (C)	450	450
Pressure (kPa)	3000	3000
Molar Flow (kg mol)	6249.131	6249.132
Cp (Kj/Kg mol/C)	-355.227	-355.587
Enthalpy (kJ)	-1E+09	-1E+09
Heat of Reaction (kJ)	-1.41E-07	
Q (kj)	**-1012154.326**	
Q (kW)	**-2732.81668**	

Table 22 HTS – 2, Case – 2 Energy Balance

5.1.10 Membrane Reactor, Case – 3:

Following is the energy balance data:

Membrane Reactor, Case - 3		
Permeate Side		
Parameters	**In**	**Out**
Temperature (C)	0	400
Pressure (kPa)	0	100
Molar Flow (kg mol)	0	495.6762
Cp (Kj/Kg mol/C)	0	100.5573
Enthalpy (kJ)	0	19937549
Retentate Side		
Parameters	**In**	**Out**
Temperature (C)	400	400
Pressure (kPa)	3447	3000
Molar Flow (kg mol)	6077.917	5582.241
Cp (Kj/Kg mol/C)	-248.014	-328.014
Enthalpy (kJ)	-6E+08	-7.3E+08
Heat of Reaction (kJ)	-17424444.53	
Q (kj)	**-19424444.53**	
Q (kW)	**-47046.00023**	

Table 23 Membrane Reactor, Case – 3 Energy Balance

CHAPTER 7

PROCESS SIMULATION

Based on real time industrial data simulations are performed for the process using ASPEN HYSYS V 8.8. Ammonia, oxygen, nitrogen, carbon dioxide, carbon monoxide, hydrogen, methane, ethane, propane, butane, and argon were selected as the components for simulation. For the process, Peng Robinson was selected as the fluid package. The process gas is preheated in a furnace and then send to the primary reformer reactor [5] [6]. We have created simulation of Case – 1 and Case – 2 on Aspen HYSYS. While the Simulation of Case – 3 will modelled mathematically in Polymath 6.0.

6.1 Simulation of Case – 1:

Following is the flow sheet:

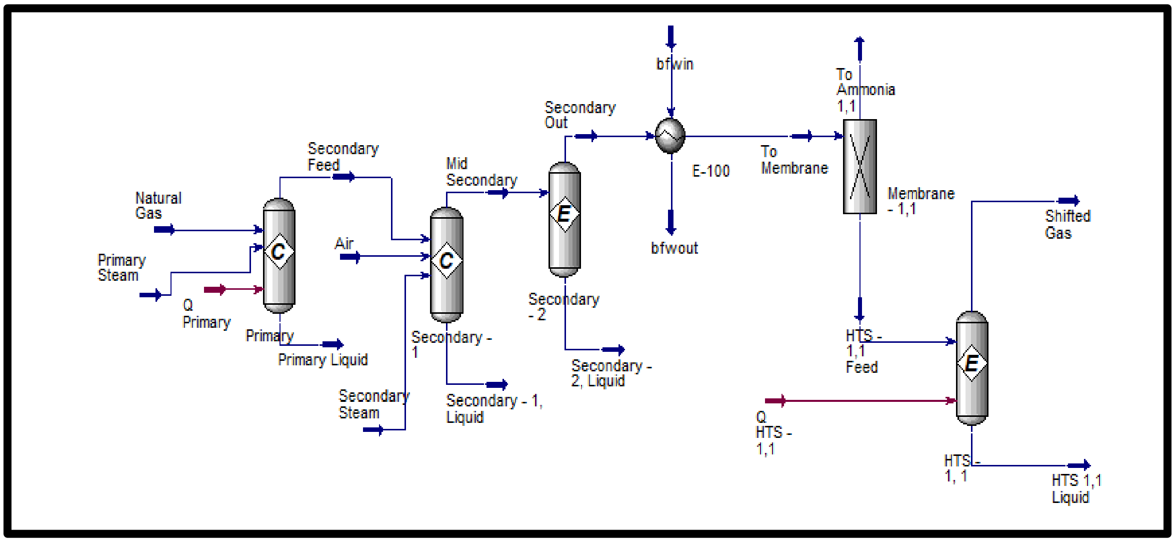
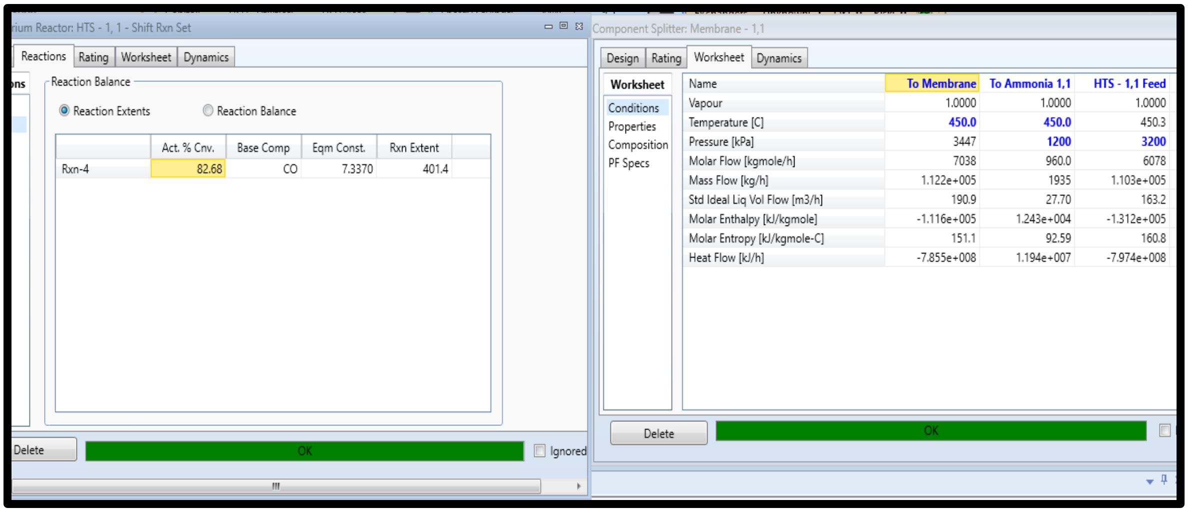


Figure 8 HYSYS Flow Sheet of Case – 1

6.1.1 Reaction Conversion in HTS Case – 1:



rium Reactor: HTS - 1, 1 - Shift Rxn Set

Reactions | Rating | Worksheet | Dynamics

Reaction Balance

● Reaction Extents ○ Reaction Balance

	Act. % Cnv.	Base Comp	Eqm Const.	Rxn Extent
Rxn-4	82.68	CO	7.3370	401.4

Delete | OK | ☐ Ignored

Component Splitter: Membrane - 1,1

Design | Rating | Worksheet | Dynamics

Worksheet: Conditions, Properties, Composition, PF Specs

Name	To Membrane	To Ammonia 1,1	HTS - 1,1 Feed
Vapour	1.0000	1.0000	1.0000
Temperature [C]	450.0	450.0	450.3
Pressure [kPa]	3447	1200	3200
Molar Flow [kgmole/h]	7038	960.0	6078
Mass Flow [kg/h]	1.122e+005	1935	1.103e+005
Std Ideal Liq Vol Flow [m3/h]	190.9	27.70	163.2
Molar Enthalpy [kJ/kgmole]	-1.116e+005	1.243e+004	-1.312e+005
Molar Entropy [kJ/kgmole-C]	151.1	92.59	160.8
Heat Flow [kJ/h]	-7.855e+008	1.194e+007	-7.974e+008

Delete | OK

Figure 9 HTS Case – 1 at Specific Hydrogen Separation

6.2 Simulation of Case – 2:

Following is the flow sheet:

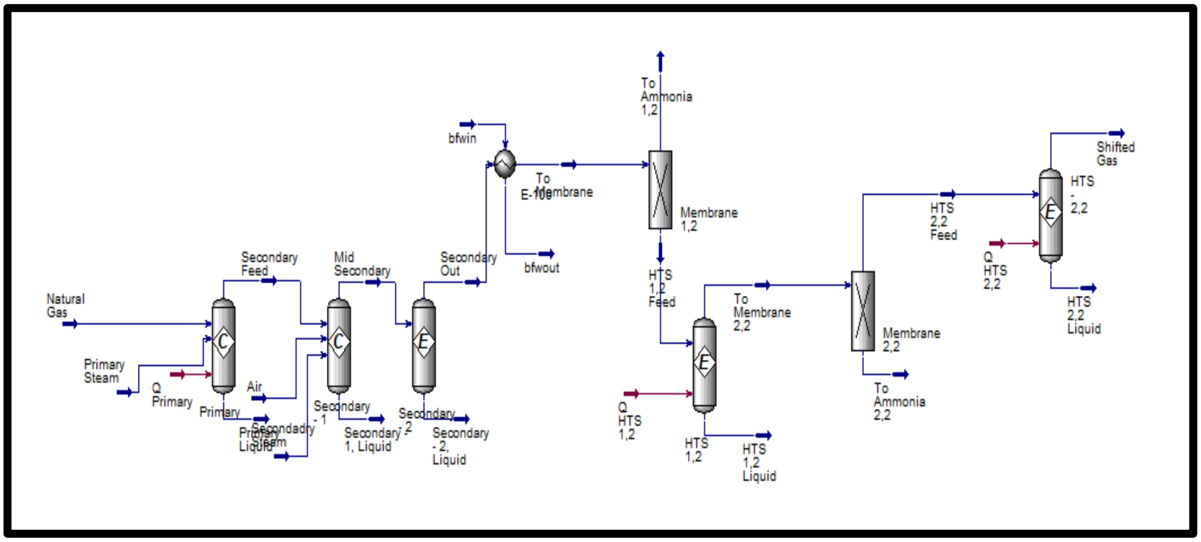
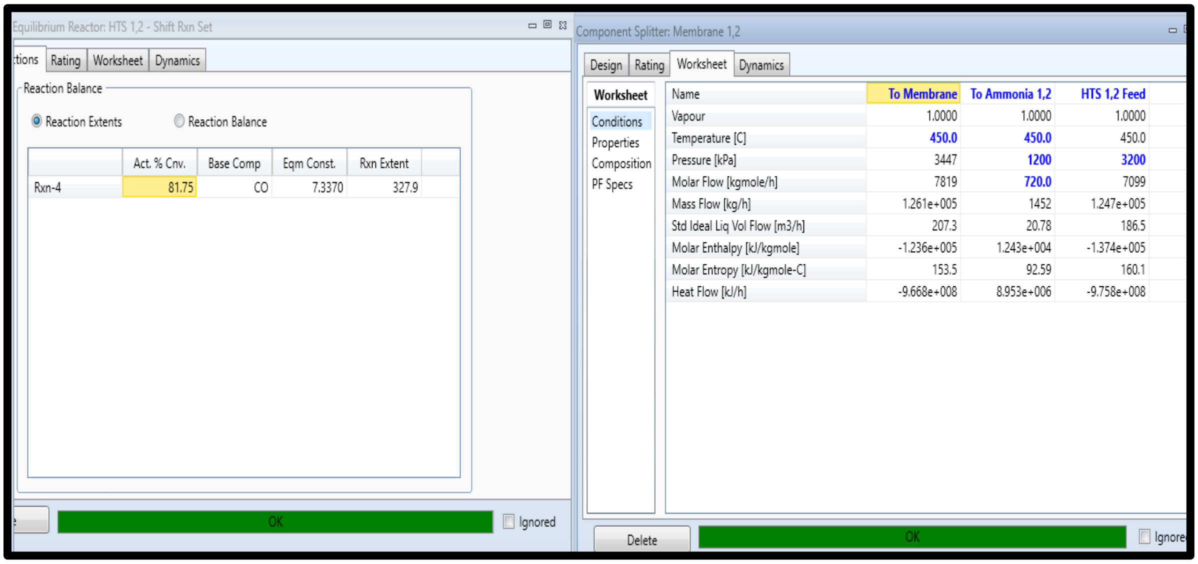


Figure 10 Aspen HYSYS Flow Sheet of Case – 2

6.2.1 Reaction Conversion in HTS – 1, Case – 2:

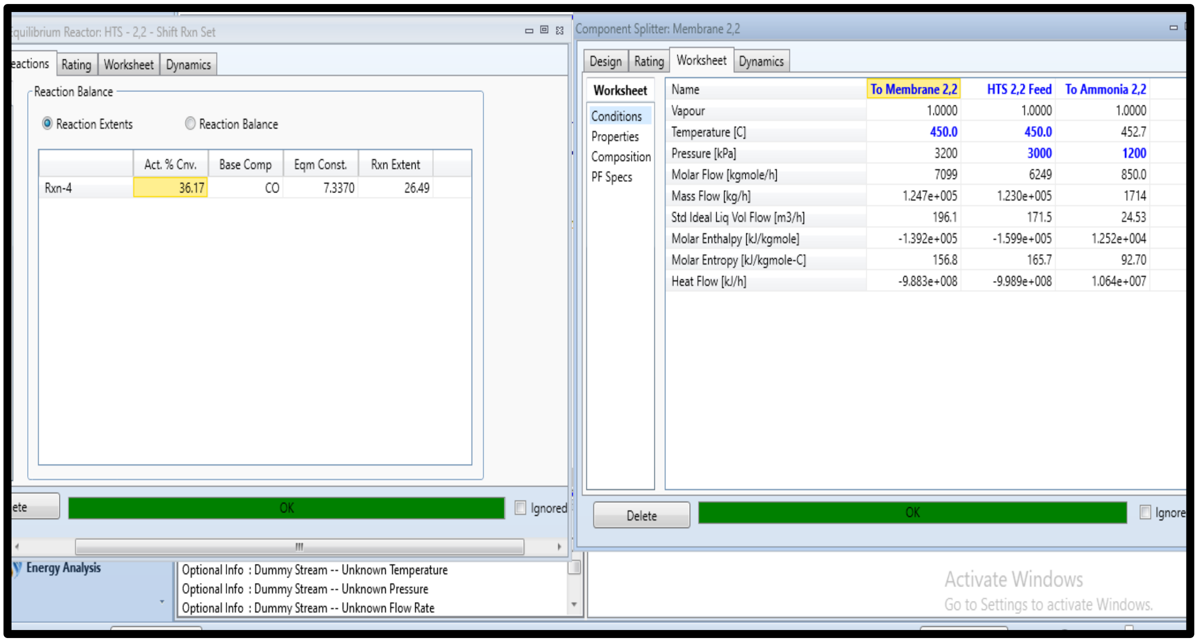


	Act. % Cnv.	Base Comp	Eqm Const.	Rxn Extent
Rxn-4	81.75	CO	7.3370	327.9

Name	To Membrane	To Ammonia 1,2	HTS 1,2 Feed
Vapour	1.0000	1.0000	1.0000
Temperature [C]	450.0	450.0	450.0
Pressure [kPa]	3447	1200	3200
Molar Flow [kgmole/h]	7819	720.0	7099
Mass Flow [kg/h]	1.261e+005	1452	1.247e+005
Std Ideal Liq Vol Flow [m3/h]	207.3	20.78	186.5
Molar Enthalpy [kJ/kgmole]	-1.236e+005	1.243e+004	-1.374e+005
Molar Entropy [kJ/kgmole-C]	153.5	92.59	160.1
Heat Flow [kJ/h]	-9.668e+008	8.953e+006	-9.758e+008

Figure 11 HTS – 1, Case – 2 Conversion at Specific Hydrogen Separation

6.2.2 Reaction Conversion in HTS – 2, Case – 2:



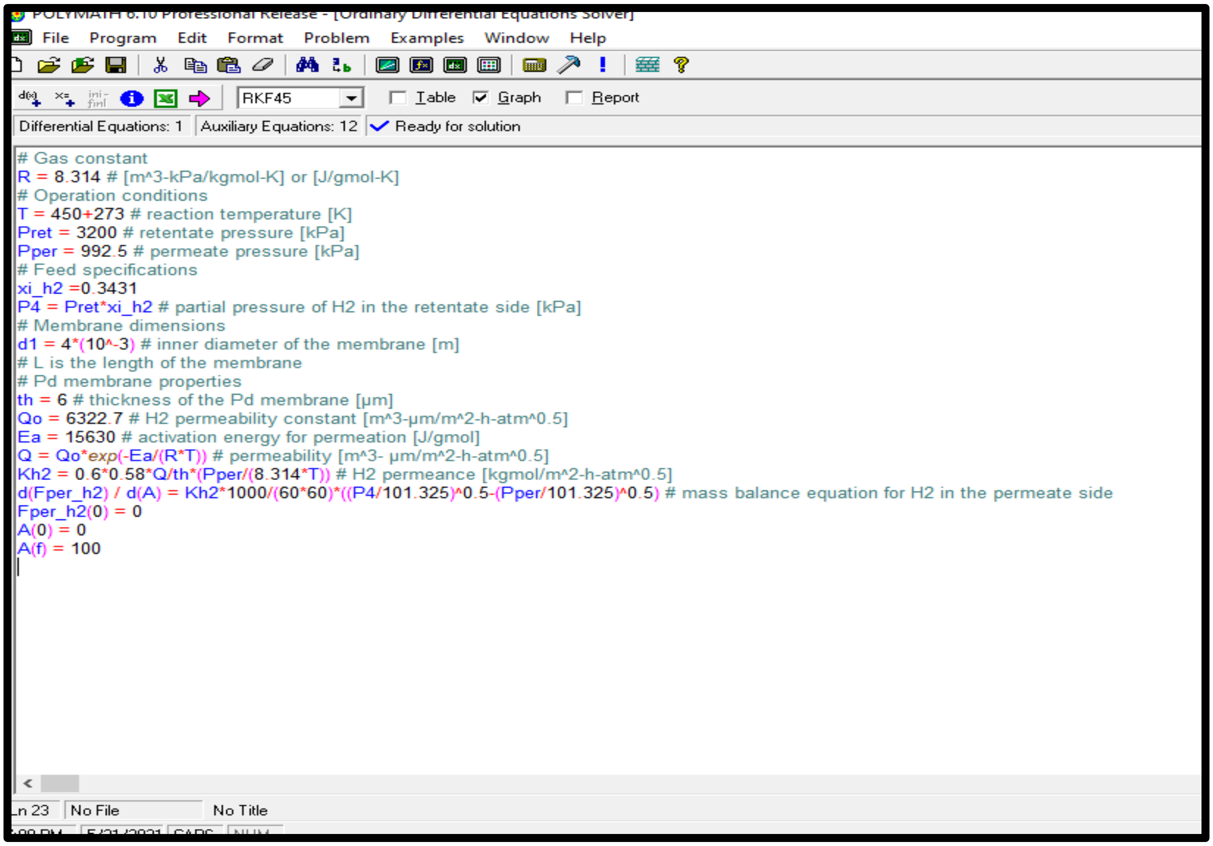
	Act. % Cnv.	Base Comp	Eqm Const.	Rxn Extent
Rxn-4	36.17	CO	7.3370	26.49

Name	To Membrane 2,2	HTS 2,2 Feed	To Ammonia 2,2
Vapour	1.0000	1.0000	1.0000
Temperature [C]	450.0	450.0	452.7
Pressure [kPa]	3200	3000	1200
Molar Flow [kgmole/h]	7099	6249	850.0
Mass Flow [kg/h]	1.247e+005	1.230e+005	1714
Std Ideal Liq Vol Flow [m3/h]	196.1	171.5	24.53
Molar Enthalpy [kJ/kgmole]	-1.392e+005	-1.599e+005	1.252e+004
Molar Entropy [kJ/kgmole-C]	156.8	165.7	92.70
Heat Flow [kJ/h]	-9.883e+008	-9.989e+008	1.064e+007

```
Optional Info  : Dummy Stream -- Unknown Temperature
Optional Info  : Dummy Stream -- Unknown Pressure
Optional Info  : Dummy Stream -- Unknown Flow Rate
```

Figure 12 HTS – 2, Case – 2 Conversion at Specific Hydrogen Separation

6.3 Membrane Modelling with Polymath 6.0:



```
# Gas constant
R = 8.314 # [m^3-kPa/kgmol-K] or [J/gmol-K]
# Operation conditions
T = 450+273 # reaction temperature [K]
Pret = 3200 # retentate pressure [kPa]
Pper = 992.5 # permeate pressure [kPa]
# Feed specifications
xi_h2 =0.3431
P4 = Pret*xi_h2 # partial pressure of H2 in the retentate side [kPa]
# Membrane dimensions
d1 = 4*(10^-3) # inner diameter of the membrane [m]
# L is the length of the membrane
# Pd membrane properties
th = 6 # thickness of the Pd membrane [µm]
Qo = 6322.7 # H2 permeability constant [m^3-µm/m^2-h-atm^0.5]
Ea = 15630 # activation energy for permeation [J/gmol]
Q = Qo*exp(-Ea/(R*T)) # permeability [m^3- µm/m^2-h-atm^0.5]
Kh2 = 0.6*0.58*Q/th*(Pper/(8.314*T)) # H2 permeance [kgmol/m^2-h-atm^0.5]
d(Fper_h2) / d(A) = Kh2*1000/(60*60)*((P4/101.325)^0.5-(Pper/101.325)^0.5) # mass balance equation for H2 in the permeate side
Fper_h2(0) = 0
A(0) = 0
A(f) = 100
```

Figure 13 Polymath Code of Membrane Separation

6.3.1 Solution of Sieverts Law with the help of Graph:

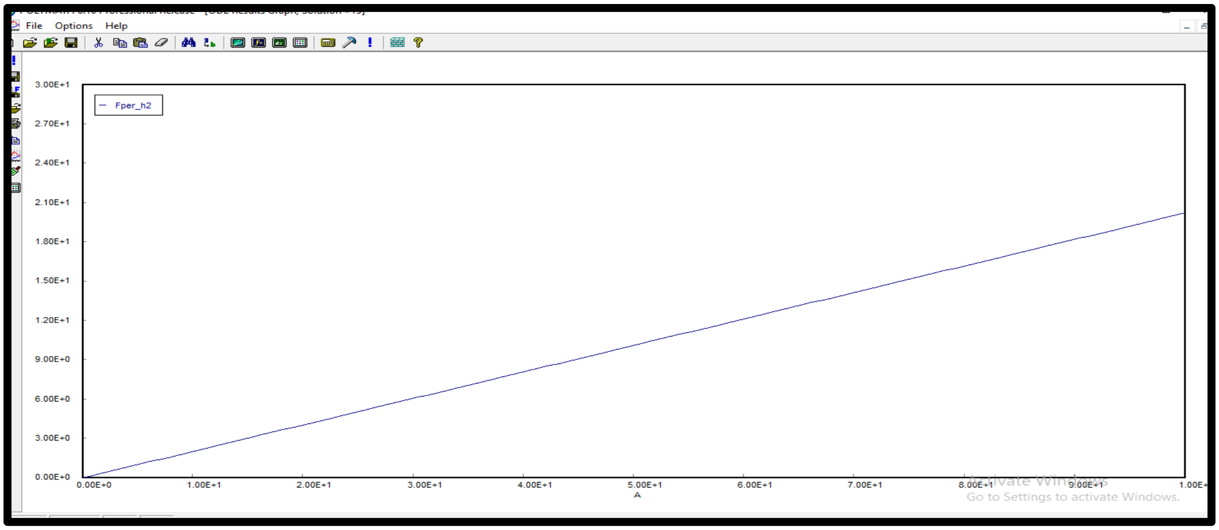
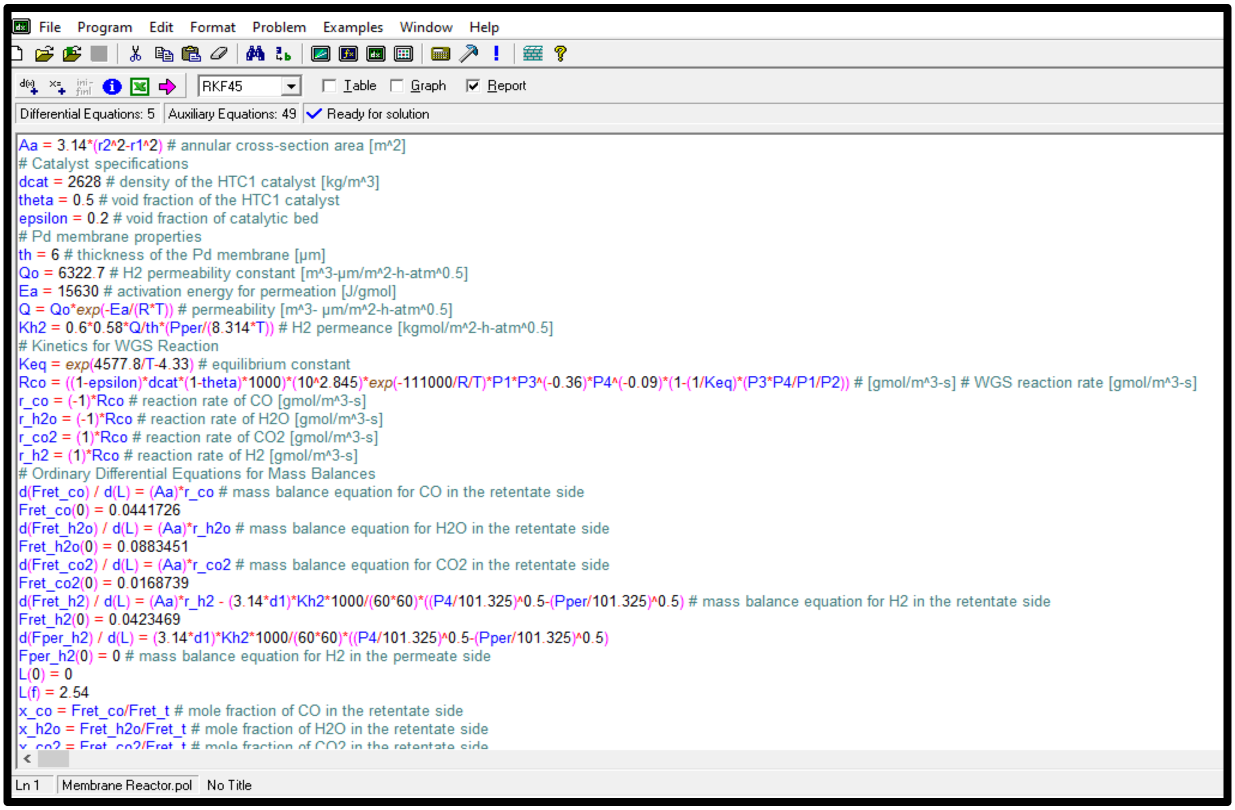
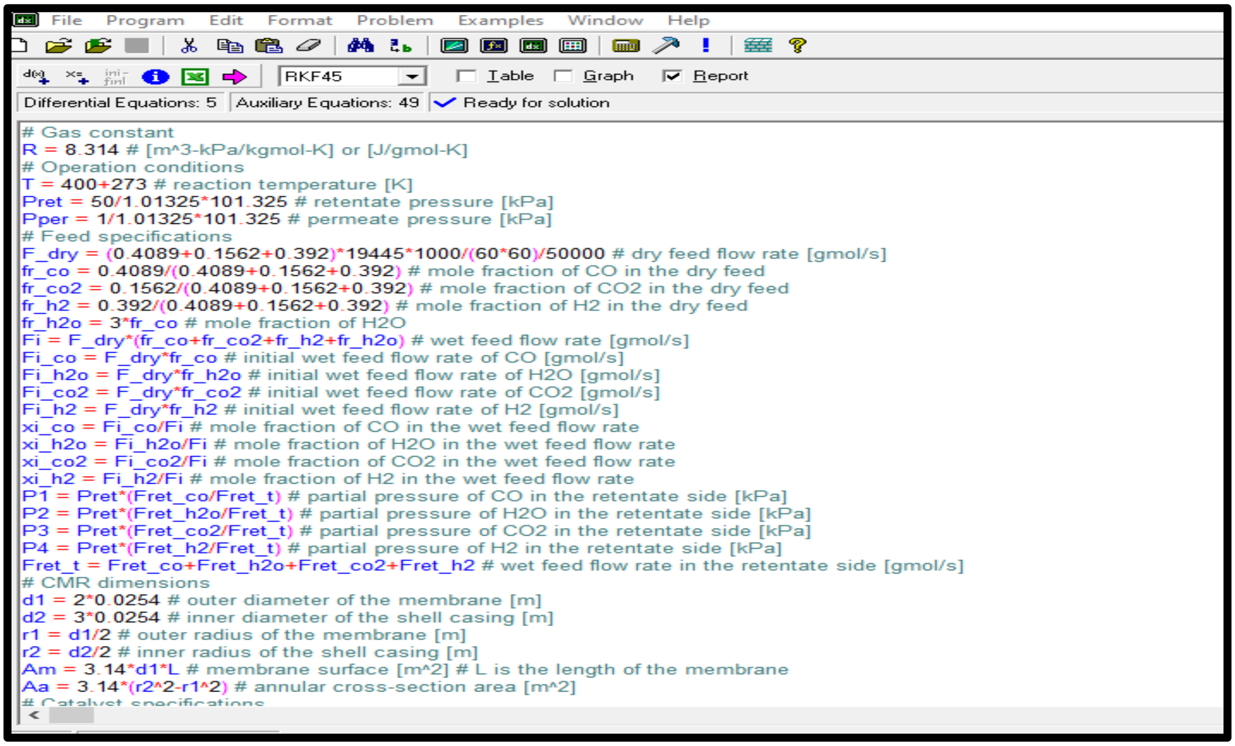


Figure 14 Flow Rate VS Area of Membrane

6.4 Membrane Reactor Modelling on Polymath 6.0:



```
Aa = 3.14*(r2^2-r1^2) # annular cross-section area [m^2]
# Catalyst specifications
dcat = 2628 # density of the HTC1 catalyst [kg/m^3]
theta = 0.5 # void fraction of the HTC1 catalyst
epsilon = 0.2 # void fraction of catalytic bed
# Pd membrane properties
th = 6 # thickness of the Pd membrane [μm]
Qo = 6322.7 # H2 permeability constant [m^3-μm/m^2-h-atm^0.5]
Ea = 15630 # activation energy for permeation [J/gmol]
Q = Qo*exp(-Ea/(R*T)) # permeability [m^3- μm/m^2-h-atm^0.5]
Kh2 = 0.6*0.58*Q/th*(Pper/(8.314*T)) # H2 permeance [kgmol/m^2-h-atm^0.5]
# Kinetics for WGS Reaction
Keq = exp(4577.8/T-4.33) # equilibrium constant
Rco = ((1-epsilon)*dcat*(1-theta)*1000)*(10^2.845)*exp(-111000/R/T)*P1*P3^(-0.36)*P4^(-0.09)*(1-(1/Keq)*(P3*P4/P1/P2)) # [gmol/m^3-s] # WGS reaction rate [gmol/m^3-s]
r_co = (-1)*Rco # reaction rate of CO [gmol/m^3-s]
r_h2o = (-1)*Rco # reaction rate of H2O [gmol/m^3-s]
r_co2 = (1)*Rco # reaction rate of CO2 [gmol/m^3-s]
r_h2 = (1)*Rco # reaction rate of H2 [gmol/m^3-s]
# Ordinary Differential Equations for Mass Balances
d(Fret_co) / d(L) = (Aa)*r_co # mass balance equation for CO in the retentate side
Fret_co(0) = 0.0441726
d(Fret_h2o) / d(L) = (Aa)*r_h2o # mass balance equation for H2O in the retentate side
Fret_h2o(0) = 0.0883451
d(Fret_co2) / d(L) = (Aa)*r_co2 # mass balance equation for CO2 in the retentate side
Fret_co2(0) = 0.0168739
d(Fret_h2) / d(L) = (Aa)*r_h2 - (3.14*d1)*Kh2*1000/(60*60)*((P4/101.325)^0.5-(Pper/101.325)^0.5) # mass balance equation for H2 in the retentate side
Fret_h2(0) = 0.0423469
d(Fper_h2) / d(L) = (3.14*d1)*Kh2*1000/(60*60)*((P4/101.325)^0.5-(Pper/101.325)^0.5)
Fper_h2(0) = 0 # mass balance equation for H2 in the permeate side
L(0) = 0
L(f) = 2.54
x_co = Fret_co/Fret_t # mole fraction of CO in the retentate side
x_h2o = Fret_h2o/Fret_t # mole fraction of H2O in the retentate side
x_co2 = Fret_co2/Fret_t # mole fraction of CO2 in the retentate side
```



```
# Gas constant
R = 8.314 # [m^3-kPa/kgmol-K] or [J/gmol-K]
# Operation conditions
T = 400+273 # reaction temperature [K]
Pret = 50/1.01325*101.325 # retentate pressure [kPa]
Pper = 1/1.01325*101.325 # permeate pressure [kPa]
# Feed specifications
F_dry = (0.4089+0.1562+0.392)*19445*1000/(60*60)/50000 # dry feed flow rate [gmol/s]
fr_co = 0.4089/(0.4089+0.1562+0.392) # mole fraction of CO in the dry feed
fr_co2 = 0.1562/(0.4089+0.1562+0.392) # mole fraction of CO2 in the dry feed
fr_h2 = 0.392/(0.4089+0.1562+0.392) # mole fraction of H2 in the dry feed
fr_h2o = 3*fr_co # mole fraction of H2O
Fi = F_dry*(fr_co+fr_co2+fr_h2+fr_h2o) # wet feed flow rate [gmol/s]
Fi_co = F_dry*fr_co # initial wet feed flow rate of CO [gmol/s]
Fi_h2o = F_dry*fr_h2o # initial wet feed flow rate of H2O [gmol/s]
Fi_co2 = F_dry*fr_co2 # initial wet feed flow rate of CO2 [gmol/s]
Fi_h2 = F_dry*fr_h2 # initial wet feed flow rate of H2 [gmol/s]
xi_co = Fi_co/Fi # mole fraction of CO in the wet feed flow rate
xi_h2o = Fi_h2o/Fi # mole fraction of H2O in the wet feed flow rate
xi_co2 = Fi_co2/Fi # mole fraction of CO2 in the wet feed flow rate
xi_h2 = Fi_h2/Fi # mole fraction of H2 in the wet feed flow rate
P1 = Pret*(Fret_co/Fret_t) # partial pressure of CO in the retentate side [kPa]
P2 = Pret*(Fret_h2o/Fret_t) # partial pressure of H2O in the retentate side [kPa]
P3 = Pret*(Fret_co2/Fret_t) # partial pressure of CO2 in the retentate side [kPa]
P4 = Pret*(Fret_h2/Fret_t) # partial pressure of H2 in the retentate side [kPa]
Fret_t = Fret_co+Fret_h2o+Fret_co2+Fret_h2 # wet feed flow rate in the retentate side [gmol/s]
# CMR dimensions
d1 = 2*0.0254 # outer diameter of the membrane [m]
d2 = 3*0.0254 # inner diameter of the shell casing [m]
r1 = d1/2 # outer radius of the membrane [m]
r2 = d2/2 # inner radius of the shell casing [m]
Am = 3.14*d1*L # membrane surface [m^2] # L is the length of the membrane
Aa = 3.14*(r2^2-r1^2) # annular cross-section area [m^2]
# Catalyst specifications
```

Figure 15 Polymath Code of Membrane Reactor

6.4.1 Membrane Reactor Modelling Results on Polymath 6.0:

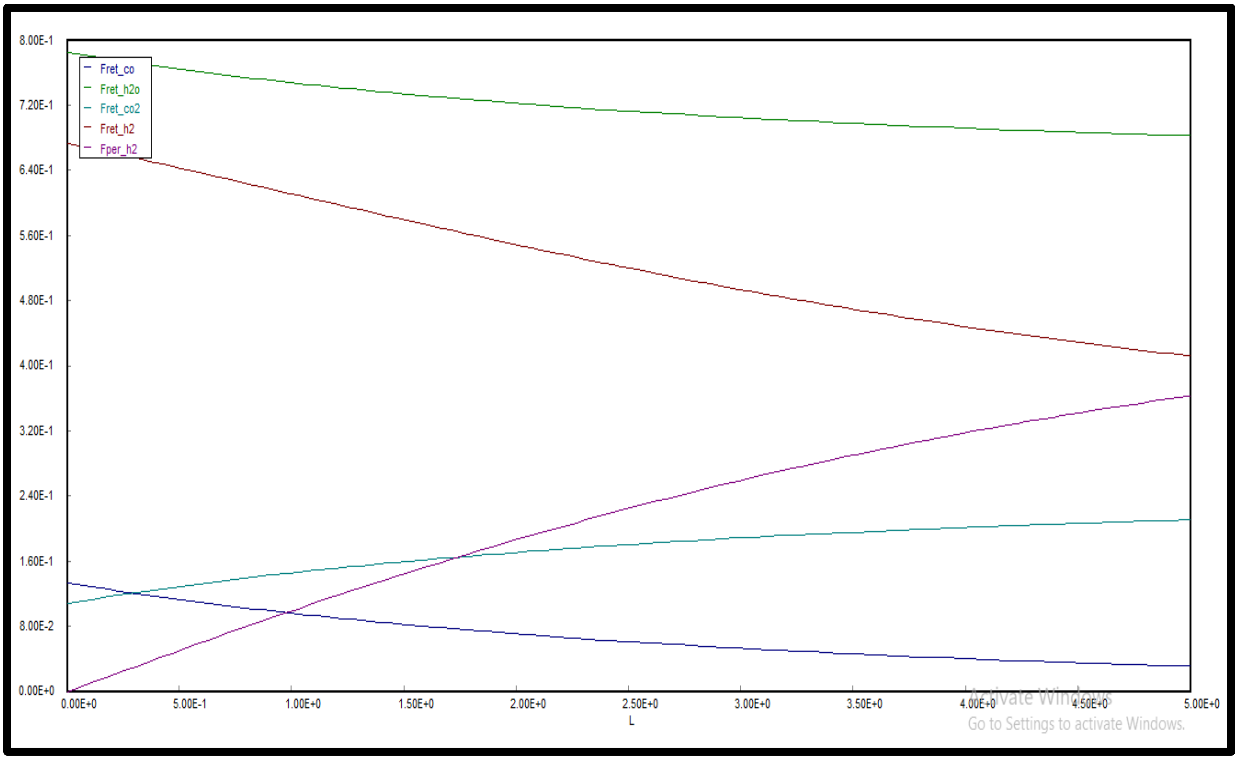


Figure 16 Membrane Reactor Flow Rate VS Length of Membrane Module

CHAPTER 7

SELECTION AND EQUIPMENT DESIGN CASE

7.1 Terminologies:

Q = Heat Flow

V_r = Volume of reactor

V_b = Volume of bed

N= No of tubes

E = Void Fraction

Q_{avg} = Average heat flux

L = Length of tube

I.D = Internal Diameter of tube

W = Weight of catalyst

V_c = Volume of catalyst

7.2 Primary Reformer R-101:

Primary reformer is a type of furnace having tubes in it. Reactions are taking place in these tubes having catalyst in it and they are heated by the burners inside the walls of furnace. For designing we chose it to be a Foster Wheeler side fired reformer due to reduced methane slip and it can bear small amount of coking because of propane and butane in our feed. Tubes and Outer body are made of stainless steel which are bearable for the reactor pressure. Design calculations are given below [7].

7.2.1 Number of tubes:

$$\boldsymbol{N = \frac{Q}{3.14 \times I.D \times L \times Q_{avg}}} \qquad \textbf{(i)}$$

Q= 5.3979173 x10^7 kcal/hr

I.D = 0.113m

L = 11m

Qavg= 65800 kcal/m²hr

By putting these values in above Equation (i) we get no of tubes,

$$\boldsymbol{N = \frac{5.39 \times 10^{7}}{3.14 \times 0.13 \times 11 \times Q_{avg}}}$$

N= 210 tubes

7.2.2 Volume of reactor:

Volume of reactor = N.π.ID².L/4

V_r=(210)*(3.14)*(0.113)2*.11/4

$V_r = 23.39\ m^3$

7.2.3 Volume of Catalyst:

Catalyst used R-67R-7H (Ni 15%, MgO25%, Al2O360%)

Bulk density of catalyst = 970 kg/m³

Voidage = E = 0.044

$E = (V_r - V_c)/V_r$

As we know E and Vr, by putting values we get V_c. (Volume of Catalyst)

$V_c = 20.133\ m^3$

7.2.4 Weight of Catalyst:

Weight of Catalyst = (Bulk density) *(Volume of catalyst)

Weight of catalyst = (970) *(20.133)

Weight of catalyst = 19527.79 kg

7.2.5 Space Velocity:

Space Velocity = Volumetric Feed Flow rate/ Volume of reactor

Space velocity = 57655.58/23.169*3600

Space velocity = 0.6912 sec^{-1}

7.2.6 Design Summary:

Parameters	Specification
Weight of Catalyst	19727 kg
Bulk density of catalyst	970kg/m^3
Volume of catalyst	20.133 m^3
Voidage	0.044
Volume of reactor	23.39 m^3
Space velocity	0.6912 sec^{-1}

Table 24 Primary Reformer Design Summary

7.3 Secondary Reformer:

There are two types of reactions that are involved in primary reformer, three of them are combustion reactions and then another type is reforming reaction which is involved in the reactor bed [8,13].

We will take into account reforming reaction which is taking place in the bed for the design of this reactor.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

7.3.1 Selection:

Is this reactor, we have combustion reactions and reforming reactions. The purpose is to extract nitrogen from air for ammonia reaction. So, we need a reaction having burner in it for combustion. And for reforming reaction we need to have a packed bed reactor under it where the reforming reaction takes place. Packed bed reaction is required as it is a catalytic reaction and gaseous phase reaction and also it gives more conversion per weight of catalyst.

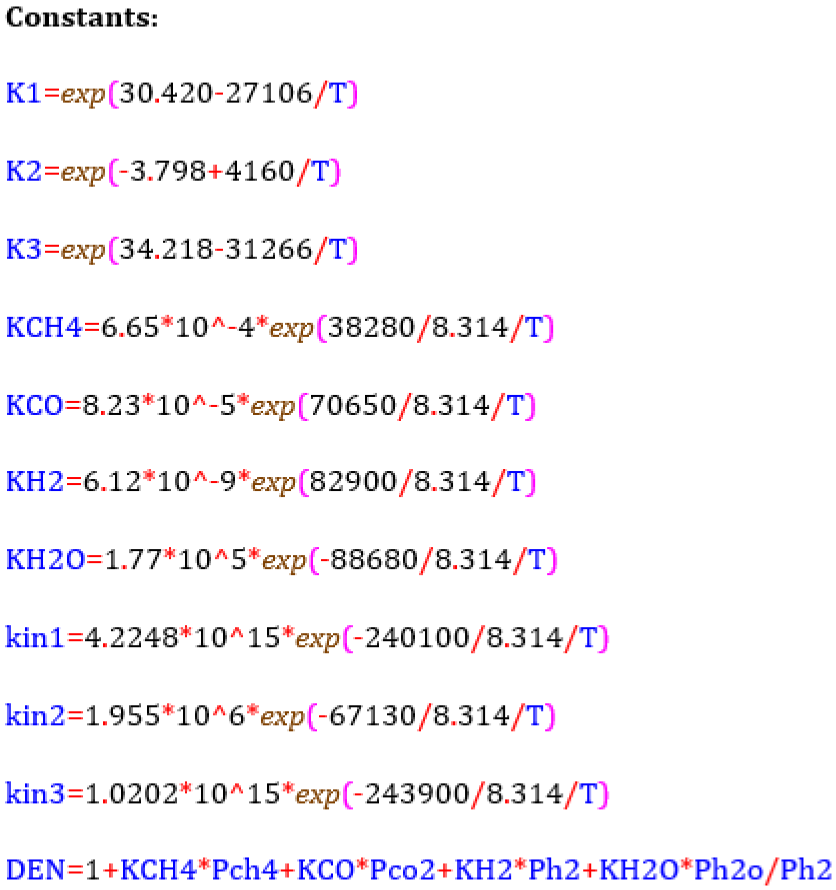
7.3.2 Weight of Catalyst:

The catalyst used in secondary reformer: RKS-2&; RKS-2-7H

Catalyst composition = NiO, Promotor/Carrier = MgO/ Al_2O_3

So the weight of the catalyst in the secondary reformer is calculated by using the polymath version 6.0. The code includes all the rate equations and the rate constants that are involved in the reactions involved in the secondary reformer and the weight of the catalyst was calculated by solving the ordinary differential equations using the Runge-Kutta method [15,13,11].

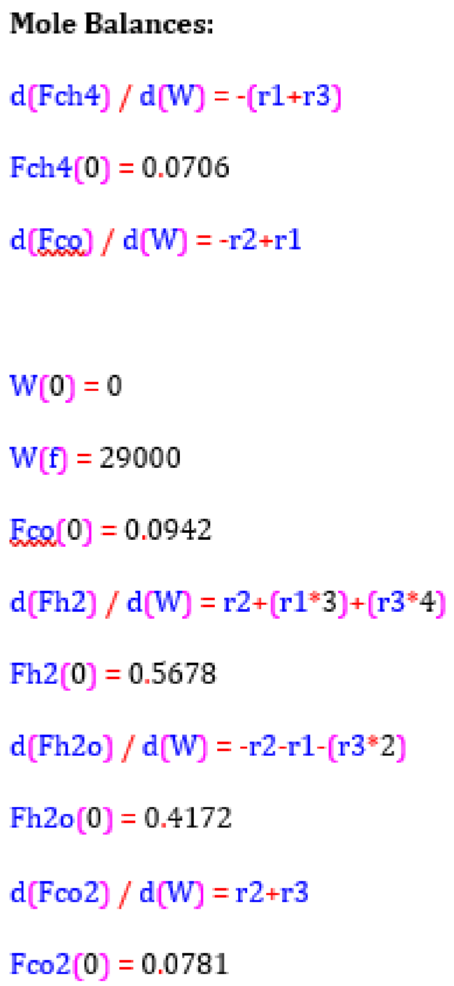
7.3.2.1 Code:



```
Constants:

K1=exp(30.420-27106/T)

K2=exp(-3.798+4160/T)

K3=exp(34.218-31266/T)

KCH4=6.65*10^-4*exp(38280/8.314/T)

KCO=8.23*10^-5*exp(70650/8.314/T)

KH2=6.12*10^-9*exp(82900/8.314/T)

KH2O=1.77*10^5*exp(-88680/8.314/T)

kin1=4.2248*10^15*exp(-240100/8.314/T)

kin2=1.955*10^6*exp(-67130/8.314/T)

kin3=1.0202*10^15*exp(-243900/8.314/T)

DEN=1+KCH4*Pch4+KCO*Pco2+KH2*Ph2+KH2O*Ph2o/Ph2
```

Rate Equations:

```
r1=kin1/Ph2^2.5/DEN^2*(Pch4*Ph2o-Ph2^3*Pco/K1)
r2=kin2/Ph2/DEN^2*(Pco*Ph2o-Ph2*Pco2/K2)*1070
r3=kin3/Ph2^3.5/DEN^2*(Pch4*Ph2o^2-Ph2^4*Pco2/K3)
Ph2 = Yh2*Ptot # Ideal Law
Pco2 = Yco2*Ptot # Ideal Law
Pco = Yco*Ptot # Ideal Law
Ph2o = Yh2o*Ptot # Ideal Law
Pch4 = Ych4*Ptot # Ideal Law
Yco=Fco/(Fh2+Fco+Fco2+Fh2o+Fch4)
Yh2o=Fh2o/(Fh2+Fco+Fco2+Fh2o+Fch4)
Yco2=Fco2/(Fh2+Fco+Fco2+Fh2o+Fch4)
Yh2=Fh2/(Fh2+Fco+Fco2+Fh2o+Fch4)
Ych4=Fch4/(Fh2+Fco+Fco2+Fh2o+Fch4)
T=600+273
Ptot=34
```



```
Mole Balances:

d(Fch4) / d(W) = -(r1+r3)

Fch4(0) = 0.0706

d(Fco) / d(W) = -r2+r1


W(0) = 0

W(f) = 29000

Fco(0) = 0.0942

d(Fh2) / d(W) = r2+(r1*3)+(r3*4)

Fh2(0) = 0.5678

d(Fh2o) / d(W) = -r2-r1-(r3*2)

Fh2o(0) = 0.4172

d(Fco2) / d(W) = r2+r3

Fco2(0) = 0.0781
```

7.3.2.2 Results:

Weight of catalyst =21789 kg of catalyst

Bulk density of catalyst = 1070 kg/m^3 (Bulk density)

7.3.3 Volume of Catalyst:

Volume of catalyst = Weight of catalyst/ Bulk density of catalyst

Volume of catalyst =21789 kg /1070

$$\mathbf{V_c=20.839 m^3}$$

7.3.4 Volume of Reactor:

$$\text{Voidage} = 0.25$$

$$E = (V_b - V_c)/V_b$$

$$\text{With 20\% clearance, } V_r = 1.20*Vb$$

$$\mathbf{Vr = 33.33\ m^3}$$

7.3.5 Height of reactor:

$$H_r = Vr/\ \pi*D^2/4,\ D_r = 4m$$

$$\mathbf{H_r = 2.65\ m}$$

7.3.6 Space Velocity:

Space Velocity = Volumetric Feed Flow rate/ Volume of reactor

$$\mathbf{Space\ velocity = 0.6617\ sec^{-1}}$$

7.3.7 Design Summary:

Parameters	Specification
Weight of Catalyst	21789 kg
Bulk density of catalyst	1070 kg/ m^3
Volume of catalyst	20.829 m^3
Voidage	0.25
Volume of reactor	33.33 m^3
space velocity	0.6617 sec ^-1
Height of Reactor	2.65 m

Table 25 Secondary Reformer Design Summary

7.4 Heat Exchanger Design:

The calculations of the shell and tube heat exchanger is divided into two parts: shell side calculations and tube side calculations. Firstly, duty is calculated for the whole exchanger and temperatures are stated. LMTD is obtained through the formula and then corrected using the values of R, S and F_T. After this, caloric temperatures for both shell and tube side, t_c and T_c, are calculated. Then calculations for shell and tube side are made separately. Almost, all the parameters calculated for both sides are the same. The parameters include flow areas, mass velocities, Reynold's numbers, heat transfer coefficients and pressure drop for both sides. If pressure drop on both sides lie within the acceptable range, the heat exchanger is deemed suitable for the operation.

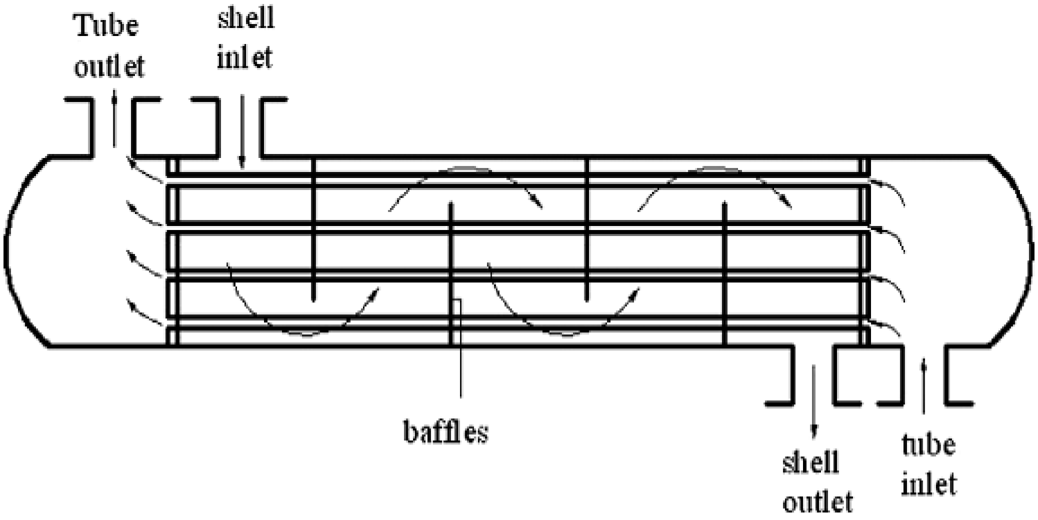


Figure 17 Shell and Tube Heat Exchanger

7.4.1 Shell and Tube Heat Exchanger Design Calculations:

Water (Shell side):	**Process gas (Tube side):**
K = 0.6108 W/m.°C	K = 0.1287 W/m.°C
$\mu = 8.9 \times 10^{-4}$ Ns/m^2	$\mu = 2.17 \times 10^{-5}$ Ns/m^2

C_p = 2.44 kJ/kg. ^oC

ρ = 1000 kg/m^3

$\dot{m}$ = 252.84 kg/s

C_p = 1.93 kJ/kg. ^oC

$\dot{m}$ = 31.4 kg/s

ρ = 8.1kg/m^3

T_{hi} = 927 ^oC ; T_{ho} = 450 ^oC

T_{ci} = 25 ^oC ; T_{co} = 99.97 ^oC

7.4.2 Heat duty*:*

Q = $\dot{m}$ x C_p x ΔT

= 31.4 x 2.44 x (927-450)

= 36545.83 KW

7.4.3 Flow rate of Water:

Q = $\dot{m}$ x C_p x ΔT → $\dot{m} = \frac{Q}{\mathrm{Cp\ x}\ \Delta T}$

$\dot{m} = \frac{36542.83}{1.93\mathrm{x}\ (99.97-25)}$

$\dot{m}$ = 252. 94kg/s

7.4.4 Log Mean Temperature Difference (LMTD):

LMTD = $\frac{\Delta T2-\Delta T1}{\ln\,(\frac{\Delta T2}{\Delta T1})}$

ΔT_2 = Temperature difference of hot fluids

ΔT_1 = Temperature difference of cold fluids

LMTD = $\frac{477-74.7}{\ln\,(477/74.7)}$

LMTD = 216.9 ^oC

$$R = \frac{T_{1-}T_2}{t_2-t_1}$$

$$S = \frac{t_2 - t_1}{t_1 - t_1}$$

$$R = \frac{927-450}{99.97-25} = 6.38$$

$$S = \frac{99.97-25}{477-25} = 0.175$$

From graph, 1 shell and 2 tube passes

So, **corrected LMTD (Δt)** = 0.98 x 216.9 = **212.56 °C**

From figure, **F_t = 0.98**

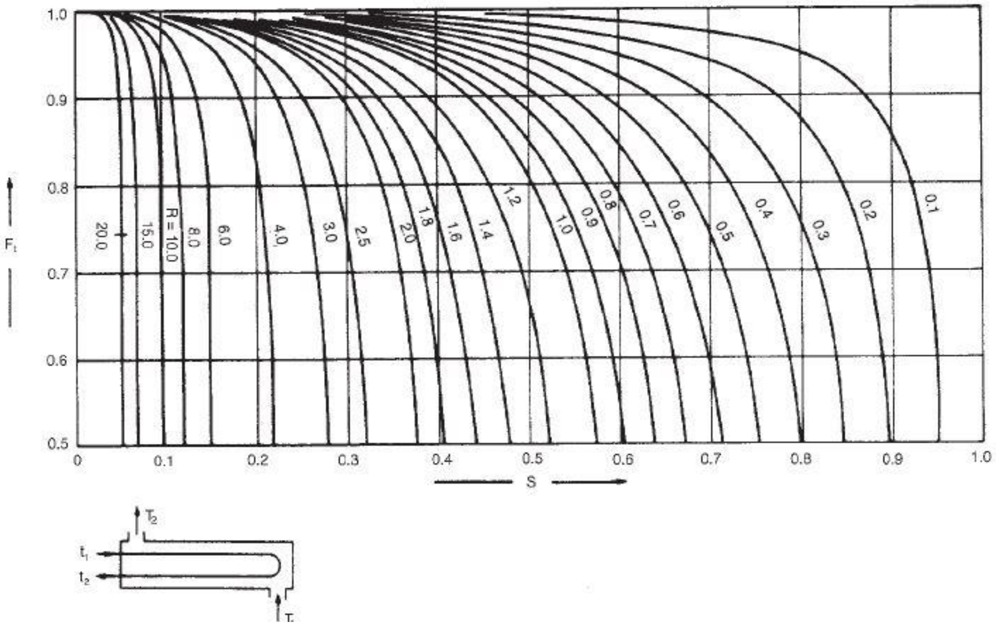
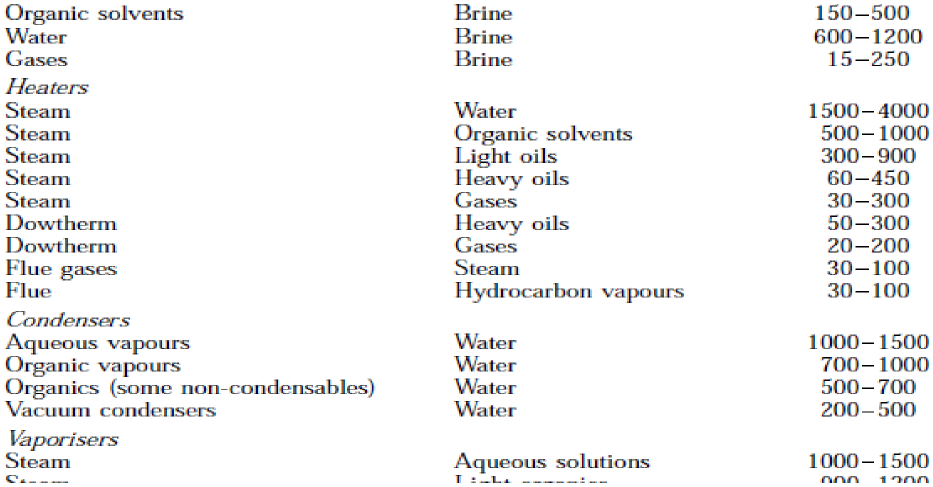


Figure 18 Correction Factor graph



Organic solvents	Brine	150–500
Water	Brine	600–1200
Gases	Brine	15–250
Heaters		
Steam	Water	1500–4000
Steam	Organic solvents	500–1000
Steam	Light oils	300–900
Steam	Heavy oils	60–450
Steam	Gases	30–300
Dowtherm	Heavy oils	50–300
Dowtherm	Gases	20–200
Flue gases	Steam	30–100
Flue	Hydrocarbon vapours	30–100
Condensers		
Aqueous vapours	Water	1000–1500
Organic vapours	Water	700–1000
Organics (some non-condensables)	Water	500–700
Vacuum condensers	Water	200–500
Vaporisers		
Steam	Aqueous solutions	1000–1500

Figure 19 Shell and tube heat exchanger 'U' ranges

U = 300 W/m^2 ^oC from above table

A = $\frac{36542.83}{300 \text{ x } 212.56}$ = **545.45m^2**

0.03m Outer diameter and 0.025m Internal diameter – BWG 17

Length of tube = L = 3.66

Area of tube = π x 3.66x 0.03 = 0.3447 m^2

Number of tubes required = $\frac{545.45}{0.334}$ = **1579 tubes**

Bundle diameter = D_b = d.($\frac{N_S}{K}$)$^{0.25}$ = **0.838 mm** … From graph

Clearance = 0.093

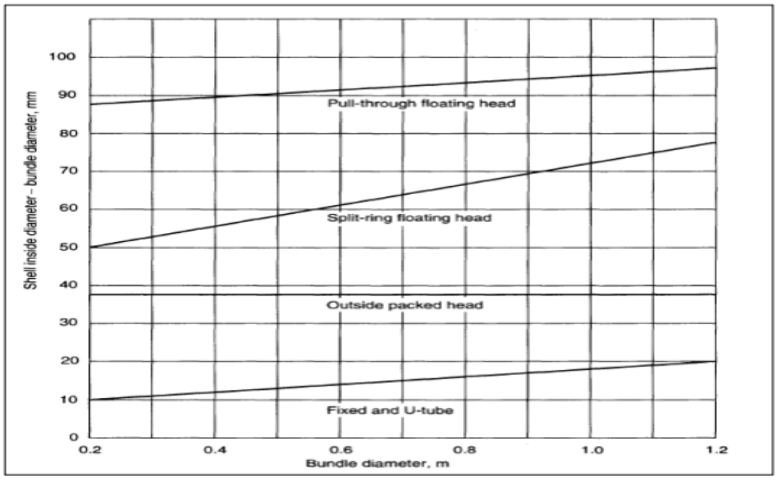
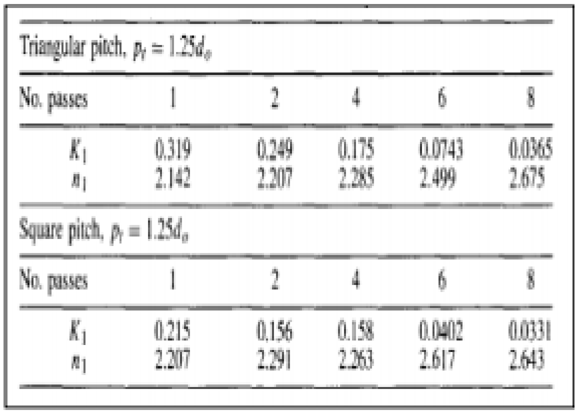


Figure 20 Bundle diameter graph



Triangular pitch, $p_t = 1.25d_o$

No. passes	1	2	4	6	8
K_1	0.319	0.249	0.175	0.0743	0.0365
n_1	2.142	2.207	2.285	2.499	2.675

Square pitch, $p_t = 1.25d_o$

No. passes	1	2	4	6	8
K_1	0.215	0.156	0.158	0.0402	0.0331
n_1	2.207	2.291	2.263	2.617	2.643

Figure 21 Pitch Factor table

Shell diameter = 0.838 +0.093 = 0.9314m

7.4.5 Shell Side Co-efficient*:*

Baffle spacing (l_B) = 0.5 x D_s = 0.4657 m

P_t = 1.25 x d_o = 0.0375m

$A_s = \frac{(P_t - d_0) \times D_s}{P_t}$ change

A_s = **0.18628 m²**

Mass velocity (Ga) = $\frac{\omega}{A_s}$ = 168.09 kg/m²s

$D_e = \frac{1.10}{d_0}(P_t^2 - 0.917 d_0^2)$

D_e = 0.021

Re_b = 3966.26

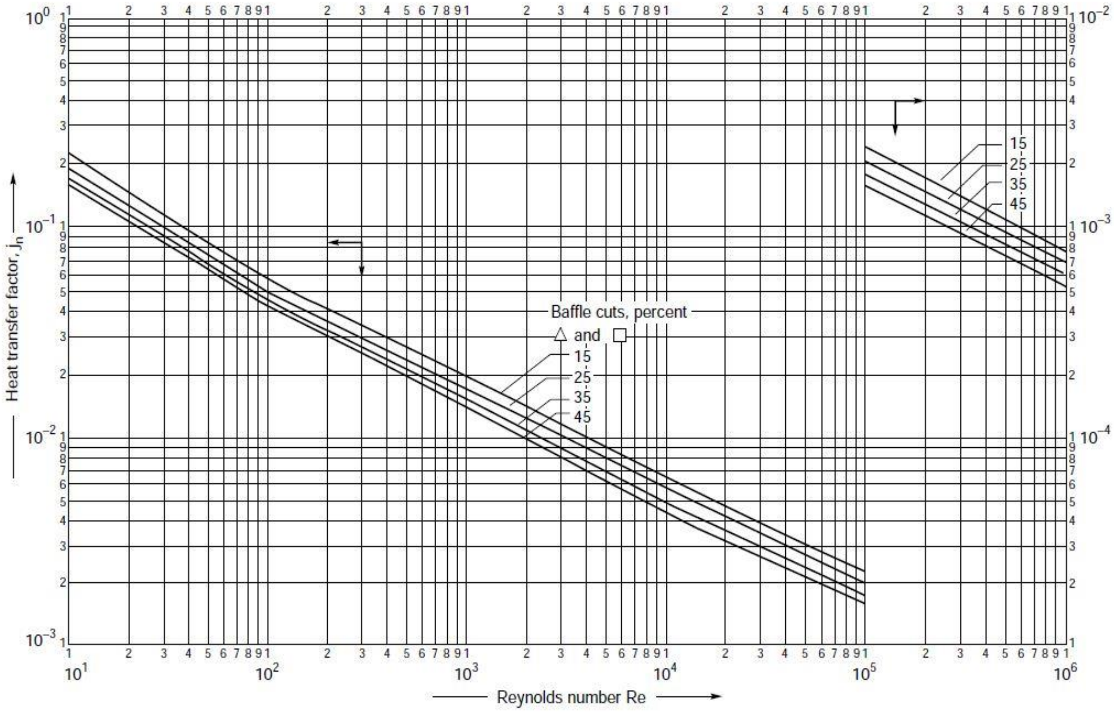


Figure 22 Reynolds number and Jh Graph

From figure, $J_h = 0.007$

$$Pr = \frac{\mu \text{ x Cp}}{K} = 5.572$$

$$\frac{h_o}{\theta_s} = \frac{J_h \text{ x Re x Pr}^{0.33} \text{ x K}_f}{\text{De}} = 1652.303 \text{ W/m}^2.\,^{o}\text{C} \qquad \theta_s = 1$$

$$h_o = \quad = 1652.303 \text{ W/m}^2.\,^{o}\text{C}$$

7.4.6 Tube side co-efficient:

$$\text{Tube cross section area} = \frac{\pi}{4} d_i^2$$

$$= 0.0005 \text{ m}^2$$

$$\text{Tube per pass} = \frac{1579}{2} = 789.5 \text{ tubes}$$

Total flow area = 790 x 0.0005 = 0.395 m^2

Mass velocity (Ga) = $\frac{\omega}{\mathrm{A}} = \frac{252.94}{0.395}$ = 640.38kg/m^{2}s

u = $\frac{640.35}{8.81}$ = 72.68 m/s

Re= $\frac{\mathrm{Di \times Ga}}{\mu}$ = 73773.2995

Pr = $\frac{\mu \times \mathrm{Cp}}{\mathrm{K}} = \frac{2.17 \times 10^{-4} \times 2.23}{0.127}$ = 0.373

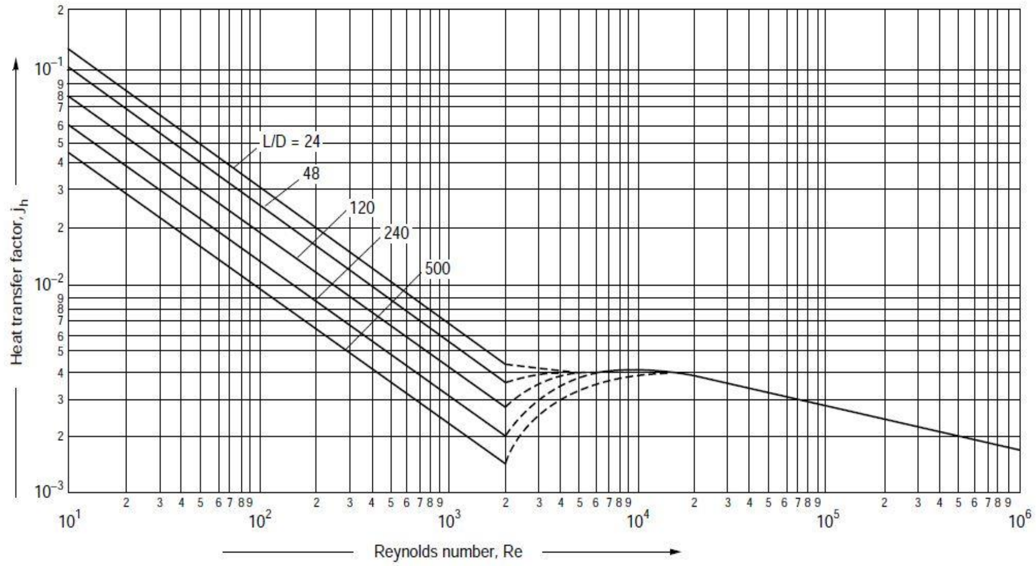


Figure 23 Jh factor graph for tube side

From figure, heat transfer factor (J_h) = 0.003

$$\frac{h_i}{\theta_t} = \frac{J_h \times \mathrm{Re} \times \mathrm{Pr}^{0.33} \times \mathrm{K_f}}{\mathrm{d_i}} = \frac{0.003 \times 111555.2995 \times (0.337)^{0.33} \times 0.1287}{0.025}$$

$\frac{h_i}{\theta_t}$ = 820.9 W/m^2.^{o}C

7.4.7 Mean Wall Temperature θ_t:

$$\left(\frac{\mu}{\mu_w}\right)^{0.14} = 1$$

$$h_i = 820.9 \text{ W/m}^2.^\circ\text{C}$$

7.4.8 Overall coefficient*:*

$$h_{io} = h_i \text{ x } \frac{\text{ID}}{\text{OD}} = h_i \, x \, \frac{0.025}{0.03}$$

$$h_{io} = 684.08 \text{ W/m}^2.\ ^\circ\text{C}$$

$$U_c = \frac{\text{hio x ho}}{\text{hio+ ho}} = 481.44 \text{ W/m}^2.\ ^\circ\text{C}$$

$$\text{For } R_d = 0.003$$

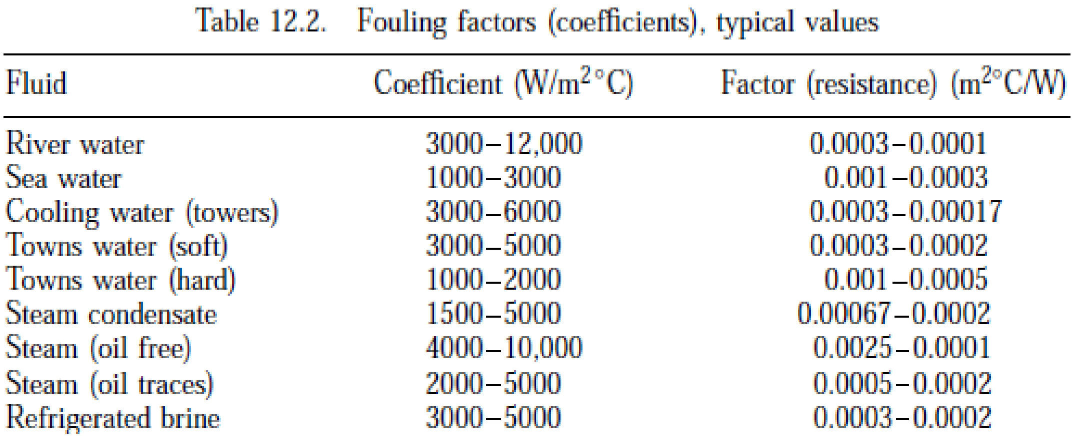


Table 12.2. Fouling factors (coefficients), typical values

Fluid	Coefficient (W/m^2 °C)	Factor (resistance) (m^2°C/W)
River water	3000–12,000	0.0003–0.0001
Sea water	1000–3000	0.001–0.0003
Cooling water (towers)	3000–6000	0.0003–0.00017
Towns water (soft)	3000–5000	0.0003–0.0002
Towns water (hard)	1000–2000	0.001–0.0005
Steam condensate	1500–5000	0.00067–0.0002
Steam (oil free)	4000–10,000	0.0025–0.0001
Steam (oil traces)	2000–5000	0.0005–0.0002
Refrigerated brine	3000–5000	0.0003–0.0002

Table 26 Fouling factor table

$$R_d = \frac{\text{Uc} - \text{UD}}{\text{UD} * \text{Uc}}$$

$$U_D = 196.96 \text{ W/m}^2.\ ^\circ\text{C}$$

Since, in the given range so acceptable design.

7.4.9 Pressure Drop Calculation:

Shell side:

$$\Delta P_s = 8 \text{ x } J_f \text{ x } \left(\frac{Ds}{d_e}\right) \left(\frac{L}{L_B}\right) \frac{\rho\mu^2}{2} (\frac{\mu}{\mu_w})^{-0.14}$$

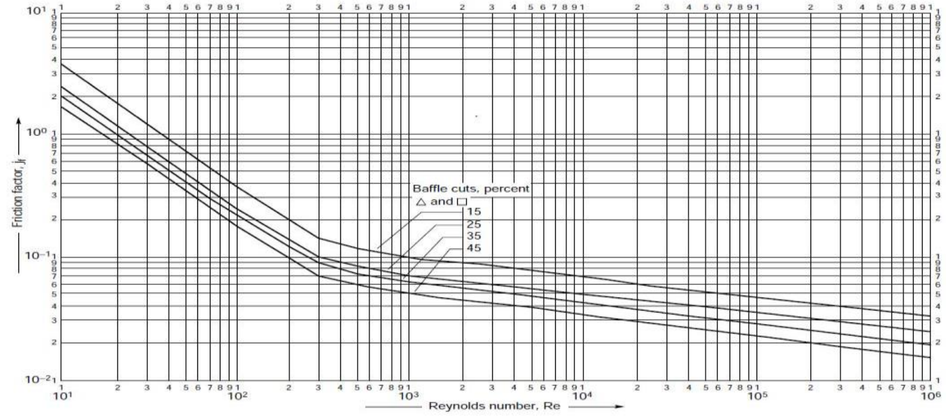


Figure 24 Jf factor graph

From figure, $J_f = 0.051$

$$= 8 \text{ x } 0.051 \text{ x } (\frac{0.9314}{0.021})(\frac{3.66}{0.4657})(\frac{997 \text{ x } 364.5}{997})^2$$

$$\Delta P_s = 2274 \text{ Pa} = 0.32\text{psi}$$

Tube side:

$$\Delta P_t = N_p \left[8 \text{ x } J_h \text{ x } \left(\frac{L}{d_i}\right) (\frac{\mu}{\mu_w})^{-m} + 2.5\right] \text{ x } \frac{\rho {u_t}^2}{2}$$

$$= 2[8 \text{ x } 0.003 \text{ x } (387.72) + 2.5] \text{ x } \frac{8.8 \ (61.21)^2}{2}$$

$$\Delta Pt = 38726.2 \text{ Pa} = 5.6 \text{ psi}$$

7.4.10 Design Summary:

Shell and Tube HX Design	
LMTD	212.6 ^oC
Baffle Spacing	1.6 in
Tubes Passes	2
Shell Passes	1
Pitch	1.25 in (square)
BWG	17
Duty	36545.83 KW
Design Overall Coefficient	196.96 $W/m^2. ^oC$
Pressure Drop Shell Side	0.32psi
Pressure Drop Tube Side	5.60 psi

Table 27 Design Summary of Heat Exchanger

7.5 Membrane Case – 1 Design:

So, the area of the membrane separator unit is calculated by using the polymath version 6.0. The code includes the systems operating temperatures and the pressures on the retentate and the permeate sides of the membrane it also incorporates the pressure drop across the surface of the membrane [14]. Now using the tubular membrane module of a specific length and area and permeability Qo the area of the membrane separator unit was calculated by solving the ordinary differential equations using the Runge-Kutta method.

7.5.1 Code:

```
R = 8.314 [J/gmol-K]


T = 450+273 # reaction temperature [K]

P|ret = 3200 [kPa]

P|per = 992.5 [kPa]

xi_h2 =0.3431

P4 = P|ret*xi_h2 [kPa]


d1 = 4*(10^-3) [m]


th = 6 [µm]

Qo = 6322.7 [m^3-µm/m^2-h-atm^0.5]

E|a = 15630 [J/gmol]

Q = Qo*exp(-E|a/(R*T)) [m^3- µm/m^2-h-atm^0.5]

Kh2 = 0.6*0.58*Q/th*(P|per/(8.314*T)) [kgmol/m^2-h-atm^0.5]

d(Fper_h2) / d(A) = Kh2*1000/(60*60)*((P4/101.325)^0.5-(P|per/101.325)^0.5)
# mass balance equation for H2 in the permeate side

Fper_h2(0) = 0

A(0) = 0

A(f) = 100
```

7.5.2 Results:

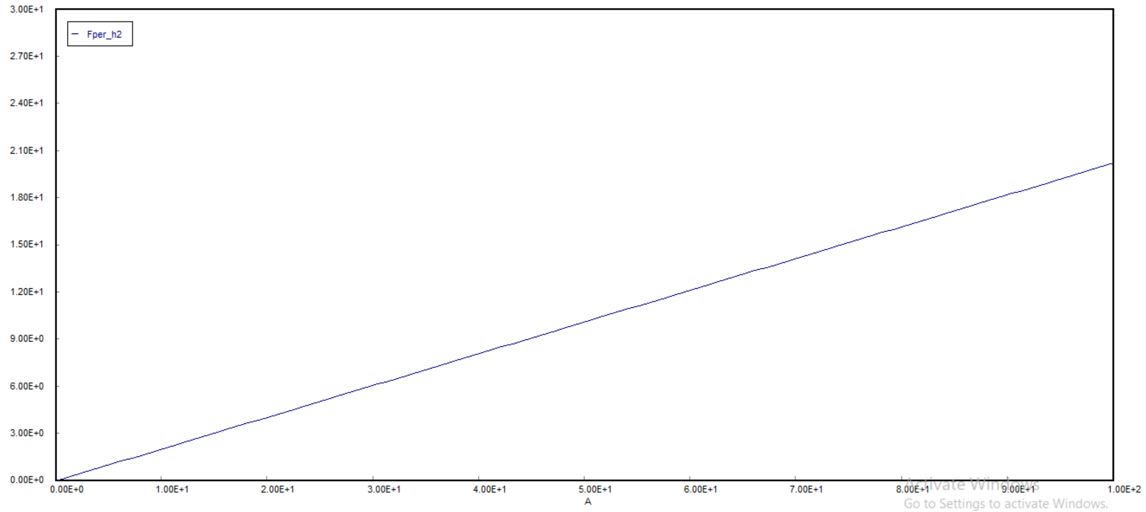


Figure 25 Membrane Case – 1 Plot on Polymath 6.0

Area of Membrane = 18.52046 m^2

One Module Specification:

L= 5 m

D = 4*10^-2 m.

Area of 1 tube= L*D = 2*pi*D/2*L = 0.62 m2

Number of Modules needed= 18.52046/0.62 = 29.8709 = **30 modules in parallel**

7.5.3 Design Summary:

Parameters	Specifications
Area of Membrane	18.52046 m^2
Length of Module	5 m
Diameter of Module	4 x 10^{-2} m
Area of one Tube	0.62 m^2
Number of modules	30

Table 28 Membrane Case – 1, Design Summary,

7.6 HTS, Case – 1 Design:

So, for the design of the HTS we need to calculate the weight of the catalyst and the weight of the catalyst is calculated using the polymath version 6.0. The code incorporates the operating temperature and pressure conditions for the HTS along with the partial pressures of all the reaction gases. It also incorporates the equilibrium constant for the HTS reaction rate equation and the weight of the catalyst is calculated by solving the ordinary differential equation using the Runge-kutta method.

7.6.2 Code:

```
R = 8.314 [J/gmol-K]

T = 450+273 [K]

P|ret = 31.58154 [atm]



P1 = P|ret*(F|ret_co/F|ret_t) [kPa]

P2 = P|ret*(F|ret_h2o/F|ret_t) [kPa]
```

```
P3 = P|ret*(F|ret_co2/F|ret_t) [kPa]

P4 = P|ret*(F|ret_h2/F|ret_t) [kPa]

F|ret_t = F|ret_co+F|ret_h2o+F|ret_co2+F|ret_h2 # wet feed flow rate in the
retentate side [gmol/s]


Keq = exp(4577.8/T-4.33)

Rco = (10^2.84)*exp(-111000/R/T)*P1*P3^(-0.36)*P4^(-0.09)*(1-
(1/Keq)*(P3*P4/P1/P2)) [gmol/kg-s]

r_co = (-1)*Rco # reaction rate of CO [gmol/m^3-s]

r_h2o = (-1)*Rco [gmol/m^3-s]

r_co2 = (1)*Rco [gmol/m^3-s]

r_h2 = (1)*Rco [gmol/m^3-s]


d(F|ret_co) / d(W) = r_co # mass balance equation for CO in the retentate side

F|ret_co(0) = 0.1341

d(F|ret_h2o) / d(W) = r_h2o

F|ret_h2o(0) = 0.7863

d(F|ret_co2) / d(W) = r_co2

F|ret_co2(0) = 0.1089

d(F|ret_h2) / d(W) = r_h2

F|ret_h2(0) = 0.4070

W(0)=0

W(f)= 100000
```

7.6.3 Results:

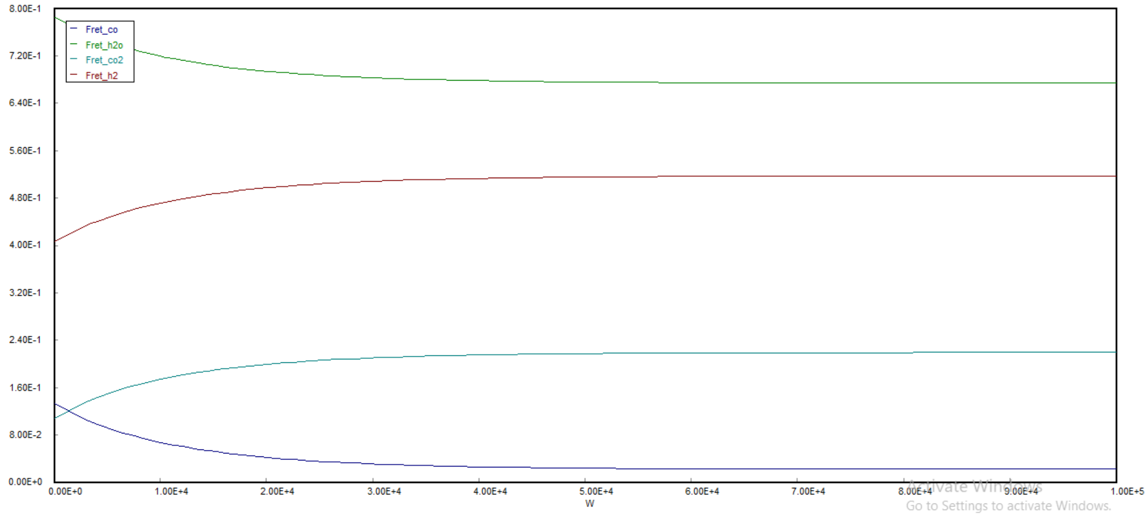


Figure 26 HTS, Case – 1 Flow Rate VS Weight of Catalyst Plot on Polymath

Weight of Catalyst = 99240 Kg

Conversion = 82 %

7.6.4 Volume of Catalyst:

Bulk density of catalyst: 1050kg/m^3

Volume of catalyst = Weight of catalyst/ Bulk density of catalyst

Volume of catalyst = 99240/1050

Volume of catalyst = 94.51 m^3

7.6.5 Volume of Reactor:

Voidage = 0.044

$E = (V_b - V_c)/V_b$

Catalyst bed Volume = V_b = 98.86 m^3

29% clearance gives the volume of reactor,

$Vr = 1.29*V_b$

Volume of reactor = Vr= 127.53 m^3

7.6.6 Height of Reactor:

Height of reactor = Vr/ π*D^2/4

Take, D = 4 m

H = 10.1485 m

7.6.7 Space Velocity:

Space Velocity = Volumetric Feed Flow rate/ Volume of reactor

Space Velocity = 11441.4092/3600*127.53

Space Velocity = 0.024/s

7.6.8 Pressure Drop:

Pressure Drop = Delta P = $(150 * ((1 - e)^\wedge 2) * G * L * u)/((Dp^\wedge 2) * rho * (e^\wedge 3)) + (1.75 * G^\wedge 2 * L * (1 - e))/(rho * Dp * (e^\wedge 3))$

Where e is voidage, G is mass velocity, L is length of reactor, Dp is particle diameter and rho and u are fluid density and viscosity respectively. Finding all these vales gave us the pressure drop by Ergun's equation as stated above.

Pressure Drop = 282.20 kPa

7.6.9 Design Summary:

Parameters	**Specification**
Conversion	**82%**
Weight of Catalyst	**99240 Kg**

Bulk density of catalyst	**1050kg/m^3**
Volume of catalyst	**94.51 m^3**
Voidage	**0.044**
Catalyst Bed Volume	**98.86 m^3**
Volume of reactor	**127.53^3**
Pressure Drop	**282.20 kPa**
Height	**10.1485 m**
Space velocity	**0.024 sec^{-1}**

Table 29 HTS Case – 1 Design Summary

7.7 Membrane – 1, Case - 2 Design:

The area of the membrane separator unit is calculated by using the polymath version 6.0. The code includes the systems operating temperatures and the pressures on the retentate and the permeate sides of the membrane it also incorporates the pressure drop across the surface of the membrane. Now using the tubular membrane module of a specific length and area and permeability Qo the area of the membrane separator unit was calculated by solving the ordinary differential equations using the Runge-Kutta method.

7.7.1 Code:

```
R = 8.314


T = 450+273 K

P|ret = 3200 [kPa]

P|per =  920.3 [kPa]
```

```
xi_h2 = 0.29

P4 = P|ret*xi_h2


d1 = 4*(10^-3) [m]

th = 6 [µm]

Qo = 6322.7 [m^3-µm/m^2-h-atm^0.5]

E|a = 15630 [J/gmol]

Q = Qo*exp(-E|a/(R*T)) [m^3- µm/m^2-h-atm^0.5]

Kh2 = 0.6*0.58*Q/th*(P|per/(8.314*T)) [kgmol/m^2-h-atm^0.5]

d(Fper_h2) / d(A) = Kh2*1000/(60*60)*((P4/101.325)^0.5-(P|per/101.325)^0.5)
# mass balance equation for H2 in the permeate side

Fper_h2(0) = 0

A(0) = 0

A(f) = 100
```

7.7.2 Results:

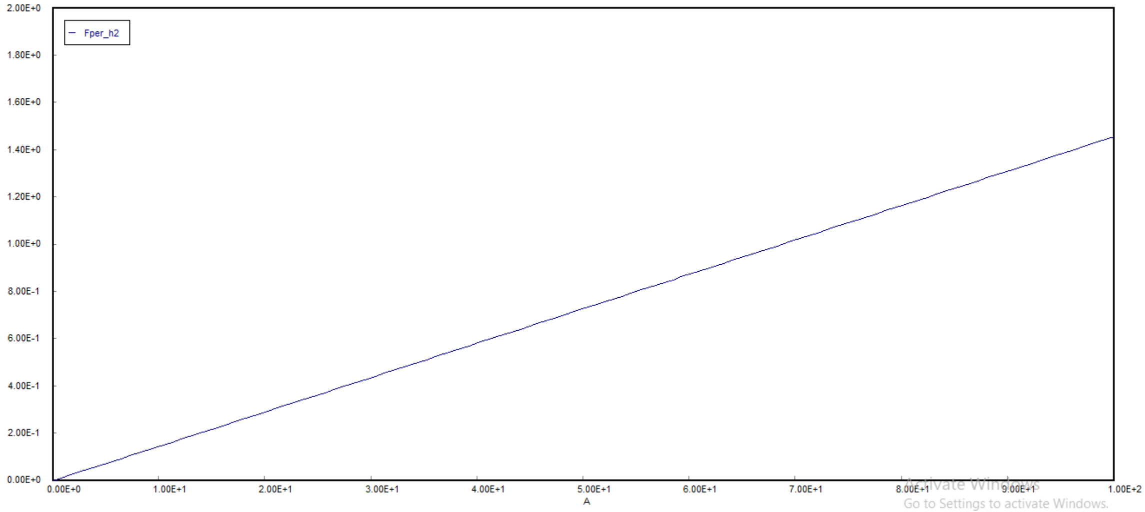


Figure 27 Flow Rate VS Area of Membrane using Polymath

Area of Membrane = 14.41971 m2

One Module Specification:

L= 5 m

D = 4*10^-2 m.

Area of 1 tube= L*D = 2*pi*D/2*L = 0.62 m2

Number of Modules needed= 14.41971/0.62 = 23.24 = **24 modules in parallel**

7.7.3 Design Summary:

Parameters	Specifications
Area of Membrane	14.41971 m^2
Length of Module	5 m
Diameter of Module	4 x 10^{-2} m
Area of one Tube	0.62 m^2
Number of modules	24

Table 30 Design Summary of Membrane – 1, Case – 2

7.8 HTS – 1, Case – 2 Design:

So, for the design of the HTS we need to calculate the weight of the catalyst and the weight of the catalyst is calculated using the polymath version 6.0. The code incorporates the operating temperature and pressure conditions for the HTS along with the partial pressures of all the reaction gases [8]. It also incorporates the equilibrium constant for the HTS reaction rate equation and the weight of the catalyst is calculated by solving the ordinary differential equation using the Runge-kutta method.

7.8.1 Code:

```
R = 8.314 # [m^3-kPa/kgmol-K] or [J/gmol-K]


T = 450+273 [K]

P|ret = 31.58154 [atm]
```

```
P1 = P|ret*(F|ret_co/F|ret_t) [kPa]
P2 = P|ret*(F|ret_h2o/F|ret_t) [kPa]
P3 = P|ret*(F|ret_co2/F|ret_t) [kPa]
P4 = P|ret*(F|ret_h2/F|ret_t) [kPa]
F|ret_t = F|ret_co+F|ret_h2o+F|ret_co2+F|ret_h2

Keq = exp(4577.8/T-4.33)
Rco=(10^2.84)*exp(-111000/R/T)*P1*P3^(-0.36)*P4^(-0.09)*(1-(1/Keq)*(P3*P4/P1/P2))  [gmol/kg-s]
r_co = (-1)*Rco [gmol/m^3-s]
r_h2o = (-1)*Rco [gmol/m^3-s]
r_co2 = (1)*Rco [gmol/m^3-s]
r_h2 = (1)*Rco [gmol/m^3-s]

d(F|ret_co) / d(W) = r_co
F|ret_co(0) = 0.1156
d(F|ret_h2o) / d(W) = r_h2o
F|ret_h2o(0) = 1.0413
d(F|ret_co2) / d(W) = r_co2
F|ret_co2(0) = 0.1274
d(F|ret_h2) / d(W) = r_h2
F|ret_h2(0) = 0.4583
```

W(0)=0

W(f)= 55000

7.8.2 Results:

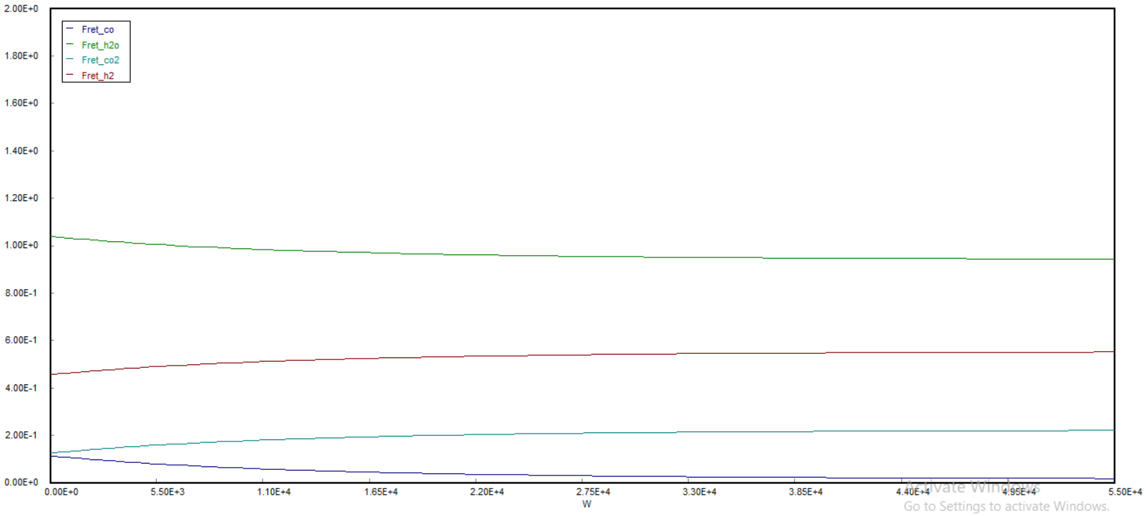


Figure 28 HTS – 1, Case – 2, Flow Rate VS Weight of Catalyst using Polymath

Weight of Catalyst = W = 54269 kg

7.8.2.1 Volume of Catalyst:

Bulk density of catalyst: 1050kg/m^3

Volume of catalyst = Weight of catalyst/ Bulk density of catalyst

Volume of catalyst = 54269/1050

Volume of catalyst = 51.68 m^3

7.8.2.2 Volume of Reactor:

Voidage = 0.044

$E = (V_b - V_c)/V_b$

Catalyst bed Bolume = V_b = 54.0585 m^3

29% clearance gives the volume of reactor,

Vr = 1.29 × Vb

Volume of reactor = Vr= 69.735 m^3

7.8.2.3 Height of Reactor:

Height of reactor = Vr/ π*D^2/4

Take, D = 3 m

Height of reactor =9.865 m

7.8.2.4 Space Velocity:

Space Velocity = Volumetric Feed Flow rate/ Volume of reactor

Space Velocity = 13904.9030841645/3600 × 69.735

Space Velocity = 0.0553/s

7.8.2.5 Pressure Drop:

Pressure Drop = Delta P = $(150 * ((1 - e)^\wedge 2) * G * L * u)/((Dp^\wedge 2) * rho * (e^\wedge 3)) + (1.75 * G^\wedge 2 * L * (1 - e))/(rho * Dp * (e^\wedge 3))$

Where e is voidage, G is mass velocity, L is length of reactor, Dp is particle diameter and rho and u are fluid density and viscosity respectively. Finding all these vales gave us the pressure drop by Ergun's equation as stated above.

Pressure Drop = 274.41 kpa

7.8.3 Design Summary:

Parameters	Specification
Weight of Catalyst	54269 kg
Bulk density of catalyst	1050kg/m^3
Volume of catalyst	51.68 m^3
Voidage	0.044
Catalyst Bed Volume	50.05 m^3
Volume of reactor	69.73 m^3
Pressure Drop	274.41 kpa
Height	9.865 m

Table 31 HT2 – 1, Case – 2 Design Summary

7.9 Membrane – 2. Case – 2 Design:

The area of the membrane separator unit is calculated by using the polymath version 6.0. The code includes the systems operating temperatures and the pressures on the retentate and the permeate sides of the membrane it also incorporates the pressure drop across the surface of the membrane. Now using the tubular membrane module of a specific length and area and permeability Qo the area of the membrane separator unit was calculated by solving the ordinary differential equations using the Runge-Kutta method.

7.9.1 Code:

```
R = 8.314 [J/gmol-K]


T = 450+273 [K]

P|ret = 3200 [kPa]
```

```
P|per = 826 [kPa]



xi_h2 = 0.26

P4 = P|ret*xi_h2 [kPa]


d1 = 4*(10^-3) [m]

th = 6 [µm]

Qo = 6322.7 [m^3-µm/m^2-h-atm^0.5]

E|a = 15630 [ J/gmol]

Q = Qo*exp(-Ea/(R*T)) [m^3- µm/m^2-h-atm^0.5]

Kh2 = 0.6*0.58*Q/th*(P|per/(8.314*T)) [kgmol/m^2-h-atm^0.5]

d(Fper_h2) / d(A) = Kh2*1000/(60*60)*((P4/101.325)^0.5-(P|per/101.325)^0.5)
#


Fper_h2(0) = 0

A(0) = 0

A(f) = 100
```

7.9.2 Results:

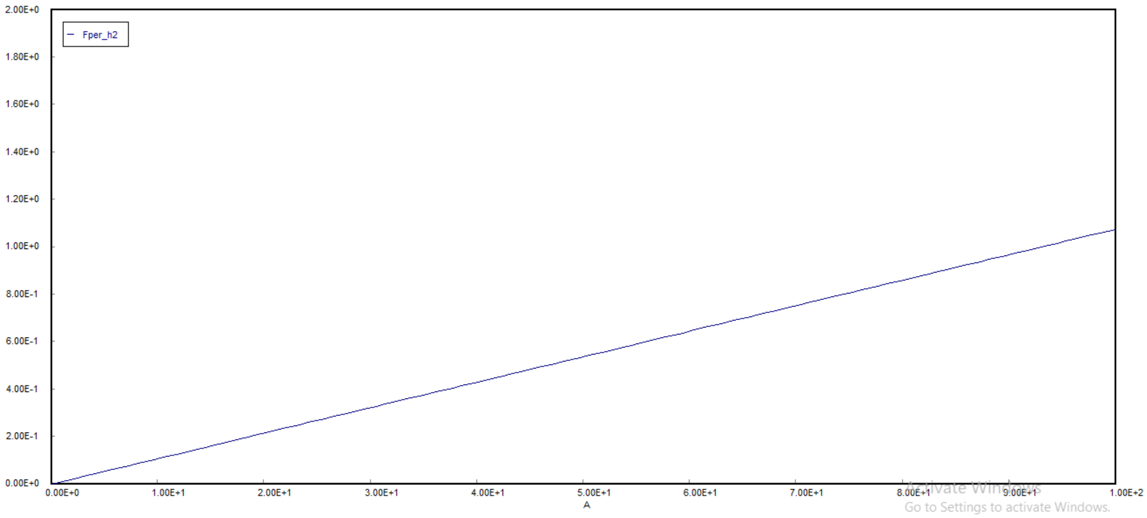


Figure 29 Flow Rate VS Membrane – 2, Case – 2 Area with Polymath

Area of Membrane = 21.72046 m2

One Module Specification:

L= 5 m

D = 4*10^-2 m.

Area of 1 tube= L*D = 2*pi*D/2*L = 0.62 m2

Number of Modules needed= 21.72046/0.62 = 16.82 = 35 modules in parallel

7.9.3 Design Summary:

Parameters	Specifications
Area of Membrane	21.72046 m^2
Length of Module	5 m
Diameter of Module	4×10^{-2} m
Area of one Tube	0.62 m^2
Number of modules	35

Table 32 Membrane – 2, Case – 2 Design Summary

7.10 HTS – 2, Case – 2 Design:

So, for the design of the HTS we need to calculate the weight of the catalyst and the weight of the catalyst is calculated using the polymath version 6.0. The code incorporates the operating temperature and pressure conditions for the HTS along with the partial pressures of all the reaction gases [9]. It also incorporates the equilibrium constant for the HTS reaction rate equation and the weight of the catalyst is calculated by solving the ordinary differential equation using the Runge-Kutta method.

7.10.1 Code:

```
R = 8.314 [J/gmol-K]


T = 450+273 [K]

P|ret = 31.58154 [atm]
```

```
P1 = P|ret*(F|ret_co/F|ret_t)
P2 = P|ret*(F|ret_h2o/F|ret_t) [kPa]
P3 = P|ret*(F|ret_co2/F|ret_t) [kPa]
P4 = P|ret*(F|ret_h2/F|ret_t) [kPa]
F|ret_t = F|ret_co+F|ret_h2o+F|ret_co2+F|ret_h2 [gmol/s]

Keq = exp(4577.8/T-4.33)
Rco = (10^2.84)*exp(-111000/R/T)*P1*P3^(-0.36)*P4^(-0.09)*(1-(1/Keq)*(P3*P4/P1/P2)) [gmol/kg-s]
r_co = (-1)*Rco [gmol/m^3-s]
r_h2o = (-1)*Rco [gmol/m^3-s]
r_co2 = (1)*Rco [gmol/m^3-s]
r_h2 = (1)*Rco [gmol/m^3-s]

d(F|ret_co) / d(W) = r_co
F|ret_co(0) = 0.01806
d(F|ret_h2o) / d(W) = r_h2o
F|ret_h2o(0) = 0.9437
d(F|ret_co2) / d(W) = r_co2
F|ret_co2(0) = 0.225
d(F|ret_h2) / d(W) = r_h2
F|ret_h2(0) = 0.3198
W(0)=0
```

W(f)= 27000

7.10.2 Results:

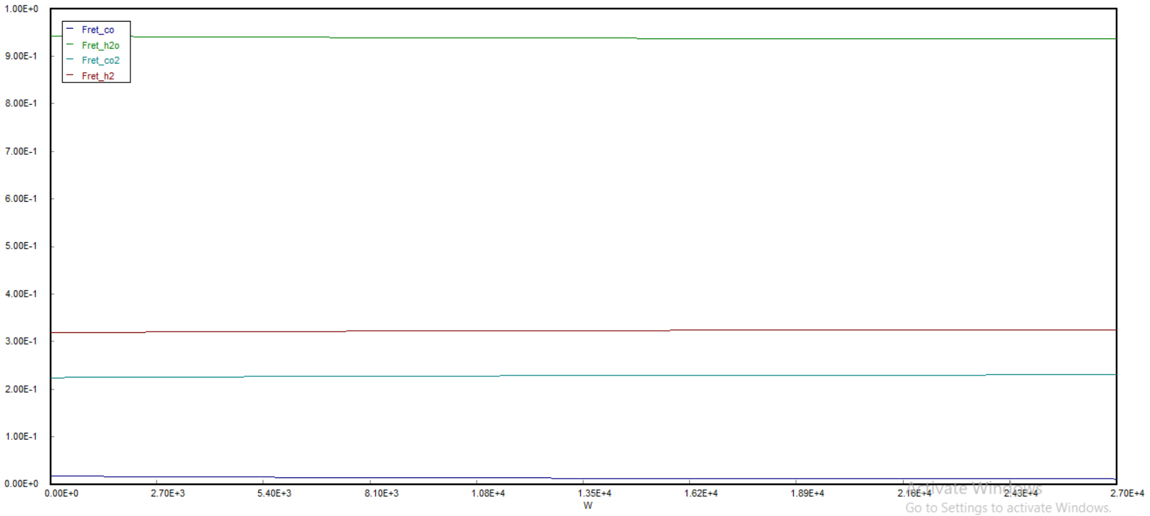


Figure 30 HTS – 2, Case – 2 Flow Rate VS Catalyst Weight

7.10.2.1 Weight of Catalyst:

Weight of Catalyst = 26390 kg

Bulk density of catalyst: 1050kg/m^3

7.10.2.2 Volume of Catalyst:

Volume of catalyst = Weight of catalyst/ Bulk density of catalyst

Volume of catalyst = 26390/1050

Volume of catalyst = 25.13 m^3

7.10.2.3 Volume of Reactor:

Voidage = 0.044

$E = (V_b - V_c)/V_b$

Catalyst bed Bolume = V_b = 26.29 m^3

29% clearance gives the volume of reactor,

Vr = 1.29*Vb

Volume of reactor = Vr= 33.91 m^3

7.10.2.4 Height of Reactor:

Height of reactor = Vr/ π*D^2/4

Take, D = 2.5 m

H = 6.90 m

7.10.2.5 Space Velocity:

Space Velocity = Volumetric Feed Flow rate/ Volume of reactor

Space Velocity = 13127.9952917201/3600*69.735

Space Velocity = 0.107/s

7.10.2.6 Pressure Drop:

Pressure Drop = Delta P = $(150 * ((1-e)^{\wedge}2) * G * L * u)/((Dp^{\wedge}2) * rho * (e^{\wedge}3)) + (1.75 * G^{\wedge}2 * L * (1-e))/(rho * Dp * (e^{\wedge}3))$

Where e is voidage, G is mass velocity, L is length of reactor, Dp is particle diameter and rho and u are fluid density and viscosity respectively. Finding all these vales gave us the pressure drop by Ergun's equation as stated above.

Pressure Drop = 192.03 kPa

7.10.3 Design Summary:

Parameters	Specification
Weight of Catalyst	26390 kg
Bulk density of catalyst	1050kg/m^3
Volume of catalyst	25.13 m^3
Voidage	0.044
Catalyst Bed Volume	26.29 m^3
Volume of reactor	33.91 m^3
Pressure Drop	192.03 kPa
Height	6.90 m

Table 33 Design Summary of HTS – 2, Case – 2

7.11 Membrane Reactor Design:

The area of the membrane and the weight of the catalyst needed are calculated using the polymath version 6.0. The code includes the systems operating temperatures and the pressures on the retentate and the permeate sides of the membrane it also incorporates the pressure drop across the surface of the membrane and the rate equation for the water gas shift reaction[14,8,9,7]. Now using the tubular membrane module of a specific length and permeability Qo the area of the membrane and the weight of the Catalyst used in the HTS is calculated by solving the ordinary differential equations using the Runge-Kutta method.

7.11.1 Code:

```
R = 8.314 [J/gmol-K]


T = 380+273 [K]
```

```
P|ret =34.47 [kPa]
P|per = 1.00 [kPa]

P1 = P|ret*(F|ret_co/F|ret_t) [kPa]
P2 = P|ret*(F|ret_h2o/F|ret_t) [kPa]
P3 = P|ret*(F|ret_co2/F|ret_t) [kPa]
P4 = P|ret*(F|ret_h2/F|ret_t) [kPa]
F|ret_t = F|ret_co+F|ret_h2o+F|ret_co2+F|ret_h2 # wet feed flow rate in the retentate side [gmol/s]
# CMR dimensions
d1 = 2*0.025 # outer diameter of the membrane [m]
d2 = 6*0.025 # inner diameter of the shell casing [m]
r1 = d1/2 [m]
r2 = d2/2 [m]
#Am = 3.14*d1*L # membrane surface [m^2] # L is the length of the membrane
Aa = 3.14*(r2^2-r1^2) # annular cross-section area [m^2]

# Catalyst specifications
d|cat = 1070 [kg/m^3]
theta = 0.5
epsi = 0.2

th = 6 [µm]
```

```
Qo = 6322.7 [m^3-µm/m^2-h-atm^0.5]
E|a = 15630 [ J/gmol]
Q = Qo*exp(-Ea/(R*T)) # permeability [m^3- µm/m^2-h-atm^0.5]
Kh2 = 0.6*0.58*Q/th*(P|per/(8.314*T)) [kgmol/m^2-h-atm^0.5]

Keq = exp(4577.8/T-4.33)
Rco = ((1-epsi)*d|cat*(1-theta)*1000)*(10^2.845)*exp(-111000/R/T)*P1*P3^(-0.36)*P4^(-0.09)*(1-(1/Keq)*(P3*P4/P1/P2)) [gmol/m^3-s]
r_co = (-1)*Rco [gmol/m^3-s]
r_h2o = (-1)*Rco [gmol/m^3-s]
r_co2 = (1)*Rco [gmol/m^3-s]
r_h2 = (1)*Rco [gmol/m^3-s]

d(F|ret_co) / d(W) = r_co/(d|cat*1000) # mass balance equation for CO in the retentate side
F|ret_co(0) = 0.1347
d(F|ret_h2o) / d(W) = r_h2o/(d|cat*1000)
F|ret_h2o(0) = 0.7795
d(F|ret_co2) / d(W) = r_co2/(d|cat*1000)
F|ret_co2(0) = 0.1083
d(F|ret_h2) / d(W) = r_h2/(d|cat*1000) - Kh2*1000/(60*60)*((P4/101.325)^0.5-(P|per/101.325)^0.5)/(d|cat*1000)
F|ret_h2(0) = 0.6745
```

```
d(Fper_h2) / d(W) = (Kh2*1000/(60*60)*((P4/101.325)^0.5-(P|per/101.325)^0.5))/(d|cat*1000)

Fper_h2(0) = 0

W(0) = 0

W(f) = 99000000
```

7.11.2 Results:

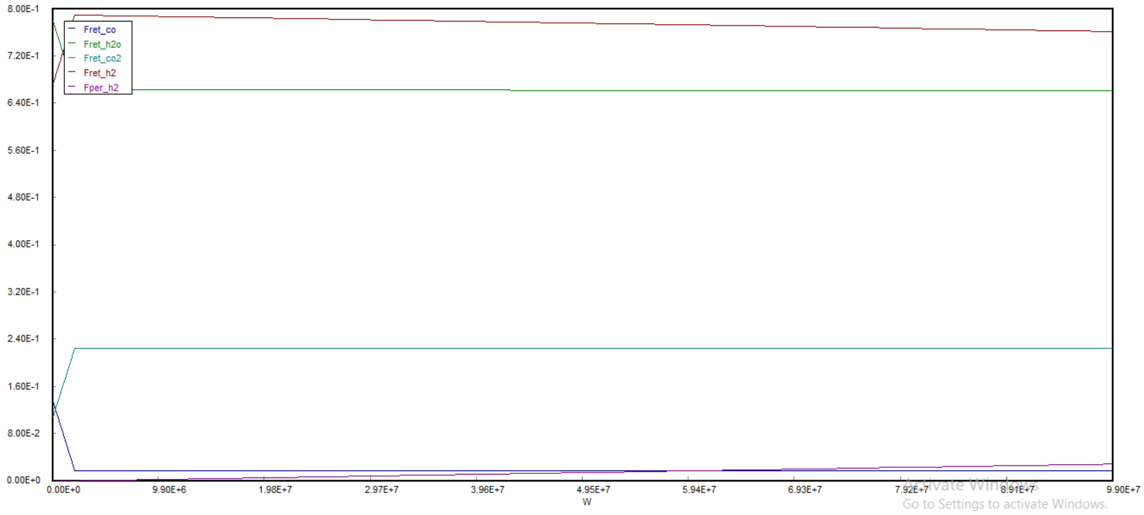


Figure 31 Membrane Reactor, Case – 3 Flow Rate VS Catalyst Weight in Polymath

7.11.2.1 Weight of Catalyst:

Weight of Catalyst = 98560 kg

Conversion = 87 %

7.11.2.2 Number of Tubes:

Weight in Single Tube = 839.95

Number of Tubes = 98560/839.9= 117.34 = **118 tubes**

7.11.2.3 Membrane Area:

Membrane Area = 118*pi*(2*0.025)^2/4 = **92.67 m^2**

7.11.2.3 Pressure Drop:

Pressure Drop = Delta P = $(150 * ((1-e)^\wedge 2) * G * L * u)/((Dp^\wedge 2) * rho * (e^\wedge 3)) + (1.75 * G^\wedge 2 * L * (1-e))/(rho * Dp * (e^\wedge 3))$

Where e is voidage, G is mass velocity, L is length of reactor, Dp is particle diameter and rho and u are fluid density and viscosity respectively. Finding all these vales gave us the pressure drop by Ergun's equation as stated above [10].

Pressure Drop = 139.153 kpa

7.11.3 Design Summary:

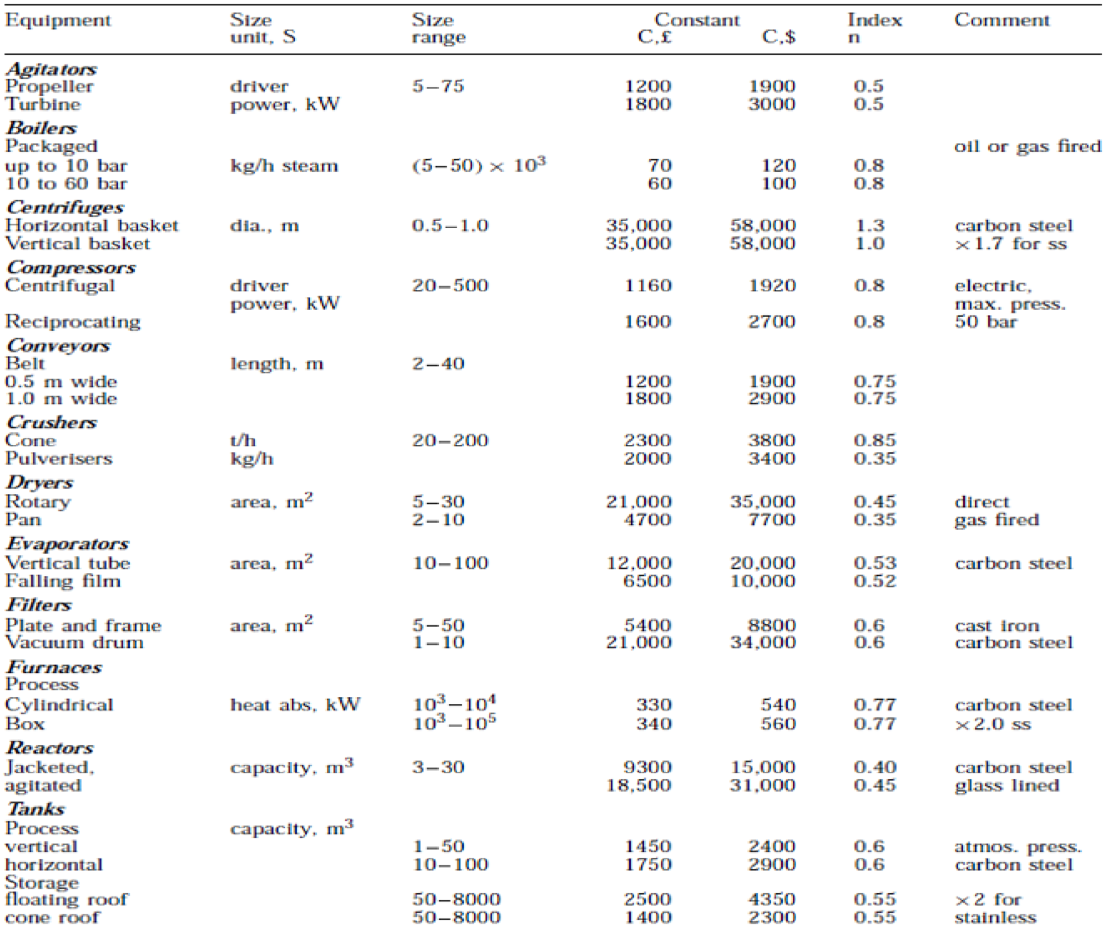
Parameters	Specification
Conversion	87%
Weight of Catalyst	98560 kg
Weight in Single Tube	839.95kg
Number of Tubes	118
Voidage	0.044
Membrane Area	92.67 m^2
Pressure Drop	139.153 kpa

Table 34 Design Summary of Membrane Reactor

CHAPTER 8

COSTING, INSTRUMENTATION AND HAZOP ANALYSIS

Costing is very important because after efficiency it is the economics that matter in designing a plant. The design Engineer must be able to make quick, fast costing estimates to decide between different processes and to choose between them. Chemical plants are made to build profits, so it is very important to do cost analysis before any plant can be placed. For calculating cost of reactors in plant following table:



Equipment	Size unit, S	Size range	Constant		Index n	Comment
			C,£	C,$		
Agitators						
Propeller	driver	5–75	1200	1900	0.5	
Turbine	power, kW		1800	3000	0.5	
Boilers						
Packaged						oil or gas fired
up to 10 bar	kg/h steam	$(5-50)\times10^3$	70	120	0.8	
10 to 60 bar			60	100	0.8	
Centrifuges						
Horizontal basket	dia., m	0.5–1.0	35,000	58,000	1.3	carbon steel
Vertical basket			35,000	58,000	1.0	×1.7 for ss
Compressors						
Centrifugal	driver power, kW	20–500	1160	1920	0.8	electric, max. press.
Reciprocating			1600	2700	0.8	50 bar
Conveyors						
Belt	length, m	2–40				
0.5 m wide			1200	1900	0.75	
1.0 m wide			1800	2900	0.75	
Crushers						
Cone	t/h	20–200	2300	3800	0.85	
Pulverisers	kg/h		2000	3400	0.35	
Dryers						
Rotary	area, m^2	5–30	21,000	35,000	0.45	direct
Pan		2–10	4700	7700	0.35	gas fired
Evaporators						
Vertical tube	area, m^2	10–100	12,000	20,000	0.53	carbon steel
Falling film			6500	10,000	0.52	
Filters						
Plate and frame	area, m^2	5–50	5400	8800	0.6	cast iron
Vacuum drum		1–10	21,000	34,000	0.6	carbon steel
Furnaces						
Process						
Cylindrical	heat abs, kW	10^3-10^4	330	540	0.77	carbon steel
Box		10^3-10^5	340	560	0.77	×2.0 ss
Reactors						
Jacketed,	capacity, m^3	3–30	9300	15,000	0.40	carbon steel
agitated			18,500	31,000	0.45	glass lined
Tanks						
Process	capacity, m^3					
vertical		1–50	1450	2400	0.6	atmos. press.
horizontal		10–100	1750	2900	0.6	carbon steel
Storage						
floating roof		50–8000	2500	4350	0.55	×2 for
cone roof		50–8000	1400	2300	0.55	stainless

Table 35 Costing Index table

8.1 Purchase Cost of Reforming Reactors:

8.1.1 Primary Reformer:

Q_{avg}= 65800lcal/hr

Qavg= 7652241W/m^2

C = 540 n = 0.77 From Table

Ce= CQ^n

Ce = (540) $(765241)^{0.77}$

Ce= $ 3111128

Cost of Catalyst = $ 450/ft^2

Vc = 20.133 m^3

Total Cost of catalyst = $97520.2

Total Cost of primary reformer = $ 3111128 + $ 97520.2

Total cost of Primary Reformer = $ 3208648.2

8.1.2 Secondary Reformer:

Weight of catalyst =21870.8 kg

Vc = 20.829 m^3

V_R = 33.33 m^3

Cost of catalyst = $ 400/ft^3

Total cost of catalyst = Cc x Vc

Total cost of catalyst = $ 89931.29

C = 540; n = 0.77;Q = 1.19x10^5 kW

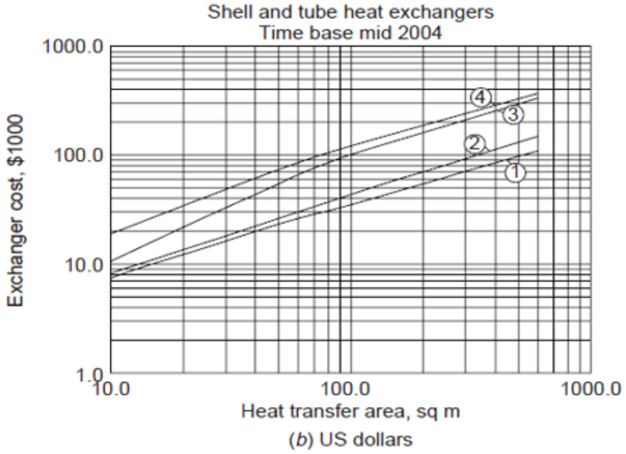
Ce = CQ^n

Ce = $ 4370840

Total cost of Secondary Reformer = $ 4460771.29

8.2 Purchase Cost of Heat Exchanger:

For costing of Heat Exchangers, the first step is to know the area of heat exchanger. By knowing the area, material of shell and tubes, pressure of heat exchanger and type of head of heat exchanger we can calculate the cost of heat exchanger in 2004 by using the following graphs.



Materials	
Shell	Tubes
① Carbon steel	Carbon steel
② C.S.	Brass
③ C.S.	Stainless steel
④ S.S.	S.S.

Pressure factors	
1–10 bar	× 1.0
10–20	× 1.1
20–30	× 1.25
30–50	× 1.3
50–70	× 1.5

Type factors	
Floating head	× 1.0
Fixed tube sheet	× 0.8
U tube	× 0.85
Kettle	× 1.3

Figure 33 index graph(A) for costing of exchangers

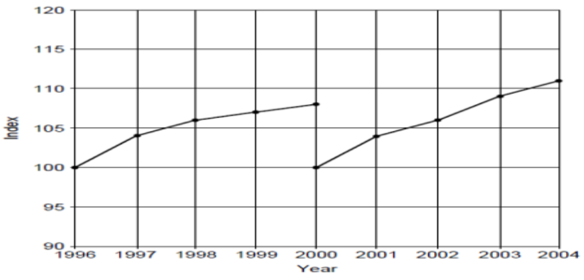


Figure 32 Cost indexing graph (B)

These graphs. We need calculate cost of heat exchanger for the 2020. For this purpose, graph (B) is used.

By using this formula, we can calculate the cost of heat exchanger in 2021.

$$Cost\ in\ 2021\ =\ (Cost\ in\ 2004)(Index\ in\ 2021)/(Index\ in\ 2004)$$

8.2.1 Cost Calculations:

Area = 545m^2

Cost in 2004 = (Bare cost from figure) x (Pres. Factor) x (T.F)

Carbon steel shell and carbon steel tubes From Figure

Cost in 2004= (105000) x (1.3) x (1) = $136500

Index in 2004 = 111 From Figure

Index in 2021 = 170

$$\boldsymbol{Cost\ in\ 2021\ =\ (Cost\ in\ 2004)(Index\ in\ 2021)/(Index\ in\ 2004)}$$

Cost in 2021 = $ 209100

8.3 Purchase Cost Membrane – 1, Case – 1:

Area = 18.52046 m^2

$$Area\ =\frac{18.52046\ m^2 \times 10.764\ ft^2}{1\ m^2}=199.35\ \ ft^2$$

Cost of the Palladium Membrane (2021) = $ 2000 $per\ \ ft^2$

$Cost$ = $ 2000 $per\ \ ft^2 \times 199.35\ ft^2$

Cost = $ 398708.4629

8.4 Purchase Cost High Temperature Shift:

Weight of catalyst = 99240 Kg

Cost of catalyst = $ 21/kg

Total cost of catalyst = $ 2084040

Vc = 94.51 m^3

Ce = CQ^n

Q = Vr = 127.52 m^3

C = 31000   n = 0.40 From Table

Total cost of HTS = $ 2299612.23

Purchase Cost of Equipment = $ **10776840. 18**

8.5 Total Cost Method:

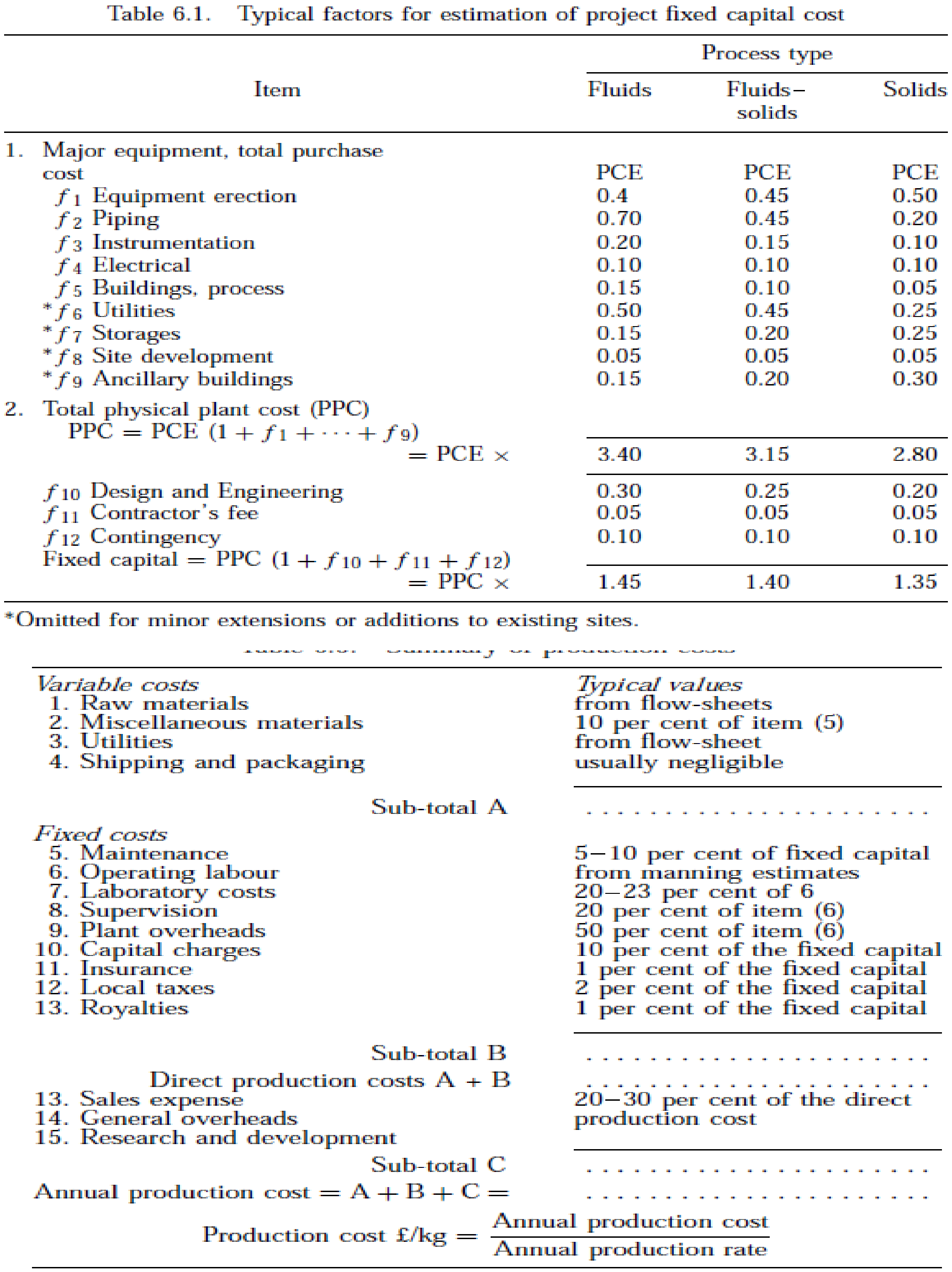


Table 6.1. Typical factors for estimation of project fixed capital cost

Item	Process type: Fluids	Process type: Fluids–solids	Process type: Solids
1. Major equipment, total purchase cost	PCE	PCE	PCE
f_1 Equipment erection	0.4	0.45	0.50
f_2 Piping	0.70	0.45	0.20
f_3 Instrumentation	0.20	0.15	0.10
f_4 Electrical	0.10	0.10	0.10
f_5 Buildings, process	0.15	0.10	0.05
*f_6 Utilities	0.50	0.45	0.25
*f_7 Storages	0.15	0.20	0.25
*f_8 Site development	0.05	0.05	0.05
*f_9 Ancillary buildings	0.15	0.20	0.30
2. Total physical plant cost (PPC) $PPC = PCE\,(1 + f_1 + \cdots + f_9)$ $= PCE \times$	3.40	3.15	2.80
f_{10} Design and Engineering	0.30	0.25	0.20
f_{11} Contractor's fee	0.05	0.05	0.05
f_{12} Contingency	0.10	0.10	0.10
Fixed capital $= PPC\,(1 + f_{10} + f_{11} + f_{12})$ $= PPC \times$	1.45	1.40	1.35

*Omitted for minor extensions or additions to existing sites.

Variable costs	*Typical values*
1. Raw materials	from flow-sheets
2. Miscellaneous materials	10 per cent of item (5)
3. Utilities	from flow-sheet
4. Shipping and packaging	usually negligible
Sub-total A	. . . .
Fixed costs	
5. Maintenance	5–10 per cent of fixed capital
6. Operating labour	from manning estimates
7. Laboratory costs	20–23 per cent of 6
8. Supervision	20 per cent of item (6)
9. Plant overheads	50 per cent of item (6)
10. Capital charges	10 per cent of the fixed capital
11. Insurance	1 per cent of the fixed capital
12. Local taxes	2 per cent of the fixed capital
13. Royalties	1 per cent of the fixed capital
Sub-total B	. . . .
Direct production costs A + B	. . . .
13. Sales expense 14. General overheads 15. Research and development	20–30 per cent of the direct production cost
Sub-total C	. . . .
Annual production cost = A + B + C =	. . . .

$$\text{Production cost £/kg} = \frac{\text{Annual production cost}}{\text{Annual production rate}}$$

Figure 34 Costing of Plant

Using the above stated tables and graphs the economic analysis was done of all the cases. The same method discussed in the above part of chapter 8 will be used for the economics analysis. As an example, the purchase cost determination of equipment has also been shown. Now we move on to calculate the macro level of costs. Following is the summary of all three cases.

8.6 Case – 1 Costing:

8.6.1 Physical Plant Cost (PPC):

Physical Plant Cost (PPC)	
Items	**Cost ($ Millions)**
Equipment Erection	0.4
Piping	0.7
Instrumentation	0.2
Electrical	0.1
Process	0.15
Utilities	0.5
Storage	0.15
Purchase Cost Equipment	10.77
Physical Plant Cost (PPC)	34.48

Table 36 Physical Cost of Case – 1

8.6.2 Fixed Capital:

Fixed Capital	
Items	**Cost ($ Millions)**
Design & Engineering	0.3
Contractor's fee	0.1
Contingencies	0.05
Fixed Capital	50.0045

Table 37 Fixed Capital of Case – 1

8.6.3 Fixed Operating Cost:

Fixed Operating Cost	
Items	**Cost ($ Million)**
Maintenance	3.75
Capital Charges	5.000453
Plant Overhead	1.075
Local Taxes	1
Royalties	0.5
Insurance	0.5
Fixed Operating Cost (FOC)	11.8

Table 38 Fixed Operating Cost of Case – 1

8.6.4 Variable Operating Cost:

Variable Operating Cost	
Items	**Cost ($ Million)**
Raw Material	0.9
Shipping and packaging	Negligible
Variable Operating Cost (VOC)	0.9

Table 39 Variable Cost of Case – 1

8.6.5 Total Operating Cost:

Total Operating Cost	
Items	**Cost ($ Million)**
Direct Production Cost	12.7
Sales Expense	2.54
General Overheads	
Research & Development	
Total Operating Cost	15.27

Table 40 Total Operating Cost of Case – 1

8.6.6 Revenue & Net Profit:

Revenue & Net Profit	
Cost of Product gas	$ 185/ton
Per annum product gas production	40560.40 tons
Cost of Hydrogen	$ 1.25/kg
Per annum production of Hydrogen	16952.75 tons
Revenue	28.6 Million
Net Profit	13.3 Million
Payout period	2.3 years

Table 41 Cost Summary of Case – 1

These are the values beneficial for making decisions. All the previous values are calculated from the previous values in series. This is final economic analysis for our Case – 1.

Now we will be following the same methodology for Case – 2 and Case – 3 and will be showing the final significant results of our economic analysis.

8.7 Case – 2 Costing:

Same calculations as in Case – 1 were done in order to reach to final revenue, profit and cost of the Case – 2.

8.7.1 Total Operating Costs:

Total Operating Cost	
Items	**Cost ($ Million)**
Direct Production Cost	12.5
Sales Expense	2.51
General Overheads	
Research & Development	
Total Operating Cost	15..099

Table 42 Total Operating Cost of Case – 2

8.7.2 Revenue & Net Profit:

Revenue & Net Profit	
Cost of Product gas	$ 185/ton
Per annum product gas production	48869 tons
Cost of Hydrogen	$ 1.25/kg
Per annum production of Hydrogen	27726.4 tons
Revenue	29.1 Million
Net Profit	14.001 Million
Payout period	2.21 years

Table 43 Cost Summary of Case – 2

8.8 Case – 3 Costing:

Some calculations as in Case – 1 were done in order to reach to final revenue, profit and cost of the Case – 3. However, for modified equipment like membrane reactors. Following were the costing ways:

8.8.1 Membrane Reactor Purchase Cost:

Weight of catalyst = $ 98560

$V_c = 219.02 m^3$

$$\mathbf{C_e = CQ^n}$$

$Q = V_r = 229.100\ m^3$

$C = 31000 \quad n = 0.40$ From Table

Cost of reactor vessel = $ 293110.6441

Cost of the membrane inside the vessel is calculated based on the area of the membrane.

$$\text{Area} = 97.62 \ \text{m}^2$$

$$\text{Area} = \frac{97.62 \ \text{m}^2 \times 10.764 \ \text{ft}^2}{1 \ \text{m}^2} = 997.491 \ \text{ft}^2$$

Cost of the Palladium Membrane (2021) = \$ 2000 per ft^2

Cost = \$ 2000 per $\text{ft}^2 \times 997.491 \ \text{ft}^2$

Cost = \$ 1994982

Cost of Membrane Reactor = \$ 2288092.644

Purchase Cost of Equipment = \$ **10166612. 13**

8.8.2 Total Operating Cost:

Rest of the calculations were same as in Case – 1 and Case – 2. Moving on to Total Operating Cost.

Total Operating Cost	
Items	**Cost ($ Million)**
Direct Production Cost	12.05
Sales Expense	2.41
General Overheads	
Research & Development	
Total Operating Cost	14.46

Table 44 Operating Cost of Case – 3

8.8.3 Revenue & Net Profit:

Revenue & Net Profit	
Cost of Product gas	$ 185/ton
Per annum product gas production	40560.4tons
Cost of Hydrogen	$ 1.25/kg
Per annum production of Hydrogen	17110.908 tons
Revenue	28.69 Million
Net Profit	14.23 Million
Payout period	2.15 years

Table 45 Cost Summary of Case – 3

8.9 HAZOP Analysis:

HAZOP analysis stands for hazard and operability analysis. This safety analysis finds its application in identifying potential risks and hazards surrounding an industrial process. HAZOP analysis deals to minimize accidents at plants that can lead to undesirable products. Following are the goals achieved by HAZOP hazard analysis:

1. Identification of hazard.
2. Extent of the damage.
3. Gguidelines to solve the problem.

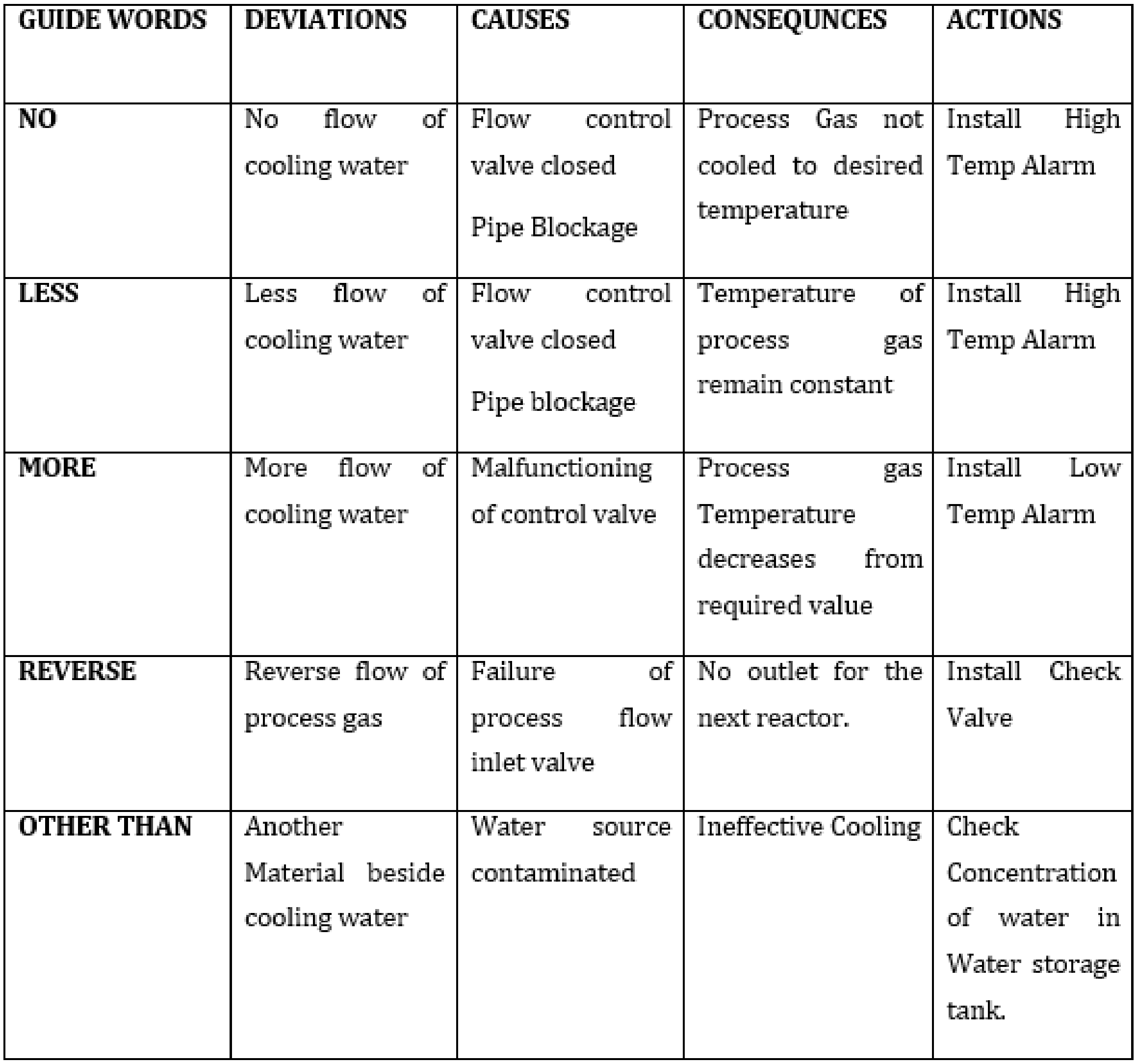
8.9.1 HAZOP Guide Words:

HAZOP utilizes a set of Guide words that identify probable deviations that can occur during a chemical process. These guide words prove their worth by allowing a systematic and consistent procedure through brainstorming. Some of these guide words which are selected by the risk management teams and are used for hazard management are as follows:

Sr. No.	**Guide Word**	**Meaning**
1	NO or NOT	Complete contradiction of original design
2	LESS	Decrease quantitatively
3	MORE	Increase quantitatively
4	AS WELL AS	Qualitative enhancement
5	REVERSE	Opposite to the original design
6	OTHER THAN/INSTEAD	Entire design
7	PART OF	Qualitative modification/decrease

Table 46 Guide of HAZOP Analysis

8.9.2 HAZOP Analysis of Heat Exchanger:



GUIDE WORDS	DEVIATIONS	CAUSES	CONSEQUNCES	ACTIONS
NO	No flow of cooling water	Flow control valve closed Pipe Blockage	Process Gas not cooled to desired temperature	Install High Temp Alarm
LESS	Less flow of cooling water	Flow control valve closed Pipe blockage	Temperature of process gas remain constant	Install High Temp Alarm
MORE	More flow of cooling water	Malfunctioning of control valve	Process gas Temperature decreases from required value	Install Low Temp Alarm
REVERSE	Reverse flow of process gas	Failure of process flow inlet valve	No outlet for the next reactor.	Install Check Valve
OTHER THAN	Another Material beside cooling water	Water source contaminated	Ineffective Cooling	Check Concentration of water in Water storage tank.

Table 47 Heat Exchanger HAZOP

8.9.3 HAZOP Analysis of Secondary Reformer:

GUIDE WORDS	DEVIATIONS	CAUSES	CONSEQUNCES	ACTIONS
NO	No Flow of reactant	Feed Line valve is closed	No reaction takes place	Open Valve to Allow Reactant into the reactor
		Feed Line is blocked	No reactant enters the reactor	Clear Blockage in feedline
Less	Less Flow of Reactant	Feed Line is loose.	Reactants falls out from field line before entering reactor	Join/Repair and seal Feed line.
	Less Temperature	Fuel Line is loose.	Incomplete Combustion will take place.	Repair and seal fuel line
	Less Pressure	Opening of PCV.	Required conversion is not achieved.	Install pressure Control Loop.
	Less Residence Time	Valve Opening Malfunction	Less optimum yield	Periodic maintenance or check up on the valve
More	More Pressure	Compressor Control Failure	Reactor operate at high Temperature than required.	Trigger automatic Shutdown.
	More Temperature	Very high amount of fuel and air flow inside the reactor.	Damage catalyst and equipment inside the reactor	Equip reactor system with fail open or fail close valve system.
As well as	Another Material beside Fuel.	Contamination of fuel storage tank.	Inadequate Combustion in reactor.	Check Composition of fuel in storage tank

Table 48 HAZOP of Secondary Reformer

8.9.4 HAZOP Analysis of Membrane Unit:

Intention: To separate Hydrogen from the Ammonia free purge gas mixture.

Guide Word	deviations	Possible Causes	Consequences	Actions
Flow	More flow	1)Feed flow rate increased 2)Temperature increase 3)Valve closed on retentate side partially closed 4)Membrane failure	Purity loss, Overpressure. Recovery increases- purity loss occurs. No separation occurs.	Fitting a high temperature alarm, Changing the membrane, split the feed stream into parallel modules
None/less	Less or flow at all.	1)Feed line blockage 2)Particulate or condensate film on membrane 3)Temperature decrease	No efficient separation, overpressure, condensate formation on membrane surface	Cleaning of feed line, installation of pressure alarm, membrane changing, checking filtration system
Less	Less temperature	Heat exchanger not functioning properly	Formation of condensate film on membrane surface would lead to inefficient separation	Installation of low temperature alarm, heat exchanger functioning inspection
More	More temperature than intention	Decreased supply of cold water to heat exchanger	Membrane damage, Permeate flow rate high, not efficient separation	Install high temperature alarm, check cold water supply valve to heat exchanger

Table 49 HAZOP of Membrane Unit

8.10 Instrumentation:

Following are the instrumentations being placed in various equipment in our plants:

Equipment	**Name of Controller**	**Type of Controller**	**Manipulated Variable**	**Controlled Variable**
Primary Reformer	LC	PI	Valve opening	Level of Reactor
	TC	PI	Cooling water flowrate	Reactor Temperature
	PC	PI	Valve opening	Reactor pressure
Secondary Reformer	LC	PI	Valve opening	Level of Reactor
	TC	PI	Flow rate of the hot inlet gas	Reactor Temperature
	PC	PI	Valve opening	Reactor pressure
HTS	LC	PI	Valve opening	Level of Reactor
	TC	PI	Flow rate of the hot inlet gas	Reactor Temperature
	FC	PI	Valve opening	pH
Membrane Reactor	PC	PI	Valve opening	Reactor pressure
	LC	PI	Valve opening	Level of Reactor
	TC	PI	Cooling water flowrate	Reactor Temperature
H**eat Exchanger**	PC	PI	Valve opening	Heat exchanger pressure
	TC	PI	Cooling water flowrate	Exchanger Temperature
	LC	PI	Valve opening	Level of liquid inside the HX
Membrane	TC	PI	Cooling water flowrate	Reactor Temperature
	PC	PI	Valve opening	Reactor pressure

Table 50 Instrumentation

8.10.1 Instrumentation and Process control

Instrumentation is termed as the use of measuring instruments to look and control a process variable such as level, pressure, flow, temperature, speed. The process control is an emerging field of study in engineering which deals with designing of algorithms and devices for maintaining the output of a specific process with a required range. In process control, control loops and controllers are used to regulate a chemical process and improve effectiveness of the process [16]. Controller is a tool that collects data from a measurement device, contrasts that statistical information to a predetermined set point, and, if needed, suggests a control component to take remedial act. Following are the type of process variables:

1. Measured/controlled Variable-is the situation of the process fluid that must be kept at the specified set point.
2. Manipulated Variable- The factor that is changed to keep the process variable at set point.

Set point is the value for a process variable which is to be retained at a constant value.

8.10. 3 Control loop and its Components:

A control loop is the base on which the architect of process control systems that are applied in the industry. Physically a control loop consists of all the elements that are necessary to control and adjust the set point of the controlled variable.

Following are the components of the control loop:

1. Sensors- Device that can access the changes in condition, and it is the first thing to measure the variable process in control loop.
2. Transducer- Device that translates a mechanical signal into an electrical signal.
3. Converters or relay- The conversion of one signal to another signal from a device
4. Transmitters- The conversion of reading from sensor to a signal.
5. Signals which are pneumatic, analog or digital.
6. Indicators-It is a device which is readable by humans and can show information like pressure gauge.

Records- To record the output from a device.

8.10.4 Control loop Applied on Heat Exchanger:

Temperature control loop is applied on the heat exchangers in order to maintain the temperature of the process gas outlet. The control loop applied is based on feedback mechanism in which the action of the system is based on the output of the process.

Manipulated Variable: Cooling water Flow rate.
Controlled Variable: Temperature of process gas.
TIT: Temperature Indicator Transmitter.
TRC: Temperature Recorder Controller.
TY: Temperature Relay.
TCV: Temperature Control Valve.

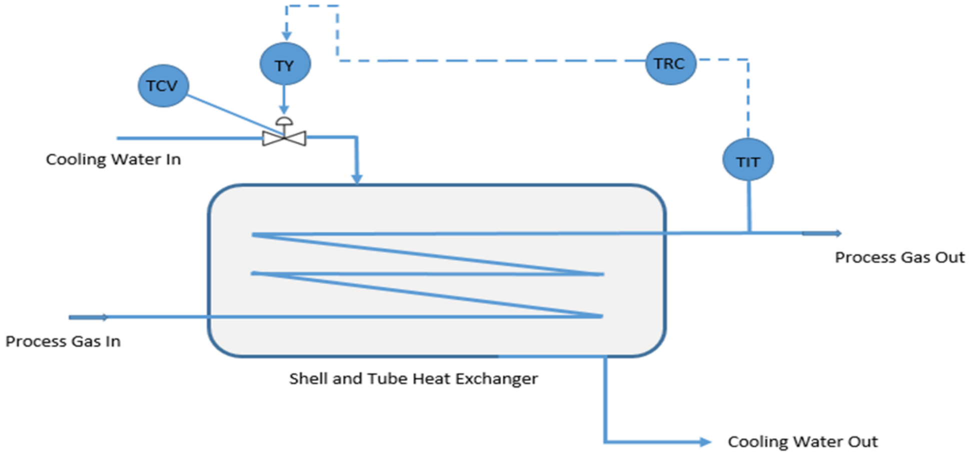


Figure 35 PID of Exchanger

8.10.5 Control Loops Applied on Secondary Reformer:

Following control loops were applied on the secondary reformer in order to maintain the temperature of outlet of the process stream and to maintain the pressure of the reactor.

Manipulated Variable	**Controlled Variable**
Flue Gases Flow rate	Reactor Pressure
Flow Rate of Fuel	Process Stream Outlet Temperature
Flow Rate of Air	Flow Rate Fuel In

Table 51 Variable table

PIT: Pressure Indicator Transmitter

PCR: Pressure Controller Recorder

PY: Pressure Relay

PCV: Pressure Control Valve

FIT: Flow Indicator Transmitter

FCR: Flow Controller Recorder

FV: Flow Relay

FCV: Flow Control Valve

Transfer functions were calculated according to the give calculations and the PID of the control loops was simulated using Simulink. The transfer calculations are given as follows with the Simulink simulation and its results.

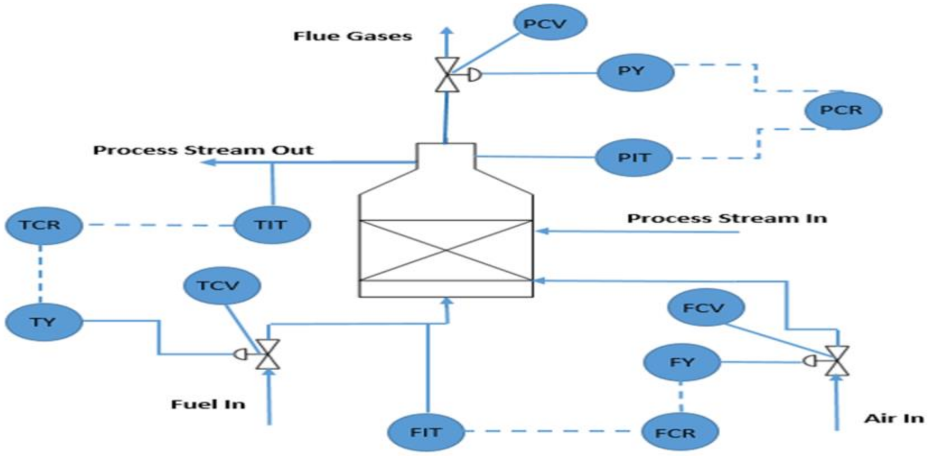


Figure 36 PID of reformer

8.10.6 Temperature Control Loop on Secondary Reformer:

Transfer Function Derivation:

Apply energy balance on the Secondary Reformer:

$$\begin{aligned}&(\text{Rate of flow of energy into tank}) - (\text{Rate of flow of energy out of tank})\\&\quad + (\text{Rate of flow of energy on from heat source})\\&\quad = (\text{Rate of energyaccumulation in tank})\end{aligned}$$

Connecting this energy balance in symbols results in:

$$wC\left(T_i - T_{ref}\right) - wC\left(T - T_{ref}\right) + q = \rho VC\frac{dT}{dt} \quad - (1)$$

Where T_{ref} is the reference of temperature and C is the capacity of heat of the fluid. At steady state, dT/dt is zero, and (1) can be written as:

$$wC(T_{is} - T_s) + q_s = 0 \quad - (2)$$

Where subscript s has been used to indicate steady state. Subtracting Eq. (2) from Eq. (1) gives:

$$wC(T_i - T_{is}) - wC(T - T_s) + q - q_s = \rho VC\frac{d(T - T_s)}{dt} \quad - (3)$$

If we assume that T_i is constant (and so $T_i = T_{is}$) and introduce the deviation variables,

$$T' = T - T_s$$

$$Q = q - q_s$$

Eq. (3) becomes:

$$-wCT' + Q = \rho VC\frac{dT'}{dt} \quad - (4)$$

Taking Laplace transforms of Eq. (4) gives:

$$-wCT'(s) + Q(s) = \rho VCsT'(s) \quad - (5)$$

Rearranging Eq. (5) produces the following first-order transfer function relating T'(s) and Q(s):

$$\frac{T'(s)}{Q(s)} = \frac{1/wC}{\left(\frac{\rho V}{w}\right)s + 1} = \frac{K}{\tau s + 1} \quad -(6)$$

Transfer Function for Thermocouple:

In order to derive it following assumptions are made:

1.Only film around bulb provide resistance to heat transfer.

2.Only mercury has thermal capacity and can attain uniform temperature instantly.

3. No expansion or contraction of glass wall containing mercury will take place

By applying unsteady-state energy balance,

$$(Input\ rate) - (Output\ rate) = (Rate\ of\ accumulation)$$

We will get:

$$hA(x - y) - 0 = mC\frac{dy}{dt} \qquad -(7)$$

In the equation above,

A = surface area of the bulb

C = heat capacity of mercury,

m = Mass in pounds of Mercury.

t = time in unit hour.

h = heat transfer coefficient, Btu/(ft3*h*°F)

This equation states when the heat flows through any film of resistance surrounding a bulb internal energy (mercury) will increase. This increment in value of internal energy can also tell us about temperature changes as well as mercury's expansion depicts thermometer reading.

Value of h always depends upon the flow rate and fluid characteristics in which it is present and also the dimensions of involving bulb, h is always constant for thermometer

For steady state process:

$$hA(x_s - y_s) = 0 \qquad -(8)$$

Difference of Equation 7 and 8 will give us

$$hA\{(x - x_s) - (y - y_s)\} = mC\frac{d(y - y_s)}{dt} \qquad -(9)$$

X=$(x - x_s)$

Y=$(y - y_s)$

Then Eq 9 will now become

$$hA(X - Y) = mC\frac{dY}{dt}$$

Now, if

$$\tau = \frac{mC}{hA}$$

Then

$$(X - Y) = \tau\frac{dY}{dt} \qquad -(10)$$

Taking Laplace of Eq 10

$$X(s) – Y(s) = \tau s\ Y(s)$$

By Rearranging,

$$\frac{Y(s)}{X(s)} = \frac{1}{\tau s + 1}$$

PID of Temperature Control Loop:

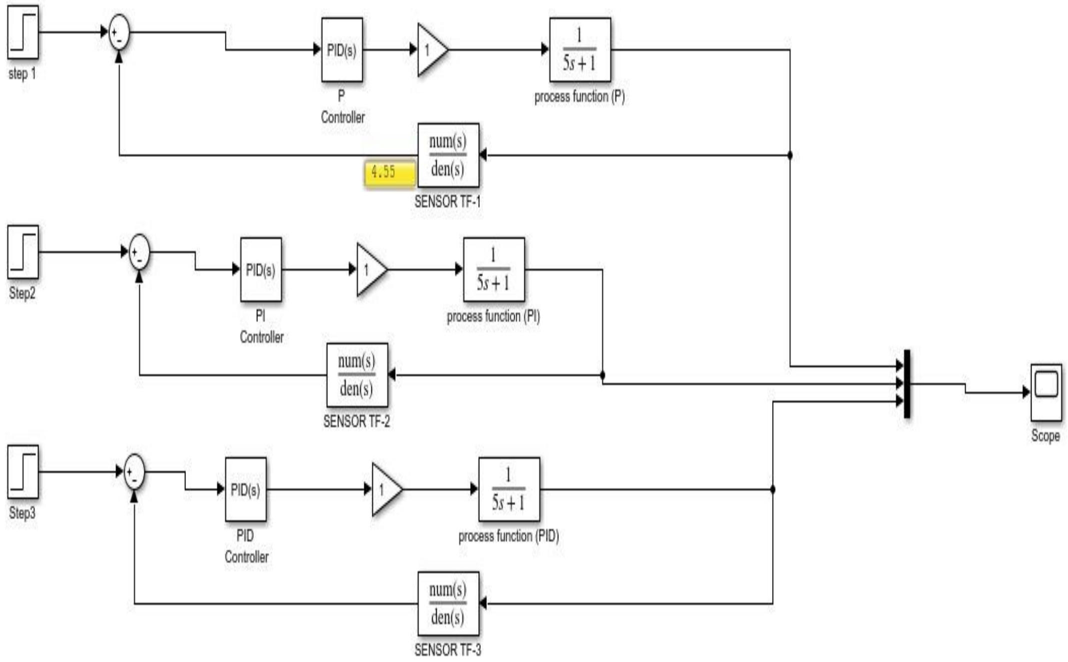


Figure 37 Simulink Screen Shot

P=10

I=3

D=3

For sensor, τ =0.5

For system, τ =0.5

Simulink Plot of Temperature Control Loop:

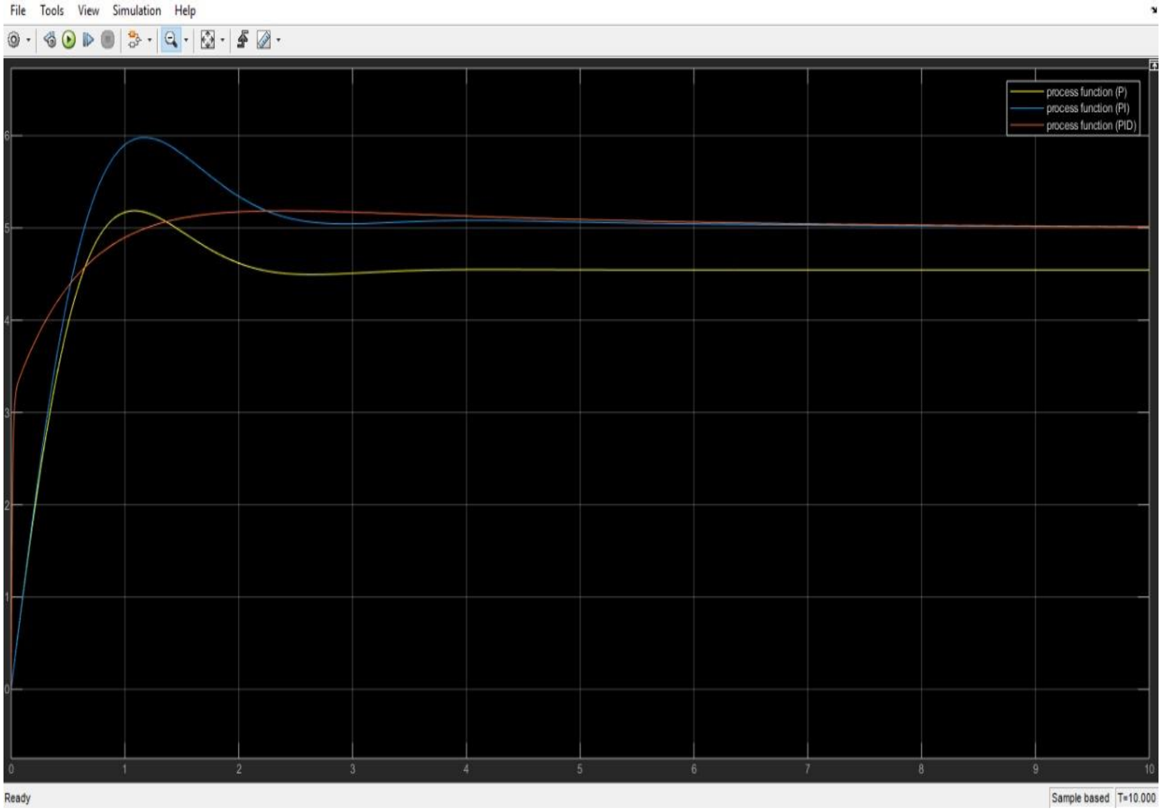


Figure 38 Simulink Plot

CONCLUSION

From the three proposed cases and their detailed study we can conclude that the membrane reactors are most effective when employed for the equilibrium reactions. If a process involves several reactions and all of them are equilibrium reactions, then the membrane reactors are most effective for high conversions in such processes. As all the reactions involved in the ammonia synthesis process are reversible reactions and their conversions are greatly influenced by, the equilibrium constant and the equilibrium conditions so we can say that ammonias synthesis with high conversions can be carried out in the membrane reactors.

Case - 2 was the most cost effective among all the three cases that we proposed however the employed membrane modules have short life spans as when put into operation on industrial scale they undergo extensive deterioration and damage. So, it must be considered as a secondary choice for the industrial applications. Also, the calculations are made based on hydrogen being the useful product however, the useful product of Ammonia plant is Ammonia not hydrogen. Once, the hydrogen fuel is as common as petrol in the world then use of such methodologies would be ideal.

So the membrane reactors are the most effective in the longer run and for industrial applications rather than separate membrane modules carrying out the separation operation and higher conversions of CO are achieved by the Membrane reactors i.e. 87% in our Case – 3 and even higher conversions can be achieved if we lower our operation temperatures however that compromise the reaction kinetics and slows down the reaction rate. In totality, it is suggested that equilibrium reactions must be now carried out in membrane based fixed bed reactors because it can change the performance of the whole process.

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