TO STUDY THE POSSIBLE CAUSES AND TO ADDRESS THE HIGH PRESSURE DROP ISSUE ACROSS THE HTS CONVERTER CATALYST BED DUE TO COKE FORMATION

By

Aleena Ahmed

Ahsan Munir

Huzaifa Bin Arshad

School of Chemical and Materials Engineering

National University of Sciences and Technology

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By

Leader -00000267196 Aleena Ahmed
Member 1 -00000244947 Ahsan Munir
Member 2 -00000251850 Huzaifa Bin Arshad

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CERTIFICATE

This is to certify that work in this thesis has been completed by Ms. Aleena Ahmed, Mr. Ahsan Munir and Mr. Huzaifa Bin Arshad under the supervision of Dr. Tayyaba Noor and Dr. Erum Pervaiz at the school of Chemical and Materials Engineering (SCME), National University of Science and Technology, H-12, Islamabad, Pakistan.

--	----------------------------------
Advisor:	Co-Advisor
Dr. Tayyaba Noor Department of Materials Engineering School of Chemical and Materials Engineering National University of Sciences and Technology	**Dr. Erum Pervaiz** Department of Materials Engineering School of Chemical and Materials Engineering National University of Sciences and Technology

Submitted Through:

HOD-------------------------------------
Dr. Erum Pervaiz
Department of Materials 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 families, teachers and friends for their continual support and help throughout this journey and without whom none of this would have been possible.
And to SCME, the place that equipped us with everything that was needed to reach this position.

ACKNOWLEDGEMENT

All praise and thanks are only for Allah, the One who, by His blessings and favor, perfected good works are accomplished.

We would like to express our thanks to **Allah Almighty** for his never-ending blessings and mercies on us. There is no doubt that it is HE who gave us all the strength and ability to get through this journey and complete this project.

We would like to thanks our supervisor **Dr. Tayyaba Noor** for her continuous guidance and moral support throughout this project. She has always helped us to ensure flawless and timely completion of every phase of this project. We would also like to thanks our co-supervisor **Dr. Erum Pervaiz** for all the assistance in technical matters and for motivating us to explore modern methods and solutions for value addition in our project.
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And lastly, we would like to mention that none of this was possible without the support, love and care provided by our families and friends.

ABSTRACT

For Diesel hydro-desulfurization (DHDS), Attock Refinery Limited (ARL) uses hydrogen produced by the Hydrogen Production Unit. High Temperature Shift (HTS) Converter is an important part of this unit in which heterogeneous catalytic Water-Gas Shift reaction takes place. A high pressure drop across the HTS catalyst bed was reported. This project aims to study and address the possible causes of this pressure drop. For this purpose, the design of monolithic HTS Converter was proposed instead of the packed bed reactor. The proposed design simulated through COMSOL Multiphysics gave significant reduction in pressure drop. Moreover, to enhance the catalyst performance by reducing coke formation, this work further focused on optimization of various operational parameters. This in turn, reduced the plant downtime. Aspen HYSYS was used for simulation of complete hydrogen production unit. Economic analysis and HAZOP study was also carried out.

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CHAPTER 1

INTRODUCTION

1.1 Scope of the Project

Hydrogen is used for the Diesel hydro-desulphurization (DHDS) in Attock Refinery Limited. Hydrogen gas is produced at the plant unit named as Hydrogen Generation unit (HYU) located in Rawalpindi, Pakistan. The production capacity of the plant is. Hydrogen is produced by steam reforming followed by water gas shift reaction which takes place in the high temperature shift converter. This HTS converter is a packed bed reactor experiencing a high pressure drop, which when viewed over the years, significantly increases the plant energy requirements. The following reaction occurs in HTS converter with Iron-Chrome as catalyst:

$$CO + H2O \leftrightarrow CO2 + H2$$

The temperature for this reaction is in the range of 300 - 450°C. At this temperature coke formation is observed and the coke is deposited on the surface of the catalyst consequently blocking the active sites for the reaction. This deactivation of catalyst leads to compromised catalytic performance. The deactivation increases with temperature and time. Hence after certain period of time the catalyst needs regeneration and sometimes replacement with new catalyst. This process adds to plant downtime. Therefore, the main objectives of this project are to study and address the possible causes of high pressure drop across the HTS catalyst bed, to enhance the catalyst performance and to reduce the plant down time.

1.2 Hydrogen

Hydrogen is the simplest of the elements and exists in abundant quantity in the universe making up nearly 75% of the visible matter. It is produced on industrial scale through well-known processes and is widely used for many major industrial and commercial purposes

1.2.1 Physical Properties

At room temperature Hydrogen is a colorless and tasteless gas without any odor. Hydrogen gas is non-toxic however it can cause asphyxiation (oxygen deficiency) as it can easily displace oxygen in the air when present in large quantities. Hydrogen has the lowest atomic weight and lowest density. Its leakage can pose a potential fire hazard.

1.2.2 Chemical Properties

Hydrogen gas exist in the form of diatomic molecules with the formula H_2. Hydrogen, as an element is non-metallic and it readily forms covalent bonds with the non-metallic elements to form compounds. Water and organic compounds are most common examples. Hydrogen also plays a significant role in acid base reactions. When present in ionic compounds, Hydrogen is present in the form of negative ion (anion) and is called hydride H^{-1}. In the cationic form Hydrogen is simply a proton H^{+1}. Hydrogen gas is highly combustible when present in the concentration ranging between its upper flammability limit (UFL) and lower flammability limit (LFL).

The following table summarizes important properties of Hydrogen

Table 1- Properties of Hydrogen

Properties of Hydrogen	
Chemical Symbol	H
Atomic Number	1
Atomic Weight	1.00794
Melting Point	-259 ◦ C
Boiling Point	-253 ◦ C
Density (gas)	0.090 g/L
Density (liquid)	0.70g/L
Explosive Limit	4-75%
Ignition Temperature	585 ◦ C

1.3 Uses of Hydrogen

Hydrogen gas has various commercial uses. Apart from its use in treating metals and reducing metal ores, as rocket fuel, welding, producing hydrochloric acid. A short description of some of these is as given below:

1.3.1 Haber Process for ammonia production

Ammonia is a vital in fertilizer and urea production. It is produced through nitrogen fixation method called Haber Bosch Process. This process utilizes the nitrogen obtained from air and hydrogen to react in the presence of metal catalyst at high temperature and pressures.

The following exothermic reaction takes place:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Apart from its use in fertilizers, ammonia is also used in the production of explosives.

1.3.2 Hydrogenation of fats and oils

Hydrogenation is a process in which hydrogen is added to oils as a result of which the number of unsaturated fatty acids is decreased and the number of saturated fatty acids is increased in the oil. The reaction also takes place in the presence of metal catalyst usually Nickel is used for this purpose. The solid or semi-solid fat as product is obtained.

1.3.3 Hydro-treating in petroleum refinery

To eliminate various oxides especially oxides of sulfur and nitrogen from the emissions during combustion of fuels, the sulfur and nitrogen content of major petroleum refinery products and fuels along is reduced to the acceptable levels. This is done by the process called hydrotreating in which high pressure hydrogen is used to remove the heteroatoms from the refinery streams. The contaminants like nitrogen, sulfur and oxygen react with the hydrogen in presence of catalyst and are removed. The particular reaction for hydrodesulfurization is:

$$\text{"[R–S]"} + H_2 \xrightarrow[300-450^{\circ}C]{\text{catalyst}} \text{"[R–H]"} + H_2S$$

Apart from these major applications, other major uses include:

- Treating metals and reducing metal ores
- As rocket fuel
- Welding
- Producing hydrochloric acid
- Renewable fuel for vehicles
- Fuel cells technology

1.4 Methods of hydrogen Production

The production of hydrogen includes the three main processes:

- Thermochemical processes
- Electrolytic processes
- Biological processes

1.4.1 Thermochemical Processes

The thermochemical processes use fossil fuels like natural gas, coal and biomass/waste as a source and use chemical reactions at high temperature conditions to obtain hydrogen from the organic sources. These include:

1.4.1.1 Steam methane reforming (SMR)

The major portion of commercially produced hydrogen is through steam reforming of natural gas. In this process, methane CH_4 from natural gas is reacted with high pressure steam in the presence of a catalyst and at high temperatures to produce Carbon monoxide CO, carbon dioxide CO_2 and hydrogen H_2. The reaction takes place normally at 3 to 5 bar pressure. The carbon monoxide produced during SMR is further reacted with steam to produce carbon dioxide and more hydrogen. This reaction us called "Water

Gas Shift Reaction". Lastly the carbon dioxide is removed using carbon capturing techniques like pressure swing adsorption leaving behind pure hydrogen.

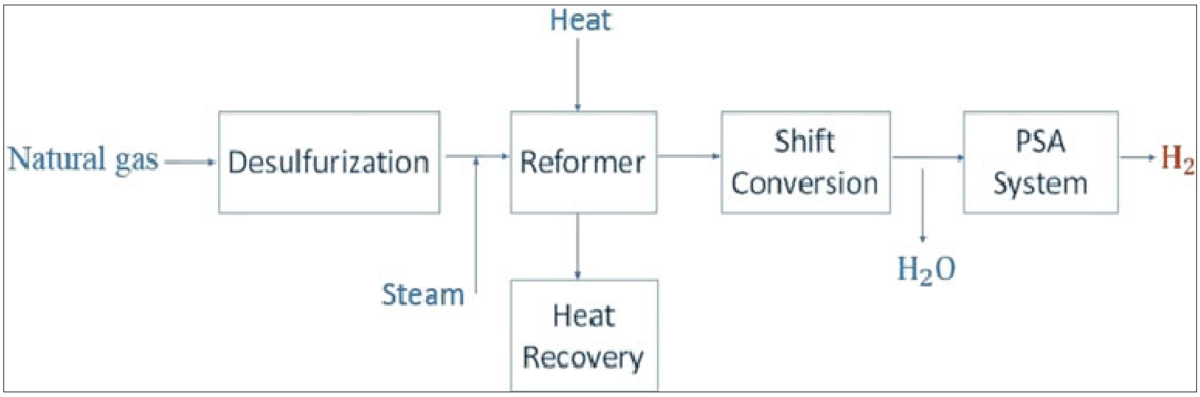
Steam methane reforming reaction:

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

Water gas shift reaction:

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

Figure 1-Block Diagram



1.4.1.2 Biomass gasification

This process involves well developed technology that uses heat, steam and oxygen to convert biomass, a carbonaceous substance into hydrogen and other products without combustion. The biomass can be any renewable organic resource like municipal solid waste, animal waste, agricultural residue and forest residue.

Simplified reaction:

$$C_6H_{12}O_6 + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + \text{other species}$$

The carbon monoxide is again converted to carbon dioxide and hydrogen through water gas shift reaction with consequent separation of CO_2.

Water gas shift reaction:

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

1.4.1.3 Biomass derived fuel reforming

Solid biomass is first converted to bio-oils and cellulosic ethanol and other bio-fuels. These liquids then undergo reforming process similar to the natural gas reforming, in the presence of catalyst, liquid fuels are reacted with steam at high temperatures and a mixture of carbon monoxide, carbon dioxide and hydrogen is produced followed by water gas shift reaction and carbon capturing.

Steam methane reforming (ethanol):

$$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$$

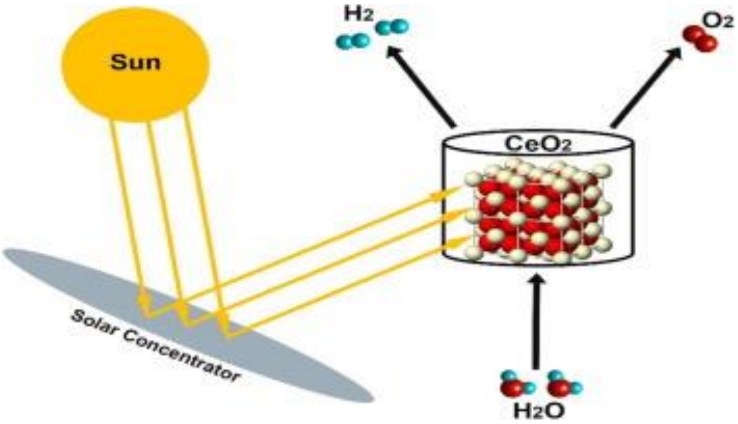
Water gas shift reaction:

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

1.4.1.4 Solar thermochemical hydrogen

This process uses thermochemical water splitting that generates oxygen and hydrogen at high temperatures ranging from $500°C \; to \; 2000°C$. These high temperatures are generated by concentrated solar power plants in which large mirror fields (heliostats) are developed to concentrate solar energy. Another method is to use waste heat from the nuclear reactions taking place at high temperatures.

Figure 2-Solar Thermochemical Hydrogen Production



1.4.2 Electrolytic Processes

This is a method that produces carbon free hydrogen from the renewable sources. In this process, electricity is used to split water into hydrogen and oxygen. This process takes place in a unit called electrolyzer. An electrolyzer consists of an anode and a cathode separated by an electrolyte. Different electrolyzers work differently based upon the type of electrolyte used. Commonly examples include:

- Alkaline Electrolyze (liquid alkaline solution of sodium or potassium hydroxide is used as an electrolyte)
- Polymer electrolyte membrane electrolyzer (solid plastic material as electrolyte)
- Solid oxide electrolyzer (solid ceramic material as electrolyte)

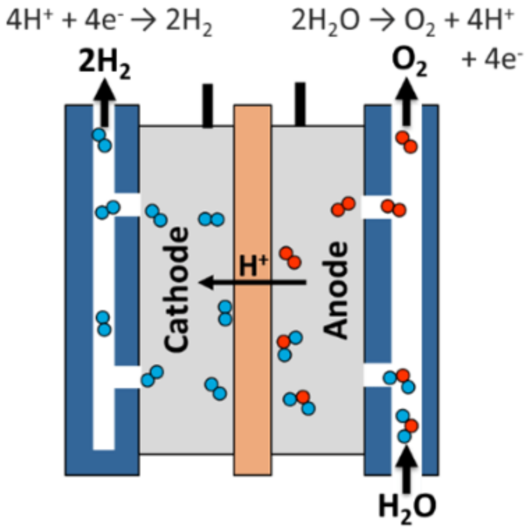


Figure 3- A Typical electrolyzer

1.4.3 Biological Processes

Biological processes use microbes like bacteria and microalgae to produce hydrogen. The microbes undergo biological reactions using sunlight and organic matter. These processes are still in research phase or are employed at only pilot scale but they have a great potential for clean and sustainable production of carbon free hydrogen. The two common biological processes are microbial biomass conversion and photo-biological process.

CHAPTER 2

LITRATURE REVIEW

2.1 Water Gas Shift Reaction

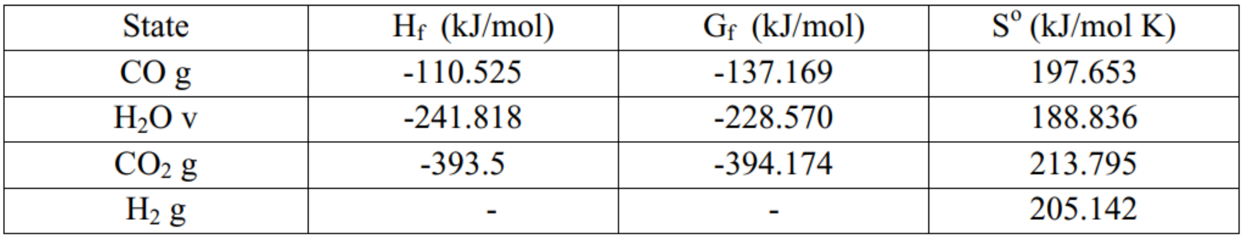
The water gas shift reaction was first discovered during the end of 19th century. Later in 1913 its first industrial application to produce hydrogen through CO shift conversion was of great success. After this, the application of WGS reaction to adjust H_2 to CO ratio after steam methane reforming and gasification of heavy hydrocarbons or other carbonaceous organic materials. CO shift conversion takes place in two stages named as high temperature shift converter (HTSC) and low temperature shift converter (LTSC) at different temperature ranges and catalysts. In this reaction of immense industrial importance, the carbon monoxide reacts with steam to produce carbon dioxide and hydrogen according to the following reaction:

$$CO + H_2 \rightarrow CO_2 + H_2O \qquad \Delta H_o = -41.7℃$$

2.1.1 Thermodynamics of WGS reaction

The reaction is exothermic and heat is evolved with the reaction. Since the reaction is reversible, according to the Le Chatellier Principle, the forward reaction is favored by removal of heat. However, the temperature cannot be too low as the kinetics of the reaction will otherwise be affected. For this reason, the reaction is carried out in two stages, at high and then at low temperatures. The composition of inlet gas and water content affect the CO conversion at equilibrium. Although the pressure does not affect the reaction equilibrium, still it can affect CO conversion due to enhanced rate of reaction. WGSR can be more effectively carried out in a two stage process. The following table summarizes the important thermodynamic parameters of the water gas shift reaction:

Table 2 – Thermodynamic Parameters of Water Gas Shift Reaction



State	H_f (kJ/mol)	G_f (kJ/mol)	S^o (kJ/mol K)
CO g	-110.525	-137.169	197.653
H_2O v	-241.818	-228.570	188.836
CO_2 g	-393.5	-394.174	213.795
H_2 g	-	-	205.142

2.1.2 Catalyst of WGS reaction

The iron oxide-based catalysts like Fe_2O_3 are very well known in high temperature water gas shift reaction (350–450°C) and these are generally doped with the chromium oxide, Cr_2O_3. This prevents the sintering of iron oxide catalyst crystallites. While in the low temperature shift converter Cu-Zn based catalyst are employed to activate the reactions. In addition to Iron and Copper bases catalysts, some noble metals also show good catalytic performance in WGS reaction. These include nickel, molybdenum, cobalt, platinum, rhodium, ruthenium, and gold. The catalyst deactivation is caused by the following three reasons:

- Thermal sintering
- Sulfur poisoning
- Chloride poisoning

2.1.3 Kinetics of WGS reaction

For the water gas shift reaction, two different reaction mechanism are proposed by the researchers named as adsorptive mechanism and regenerative mechanism. The major steps in mechanism include the adsorption of the reactants on the active sites of the catalyst where the reaction takes place after which the desorption of the product takes place. The following reaction rate equation proposed by Langmuir-Hinshelwood is the widely acceptable.

Rate expression:

$$r = k_o \, . \, e^{\frac{-E_a}{RT}} \, . \, p_{CO}^{L} \, . \, p_{H_2O}^{m} \, . p_{CO_2}^{n} \, . p_{H_2}^{q} \, . \left(1 - \frac{1}{K_{eq}} \, . \frac{p_{CO_2} . \, p_{H_2}}{p_{CO} \, . \, p_{H_2O}}\right)$$

Where,

k_o = Pre-exponential factor

E_a = Activation Energy

p = Partial pressure

K_{eq} = Reaction equilibrium constant, given as

$$\ln\left(K_{eq}\right) = \frac{5693.5}{T} + 1.077\ln(T) + 5.44 \times 10^{-4}T - 1.125 \times 10^{-7}T^2 - \frac{49170}{T^2} - 131$$

The HTS converter is usually a packed bed reactor that operates at temperature between 350-400°C with Fe-Cr as catalyst.

2.2 Pressure drop in packed bed reactor

The pressure drop in the packed bed reactor is given by the Ergun Equation as:

$$\frac{\Delta P}{L} = \frac{150\mu v_o}{{D_p}^2} \times \frac{1 - \varepsilon^2}{\varepsilon^3} + \frac{1.75\rho_g v_o^2}{D_p} \times \frac{1 - \varepsilon}{\varepsilon^2}$$

Where,

ΔP = pressure Drop

L = height of bed

μ = gas viscosity

v_o = superficial velocity

D_p = particle diameter

ε = porosity of bed

ρ_g = gas density

2.2.1 Causes of High Pressure drop

Usually the pressure in the packed bed is high due to the following 2 major reasons:

- Pressure drop due to inherent sources like frictional losses in inlet diffusers and distributors and packing material.
- Pressure drop due to fouling sources.

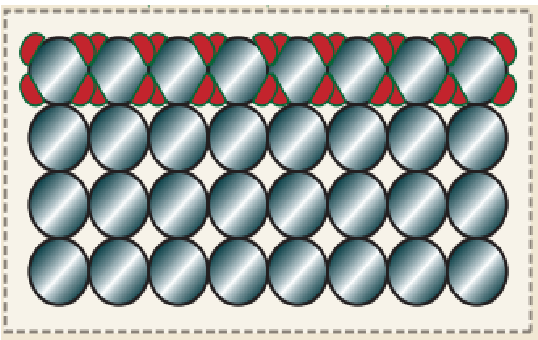


Figure 4-Deposition in catalyst particles

The pressure drop sue to the fouling sources is of greater extent than that caused by the inherent sources. There are three major fouling sources as mentioned below:

- Particulates (e.g. Iron sulfides, phosphate products and carbon particles)
- Organic species (e.g. olefins/diolefins, metal naphthanetes, asphaltenes)
- Coke formation (due to insufficient hydrogen, maldistribution, high bed temperature)

In our particular case the first two are causes are ruled out as the feed entering the HTS converter is free of sulfides, chlorides and other contaminants. However, the coke formation cannot be neglected and need further investigations.

2.2.2 Addressing high pressure drop

The high pressure drop in the packed bed can be addressed by revising and making necessary changes to overcome the pressure drop due to both inherent sources and fouling sources. The following recommendations are suggested as proposed solution to the main problem statement of this project:

- Addressing Inherent source: Redesigning of the packed bed reactor as a monolithic reactor
- Addressing fouling source: Reducing coke formation by optimizing operational parameters

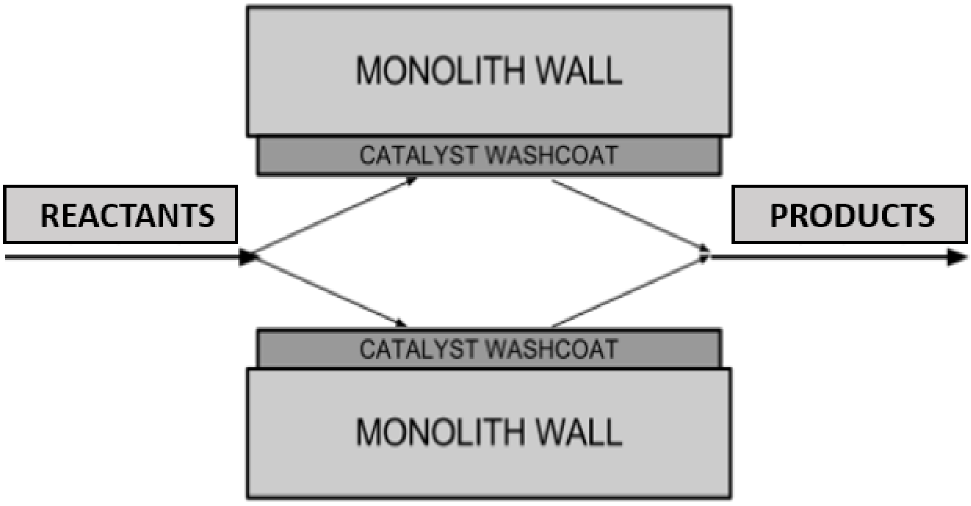
2.3 Monolith reactor

Structured reactors provide promising solution to the high pressure drop issue. Structured reactors or monolith reactors are also commonly known as honey-comb reactors. A monolithic structure consists of several parallel channels or cells. Mostly the monolith structures are made up of metal or ceramic material. The catalyst in the form of washcoat is deposited on the walls of monolith channels. The typical way of depositing washcoat on channel walls is to prepare the catalyst support or carrier (e.g. Alumina) and impregnate it with the catalyst particles followed by milling it in an aqueous media. Then the monolithic structure is dipped in the produced catalyst slurry. In this way catalyst washcoat is deposited on monolith channel walls.

Figure 5- Monolith Structure

The reactants in gas phase enter the monolith channels, react on the walls of the channel and the products flow towards the exit of the channel.

Figure 6- Schematic of reaction in monolith reactor channel



2.3.1 Advantages of Monolith reactors

Monolith reactors offer numerous advantages over convention packed bed reactors. The most important of them are mentioned below:

- They provide high geometric surface area
- High open frontal area
- High rates of mass transport
- Fast catalyst warm up
- High conversion
- Absolutely no attrition
- Laminar flow
- Ease of positioning
- Straight channels
- Extremely low pressure drop
- Low energy consumption

2.4 Reducing coke formation

In the study of water gas shift reaction, it has been observed that along with WGS there are many side reactions as well that have tendency to occur and these can significantly affect the process. The most common and most important of them being the Boudouard reaction which is given as:

$$2CO \rightleftharpoons C + CO_2$$

Temperature close to 300°C and the insufficient amount of steam during the reaction are the main factors that contribute to the boudouard reaction in which carbon monoxide converts to the solid carbon deposits also called coke. Hence, to reduce coke formation, boudouard reactions need to be eliminated. This can be done by the study of critical parameters that influence boudoudard reaction like temperature, gas-hourly space velocity and inlet steam to carbon ratio. Adjusting these parameters along with optimizing the CO conversion can solve the problem. The following plots obtained from previously performed studies were utilized to find the optimum values for the critical parameters.

2.4.1 Effect of gas-hourly space velocity (GHSV)

The following plot shows the change in CO conversion with varying GHSV at temperature of 400°C and inlet H_2O/CO ratio of 1.29 with the dashed line representing the thermodynamic equilibrium limit line. It can be seen that the maximum CO conversion takes place at GHSV of 50,000 h^{-1} without reaching the thermodynamic limit.

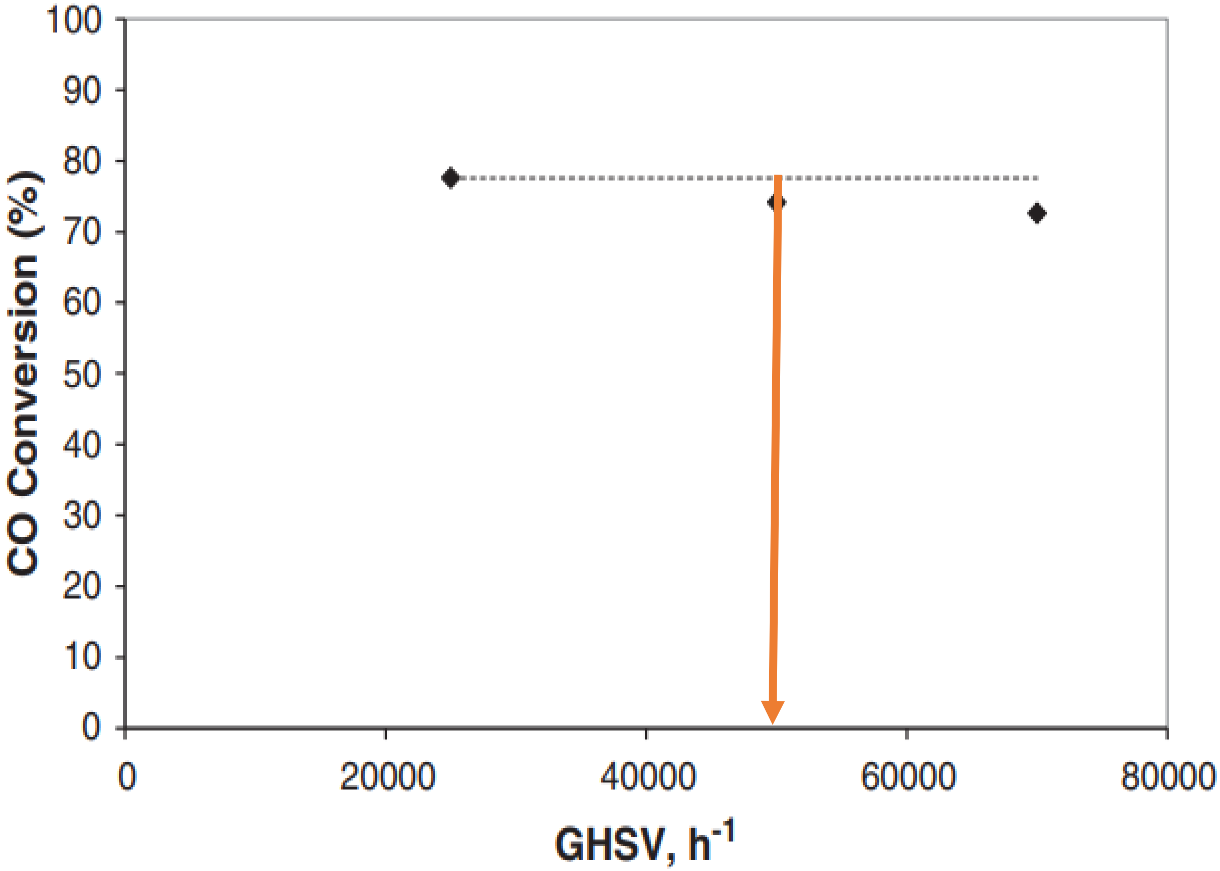


Figure 7- Change of CO conversion with GHSV

2.4.2 Effect of Temperature

The change in CO conversion with varying temperature is shown in the following plot at GHSV of 50,000 h^{-1} and inlet H_2O/CO ratio of 2 with the dashed line representing the thermodynamic equilibrium limit line. It can be seen that the maximum CO conversion takes place in the temperature range of 375 – 400 °C without reaching the thermodynamic limit.

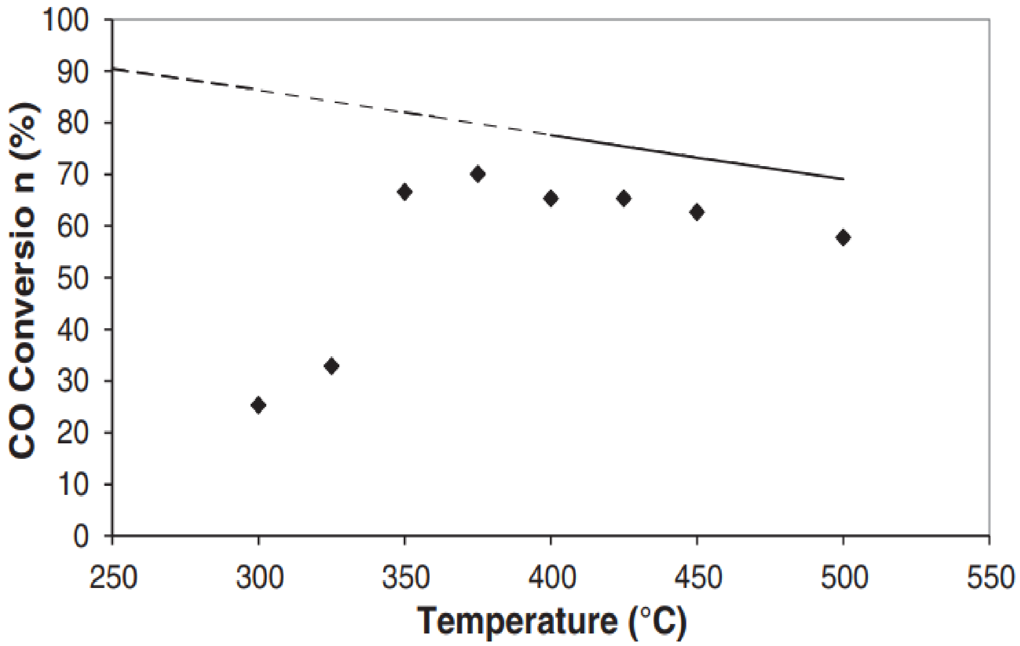


Figure 8 - Change in CO conversion with temperature

2.4.3 Effect of inlet H_2O/CO ratio

The change in CO conversion with varying H_2O/CO ratio is shown in the following plot at GHSV of 50,000 h^{-1} and temperature of 400 °C with the dashed line representing the thermodynamic equilibrium limit line. It can be seen that the maximum CO conversion takes place at the inlet H_2O/CO ratio of 2 without reaching the thermodynamic limit.

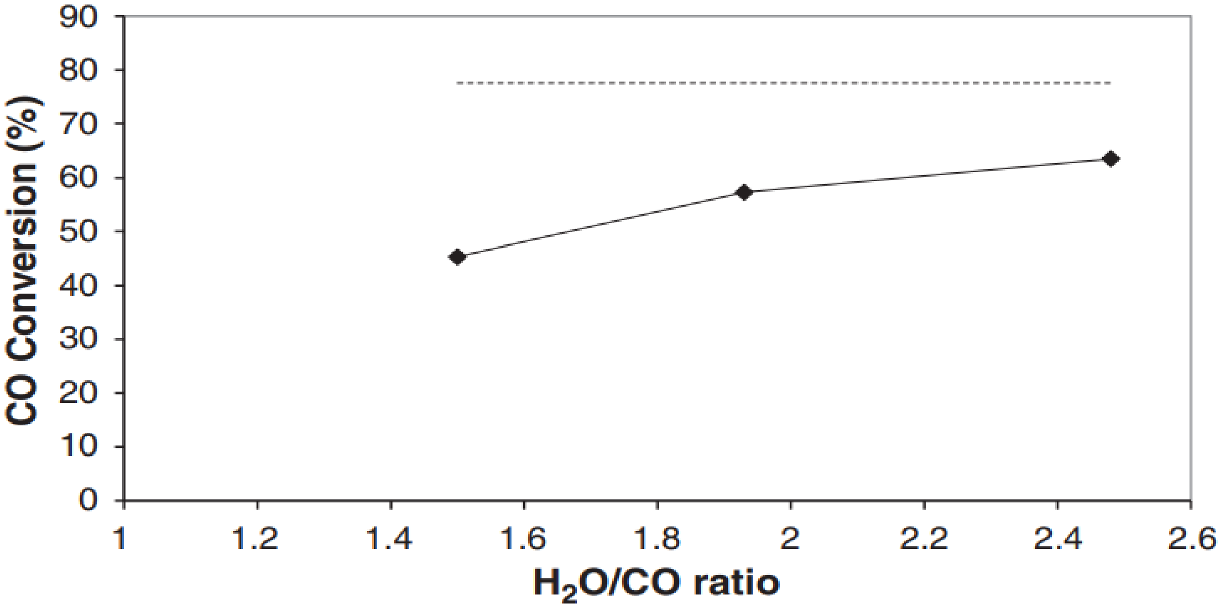


Figure 9 - Change of CO conversion with inlet steam/CO ratio

The values of the critical parameters to be used in the HTS converter for the maximum CO conversion and reduced coke formation are summarized in the following table:

Parameter	**Value**
Gas-hourly space velocity	50,000 h^{-1}
Temperature	375 – 400 ℃
Inlet steam/CO ratio	2

Table 3 - Values of critical parameters

Hence, with monolith reactor and reduced coke formation, the objectives of the project can be achieved.

CHAPTER 3

PROCESS DESCRIPTION

3.1 Hydrogen production process

In Attock Refinery Limited (ARL), hydrogen is produced by steam reforming of light naphtha followed by water gas shift reaction. Light naphtha is the substance having boiling point in the range of 30°C to 90°C and having the hydrocarbon compounds with up to 5-6 carbon atoms. The major steps in production process are discussed next.

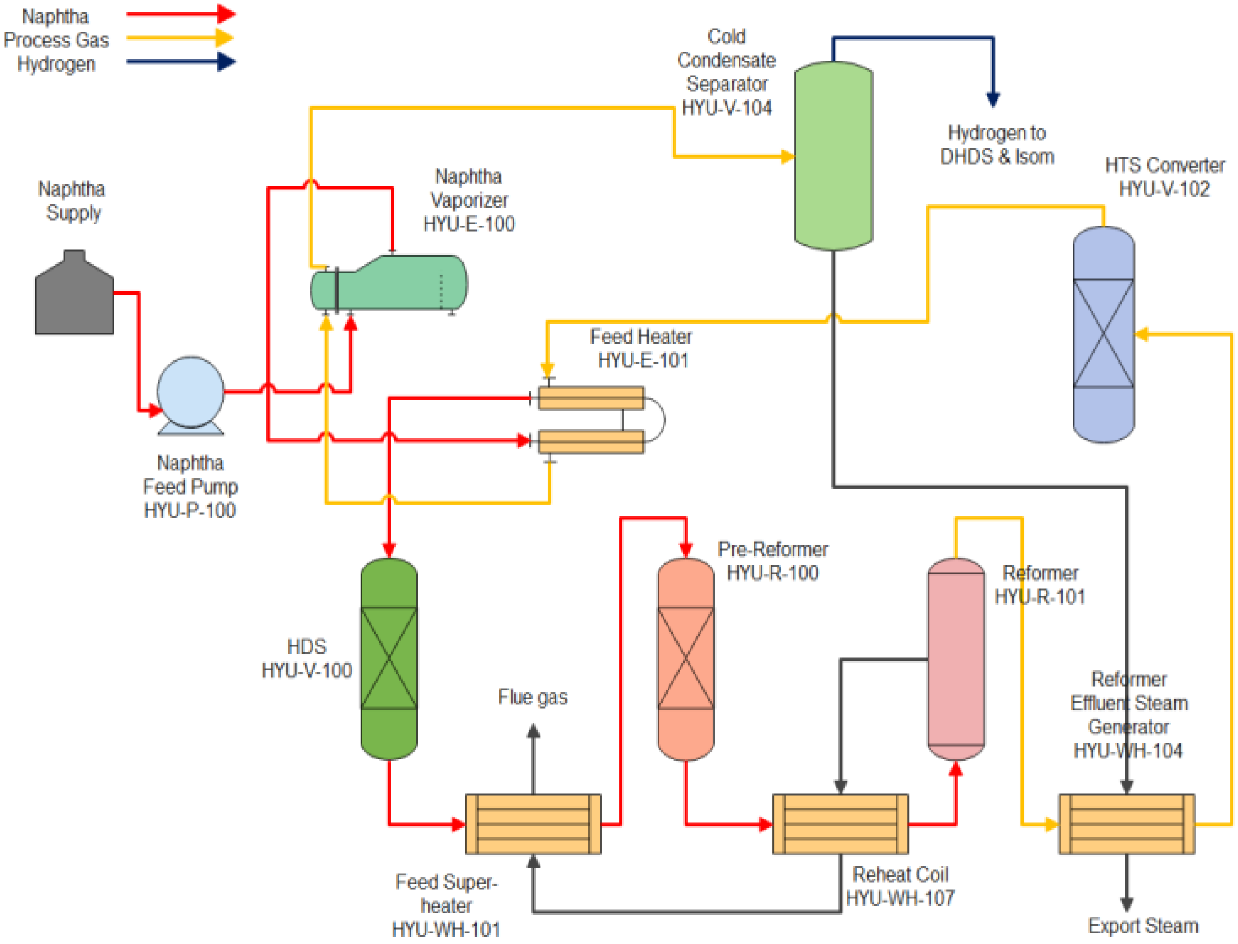


Figure 10 - Process Flow Diagram

3.1.1 Feed Treatment and feed heating

Naphtha liquid is supplied to the plant as main feedstock. Naphtha is supplied to the plant as process feed. Naphtha is pumped by the Naphtha Feed Pumps (HYU-P-100A&B) to the Naphtha Feed Vaporizer (HYU-E-100). Naphtha is vaporized using process gas. The blowdown from the vaporizer is cooled by the Naphtha Fuel Cooler (HYU-E-111) and sent to the burner as fuel. The vaporized naphtha feed plus hydrogen is heated to 399°C in the Feed Heater (HYU-E-101) using the process gas entering the feed heater at around 418-431°C and exiting at 332-394°C.

3.1.2 Hydro-desulfurization

The feed then passes through the zinc oxide catalyst in the Desulfurizer vessels (HYU-V-101A&B). The hydrogen sulfide reacts with the zinc oxide to form zinc sulfide and is adsorbed by the catalyst. The zinc oxide removes the hydrogen sulfide by the following reaction:

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

3.1.3 Pre-Reforming

After sulfur removal the feed is mixed with superheated steam and then it is fed to the pre-reformer (HYU-R-100) at 450°C in the presence of Nickel catalyst. The following reactions takes place in the pre-reformer

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2$$

$$CO + H_2 \leftrightarrow CO + H_2O$$

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

This reaction is exothermic for naphtha feed and results in a temperature rise of 39°C. Following the pre-reformer operation, the process gas passes through the Reheat Coil (HYU-WH-107) exits at around 552°C.

3.1.4 Reforming

The heated process gas then is passed through the catalyst tubes in the Reformer (HYU-R-101). The reaction of hydrocarbon gas with excess steam in the presence of a nickel reforming catalyst produces hydrogen, carbon monoxide, carbon dioxide and methane. The reforming reaction is represented by the following equation

Reforming reaction:

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

The reforming reaction is highly endothermic.
In addition to the reforming reaction, a partial water gas shift reaction occurs in the reformer furnace.

Water gas shift reaction:

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

Process gas leaves the reformer catalyst tubes at approximately 843°C.

3.1.5 Shift Conversion

The hot process gas exiting the Reformer (HYU-R-101) then flows to the reformer Effluent Steam Generator (HYU-WH-104). Here the outlet temperature is controlled to approximately 343°C for the correct operation of the shift converter. The process gas enters the high temperature Shift Converter (HYU-V-102), where in the presence of chromium promoted iron oxide catalyst, the water-gas shift reaction converts the carbon monoxide to carbon dioxide and hydrogen. There will be a temperature rise of approximately 75-88°C from the inlet to the outlet of the shift converter. The process gas will exit the shift converter at approximately 431°C.

3.1.6 Process Gas Cooling

The process gas from the shift converter flows through the Feed Heater (HYU-E101), where the stream is cooled down to 332-394°C. Then the process gas flows to the Naphtha Feed Vaporizer (HYU-E-100) to vaporize the naphtha feed. The process gas then enters the Shift Effluent Steam Generator (HYU-WH-105) where the stream is cooled to 232°C while generating process steam. Then the crude hydrogen flows to the Cold Condensate Separator (HYU-V-104) where the condensed moisture is removed from the crude hydrogen gas stream before it enters the PSA for purification.

3.1.7 PSA Hydrogen Purification System

The PSA system consists of four vessels which purify hydrogen using the pressure swing adsorption process. While under pressure, impurities are adsorbed onto various layers of adsorbents within the vessel and an ultra-pure Hydrogen product is obtained at the exit.

CHAPTER 4

MATERIAL BALANCE

In this chapter, we did material balance to find out the impact of naphtha feed on the plant. The manual calculations were done by hand and also used Aspen HYSYS for further improvements. Material balance on reactors and cold condensate separator was applied as they are the main units installed.

The material balance was carried out by assuming the plant to be at steady state, suggesting there is no accumulation.

Moreover, formulae and relevant equations are given where required and tables have been created to show input and output streams of raw materials and products. Material Balance is essential because this tells us about flow rates going in and coming out and about the equipment's performance to some extent and whether it is executing the required task. In this regard, we apply law of conservation of mass for material balance which states that mass can neither be created nor destroyed.

4.1. Material Balance on Reactors

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

1. The basis for the material balance was taken as 1 hour.
2. Steady state process was assumed meaning no accumulation.

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

Applying steady state process condition (Accumulation=0)

$$In - out = Generation - Consumption$$

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

$$Conversion(\%) = \frac{(Mass\ in\ feed\ stream - Mass\ in\ product\ stream)}{Mass\ in\ feed\ stream} \times 100\%$$

The feed composition of light naphtha is as follow:

Table 4 – Feed Composition

Components	Naphta Supply (kg/hr)
23-Mpentane	1.13
33-Mpentane	1.83
24-Mpentane	51.65
22-Mpentane	30.68
23-Mbutane	60.27
22-Mbutane	31.10
Cyclopentane	70.03
2-Mpentane	412.47
3-Mpentane	239.15
Mcyclopentan	327.05
Cyclohexane	714.34
Benzene	0
223-Mbutane	7.88
1-ci2-MCC5	8.96
3-Mhexane	2.25
2-Mhexane	7.88
E-Mercaptan	0.14
diE-Sulphide	0.12
Thiolane	5.82E-02
4-M-Pyridine	5.10E-03
Methylamine	3.00E-04
Total (Naphta)	**1967**

4.1.1. Hydro-desulfurizer (HYU-V-100)

The following reactions occur in the hydro-desulfurizer with their respective conversions shown as follow:

Conversion = 85 %

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$$

Conversion = 97 %

$$C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S$$

$$C_2H_5SC_2H_5 + 2H_2 \rightarrow 2C_2H_6 + H_2S$$

$$C_4H_8S + 2H_2 \rightarrow C_4H_{10} + H_2S$$

Conversion = 94 %

$$C_6H_7N + H_2 \rightarrow C_6H_{14} + NH_3$$

$$CH_3NH_2 + H_2 \rightarrow CH_4 + NH_3$$

Table 5 – Hydro-desulfurizer (HYU-V-100) Material Balance

Hydro-desulfurizer (HYU-V-100)		
Component	**Heated Feed + Steam (kg/hr)**	**HDS Exit (kg/hr)**
Hydrogen	10.1364	10.1239
Benzene	0	0
E-Mercaptan	0.1366	0.0041
diE-Sulphide	0.1190	0.0036
Thiolane	0.0582	0.0017
4-M-Pyridine	0.0051	0.0003
Methylamine	0.0003	0.00002
H2S	0	0.1381
Ammonia	0	0.0011
Naphtha	1966.681	1966.864
Total	**1977**	**1977**

4.1.2. Pre-Reformer (HYU-R-100)

The following reactions occur in the pre-reformer with their respective conversions shown below:

$$C_nH_m + 2nH_2O \leftrightarrow nCO_2 + \left[\frac{m+4n}{2}\right]H_2 \qquad \textit{Conversion = 100 \%}$$

$$CO_2 + 4H_2 \leftrightarrow CH4 + 2H_2O \qquad \textit{Conversion = 66.5\%}$$

Table 6 – Pre-Reformer (HYU-R-100) Material Balance

Pre-Reformer		
Component	**Pre-Reformer Feed (kg/hr)**	**Pre-Reformer Exit (kg/hr)**
Methane	0.0002	1478.63
Carbon Dioxide	0	2192.48
Carbon Monoxide	0	0
Hydrogen	10.12	91.76
Water	6774	4993.93
23-Mpentane	1.16	0
33-Mpentane	1.83	0
24-Mpentane	51.65	0
22-Mpentane	30.68	0
23-Mbutane	60.27	0
22-Mbutane	31.10	0
Cyclopentane	70.03	0
2-Mpentane	412.47	0
3-Mpentane	239.15	0
Mcyclopentane	327.05	0
Cyclohexane	714.34	0
223-Mbutane	7.88	0
1-ci2-MCC5	8.96	0
3-Mhexane	2.25	0
2-Mhexane	7.88	0
Total	**8751.22**	**8751.22**

4.1.3. Reformer (HYU-R-101)

The following reaction occur in the reformer with its conversion shown below:

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ *Conversion = 81.5 %*

Table 7 – Reformer (HYU-R-101) Material Balance

Reformer (HYU-R-101)		
Component	**Reformer Inlet (kg/hr)**	**Reformer Exit (kg/hr)**
Methane	1478.63	268.11
Carbon Dioxide	2192.48	2192.09
Carbon Monoxide	0	2126.24
Hydrogen	91.76	550.63
Water	4993.93	3611.99
Naphtha	-	-
Total	**8751.22**	**8751.22**

4.1.4. High Temperature Shift Converter (HYU-V-102)

The following reaction occur in the high temperature shift converter with its conversion shown below:

$CO + H_2O \leftrightarrow CO_2 + H_2$ *Conversion = 63 %*

Table 8 – HTS Converter (HYU-V-102) Material Balance

HTS Converter (HYU-V-102)		
	In	**Out**
Component	**HTS Feed (kg/hr)**	**HTS Exit (kg/hr)**
Methane	268.11	268.11
Carbon Dioxide	2192.09	4296.3
Carbon Monoxide	2126.239	786.997
Hydrogen	550.627	647
Water	3611.99	2750.66

Naphtha	-	-
Total	**8751.22**	**8751.22**

4.1.5. Material Balance on Cold Condensate Separator (HYU-V-104)

Table 9 – Cold Condensate Separator (HYU-V-104) Material Balance

Cold Condensate Separator (HYU-V-104)			
	In	**Out**	
Component	**Process Gas (kg/hr)**	**Hydrogen to DHDS (kg/hr)**	**Cold Condensate to Steam Generator (kg/hr)**
Methane	268.11	268.11	-
Carbon Dioxide	4296.32	4296.32	-
Carbon Monoxide	786.99	786.99	-
Hydrogen	647	647	-
Water Vapour	2750.66	31.67	-
Water Liquid	-	-	2718.93
Naphtha	-	-	-
Total	**8751.42**	**6032.49**	**2718.93**

CHAPTER 5

ENERGY BALANCE

In this chapter, energy balance of on the hydrogen plant using light naphtha was applied. The manual calculations were done by hand and also on excel sheet for further improvements. The end results were also compared with Aspen Hysys Simulation values for verification. Energy balance on pump, heat exchangers and reactors 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 being 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 Cp, Cv, average temperatures etc.).

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:

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

$$E_k = E_p = 0$$

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

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

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

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

$$H_T = \int C_p * dt \ (\text{kJ/hr})$$

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

$$C_p(mixture) = x_a C_{p,a} + x_b C_{p,b} + x_c C_{p,c} + \cdots$$

5.2. Energy Balance on Reactors

5.2.1. Hydro-desulfurizer (HYU-V-100)

Sample Calculations:

The energy balance on hydro-desulfurizer is as follow:

$$\Delta H = \Delta H_{out} - \Delta H_{in} + \Delta H_{reaction}$$

Enthalpy of inlet stream in calculated by:

$$\Delta H_{in} = mCp\Delta T = 1977 \times 2.84 \times (399 - 25) = 2.1 \times 10^6\ KJ/hr$$

Similarly, enthalpy of outlet stream in calculated by:

$$\Delta H_{out} = mCp\Delta T = 1977 \times 2.77 \times (371 - 25) = 1.9 \times 10^6\ KJ/hr$$

Heat of reaction is calculated by from heat of combustions and extents of all the reactions taking place in the hydro-desulfurizer as mentioned in material balance.

$$\Delta H_{reaction} = \sum \varepsilon \Delta H_r$$

where,

$$\varepsilon = \frac{n_{out} - n_{in}}{|\gamma|} \quad \text{and} \quad \Delta H_r = \sum H_{c,reactants} - \sum H_{c,products}$$

From calculations,

$$\Delta H_{reaction} = -3.50 \times 10^2\ KJ/hr$$

Using the values of ΔH_{in}, ΔH_{out} and $\Delta H_{reaction}$

$\Delta H = 1.9 \times 10^6 - 2.1 \times 10^6 + (-3.50 \times 10^2) = -2.0 \times 10^5\ KJ/hr$

As, flow work is zero in case hydro-desulfurizer. Hence,

$Q = -2.0 \times 10^5\ KJ/hr$

Table 10 – Hydro-desulfurizer (HYU-V-100) Energy Balance

Hydro-desulfurizer (HYU-V-100)		
	In	**Out**
Parameters	**Heated Feed + Steam**	**HDS Exit**
Temperature (℃)	399	371
Pressure (KPa)	2082	2043

C_p (KJ/Kg. ℃)	2.84	2.77
Mass Flowrate (kg/hr)	1977	1977
ΔH (KJ/hr)	2.1E+6	1.9E+6
Heat of Reaction (KJ/hr)	-3.50E+2	
Q (KJ/hr)	-2.0E+5	
Q (KW)	**-55.55**	

5.2.2. Pre-Reformer (HYU-R-100)

In the same as done for the hydro-desulfurizer, energy balance calculations for pre-reformer were carried out and the results have been tabulated and shown below.

Table 11 – Pre-Reformer (HYU-R-100) Energy Balance

Pre-Reformer (HYU-R-100)		
	In	**Out**
Parameters	**Pre-Reformer Feed**	**Pre-Reformer Exit**
Temperature (℃)	464	503
Pressure (KPa)	1974	1935
C_p (KJ/Kg. ℃)	2.358	2.33
Mass Flowrate (kg/hr)	8751	8751
ΔH (KJ/hr)	9.1E+6	9.75E+6
Heat of Reaction (KJ/hr)	1.21E+6	
Q (KJ/hr)	1.86E+6	
Q (KW)	**516.67**	

5.2.3. Reformer (HYU-R-101)

In the same way, energy balance calculations for reformer were carried out and the results have been tabulated and shown below.

Table 12 – Reformer (HYU-R-101) Energy Balance

Reformer (HYU-R-101)		
	In	**Out**
Parameters	**Reformer Inlet**	**Reformer Exit**
Temperature (℃)	538	843
Pressure (KPa)	1867	1729
C_p (KJ/Kg. ℃)	2.366	2.69
Mass Flowrate (kg/hr)	8751	8751
ΔH (KJ/hr)	1.06E+7	1.93E+7
Heat of Reaction (KJ/hr)	1.60E+7	
Q (KJ/hr)	2.46E+7	
Q (KW)	**6833.33**	

5.2.4. High Temperature Shift Converter (HTS-V-102)

In the same way, energy balance calculations for HTS Converter were carried out and the results have been tabulated and shown below.

Table 13 – HTS Converter (HYU-V-102) Energy Balance

HTS Converter (HYU-V-102)		
	In	**Out**
Parameters	**HTS Feed**	**HTS Exit**
Temperature (℃)	343	431
Pressure (KPa)	16.0	15.8
C_p (KJ/Kg. ℃)	2.409	2.50
Mass Flowrate (kg/hr)	8751	8751
ΔH (KJ/hr)	6.67E+06	8.88E+6
Heat of Reaction (KJ/hr)	-1.96E+6	
Q (KJ/hr)	-2.49E+5	
Q (KW)	**-69.44**	

5.3. Energy Balance on Heat Exchangers

Energy balance was used to work out the heat loads involved in each heat exchanger employed for the process.

The basic equation in use for all the following cases is:

$$H = mC_p\Delta T$$

$$Q = \Delta H$$

$$\sum Q_{hot} = \sum Q_{cold}$$

5.3.1. Naphtha Vaporizer (HYU-E-100)

Table 14 – Naphtha Vaporizer (HYU-E-100) Energy Balance

Naphtha Vaporizer (HYU-E-100)				
	Shell Side		**Tube Side**	
Parameters	**Naphtha from Pump**	**Vaporized Naphtha**	**Process Gas from Feed Heater**	**Process gas to condensate separator**
Temperature (℃)	47	269	389	328
Pressure (KPa)	2337	2200	1631	1612
C_p (KJ/Kg. ℃)	2.05	3.144	2.48	2.44
Mass Flowrate (kg/hr)	1967	1967	8752	8752
H (KJ/hr)	8.87E+4	1.51E+6	7.90E+6	6.48E+6
ΔH (KJ/hr)	1.42E+6		-1.42E+6	
Q (KW)	**394.4**		**-394.4**	

5.3.2. Feed Heater (HYU-E-101)

Table 15 – Feed Heater (HYU-E-101) Energy Balance

Feed Heater (HYU-E-101)				
	Shell Side		Tube Side	
Parameters	**Process Gas from HTS**	**Process Gas to Naphtha Vaporizer**	**Feed + H2**	**Heated Feed**
Temperature (℃)	431	389	249	399
Pressure (KPa)	1651	1631	2102	2082
C_p (KJ/Kg. ℃)	2.497	2.48	2.53	2.84
Mass Flowrate (kg/hr)	8752	8752	1977	1977
H (KJ/hr)	8.87E+6	7.90E+6	1.12E+6	2.10E+6
ΔH (KJ/hr)	-9.72E+5		9.72E+5	
Q (KW)	**-270**		**270**	

5.3.3. Feed Super Heater (HYU-WH-101)

Table 16 – Feed Super Heater (HYU-WH-101) Energy Balance

Feed Super-heater (HYU-WH-101)				
	Shell Side		Tube Side	
Parameters	**Flue gas to super heater**	**Flue gas to steam generator**	**Feed + Steam**	**To Pre-reformer**
Temperature (℃)	908	792	246	464
Pressure (KPa)	1306	1248	2043	1974
C_p (KJ/Kg. ℃)	1.356	1.31	2.58	2.36
Mass Flowrate (kg/hr)	21,285	21,285	8751	8751
H (KJ/hr)	2.55E+07	2.14E+07	4.99E+06	9.07E+06
ΔH (KJ/hr)	-4.1E+06		4.1E+6	
Q (KW)	**-1138.9**		**1132.9**	

5.3.4. Reheat Coil (HYU-WH-107)

Table 17 – Reheat Coil (HYU-WH-107) Energy Balance

Reheat Coil (HYU-WH-107)				
	Shell Side		Tube Side	
Parameters	**Flue Gas from Reformer**	**Flue Gas to Feed Super-heater**	**Pre-reformer Exit**	**Reformer Inlet**
Temperature (℃)	930	908	503	538
Pressure (KPa)	1373	1306	1935	1867
C_p (KJ/Kg. ℃)	1.363	1.35	2.33	2.366
Mass Flowrate (kg/hr)	21285	21285	8751	8751
H (KJ/hr)	2.63E+07	2.54E+07	9.75E+06	1.06E+07
ΔH (KJ/hr)	-8.8E+05		8.8E+5	
Q (KW)	**-244.4**		**244.4**	

5.3.5. Reformer Effluent Steam Generator (HYU-WH-104)

Table 18 – Reformer Effluent Steam Generator (HYU-WH-104) Energy Balance

Reformer Effluent Steam Generator (HYU-WH-104)				
	Shell Side		Tube Side	
Parameters	**Cold Condensate**	**Export Steam**	**Reformer Exit**	**HTS Inlet**
Temperature (℃)	171	208	843	343
Pressure (KPa)	811	1867	1729	1670
C_p (KJ/Kg. ℃)	4.42	2.14	2.69	2.409
Mass Flowrate (kg/hr)	5274	5274	8751	8751
H (KJ/hr)	2.50E+6	1.45E+07	1.93E+07	6.67E+06
ΔH (KJ/hr)	1.20E+07		-1.20E+07	
Q (KW)	**3333.3**		**-3333.3**	

5.4. Energy Balance on Pump

The main equation used for calculating the energy balance on pump is:

$$Q = \dot{m}\left(\Delta Z + \frac{\Delta P}{\rho g} + \Delta\frac{v^2}{2g}\right) + Q_{losses}$$

Ignoring elevations, changes in velocity and losses, and incorporating efficiency of pump, the equation is reduced to:

$$\eta Q = \dot{m}\left(\frac{\Delta P}{\rho}\right)$$

Required data and results tabulated as follows:

Table 19 – Pump Energy Balance

Naphtha Feed Pump (HYU-P-100)		
	In	**Out**
Parameters	**Naphtha Supply**	**Naphtha To Vaporizer**
Temperature (℃)	47	47
Pressure (Kpa)	196.12	2337
Density (kg/m3)	760.81	762.83
Mass Flowrate (kg/hr)	1967	1967
ΔH (KJ/hr)	5527.7	
W (KJ/hr)	5527.7	
Pump Efficiency	0.75	
Pump Duty (KW)	**2.047**	

CHAPTER 6

EQUIPMENT DESIGN

This section includes the design of the major equipment within the process. There are three key equipment designs tackled:

1. Reformer (HYU-R-101)
2. High Temperature Shift Converter (HYU-V-102)
3. Reformer Effluent Steam Generator (HYU-WH-104)

6.1. Reformer (HYU-R-101)

Reformer is a vertical, cylindrical, upflow and upfired 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. In the tubes of the Reformer, the hydrocarbon and steam are heated further and react in the presence of a nickel catalyst to produce a mixture of hydrogen, carbon dioxide, carbon monoxide, water, and methane. Tubes and Outer body are made of stainless steel which are bearable for the reactor pressure. Design calculations are given below:

6.1.1 Number of Tubes:

$$N = \frac{Q}{\pi \times ID \times L \times Q_{avg}} \quad --- (1)$$

$Where,$

$Q = 6594.2 \ {}^{KW}/_{m^2}$

$ID = 0.0953\, m$

$L = 12.8\, m$

$Q_{avg} = 45.68 \ {}^{KW}/_{m^2}$

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

$$N = \frac{6594.2}{\pi \times 0.0953 \times 12.8 \times 45.68}$$

$$N = 40\ tubes$$

6.1.2. Volume of Reactor:

$$V_r = \frac{\pi \times N \times ID^2 \times L}{4}$$

$$V_r = \frac{\pi \times 40 \times (0.0953)^2 \times 12.8}{4}$$

$$V_r = 3.71\ m^3$$

6.1.3. Volume of Catalyst:

$$Bulk\ Density\ of\ Catalyst = 787\ {}^{kg}/_{m^3}$$

$$Voidage = \varepsilon = 0.03$$

$$\varepsilon = \frac{V_r - V_c}{V_r}$$

$$0.03 = \frac{3.71 - V_c}{3.71}$$

$$V_c = 3.65\ m^3$$

6.1.4. Weight of Catalyst:

$$Weight\ of\ Catalyst = Bulk\ Density \times Volume\ of\ Catalyst$$

$$Weight\ of\ Catalyst = 787 \times 3.65$$

$$Weight\ of\ Catalyst = 2872\ kg$$

6.1.5. Space Velocity:

$$Space\ Velocity = \frac{Volumetric\ Feed\ Flow\ Rate}{Volume\ of\ reactor}$$

$$Space\ Velocity = \frac{3315.15}{3.71 \times 3600}$$

$$Space\ Velocity = 0.25\ s^{-1}$$

6.1.5. Design Summary:

Table 20 – Design Summary Reformer

Design Specifications		
Material of Construction	**SS Grade-304**	
Reactor Type	**Tubular Reactor**	
Parameters	Specs	Units
Weight of Catalyst	2872	kg
Bulk Density of Catalyst	787	kg/hr
Volume of Catalyst	3.65	m^3
Voidage	0.03	-
Volume of Reactor	3.71	m^3
Space Velocity	0.25	s^{-1}

6.2. Reformer Effluent Steam Generator (HYU-WH-104):

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, tc and Tc, are calculated. 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.

6.2.1. Shell and Tube Heat Exchanger Design Calculations:

Table 21 – WH-104 Operating Conditions

Water (Shell)	Process Gas (Tubeside)
$K = 0.3438\ {}^{W}/_{m°\text{C}}$	$K = 0.148\ {}^{W}/_{m°\text{C}}$
$\mu = 0.0000757\ {}^{Ns}/_{m^2}$	$\mu = 0.0000258\ {}^{Ns}/_{m^2}$
$C_p = 3.88\ {}^{kJ}/_{kg°\text{C}}$	$C_p = 2.54\ {}^{kJ}/_{kg°\text{C}}$
$\rho = 843.47\ {}^{kg}/_{m^3}$	$\rho = 3.63\ {}^{kg}/_{m^3}$
$\dot{m} = 89{,}667\ {}^{kg}/_{hr}$	$\dot{m} = 8{,}752\ {}^{kg}/_{hr}$
$T_h = 217\ °\text{C}$	$T_h' = 816\ °\text{C}$
$T_c = 217\ °\text{C}$	$T_c' = 343\ °\text{C}$

6.2.2. Heat Duty

$$Q = \dot{m} C_p \Delta T$$

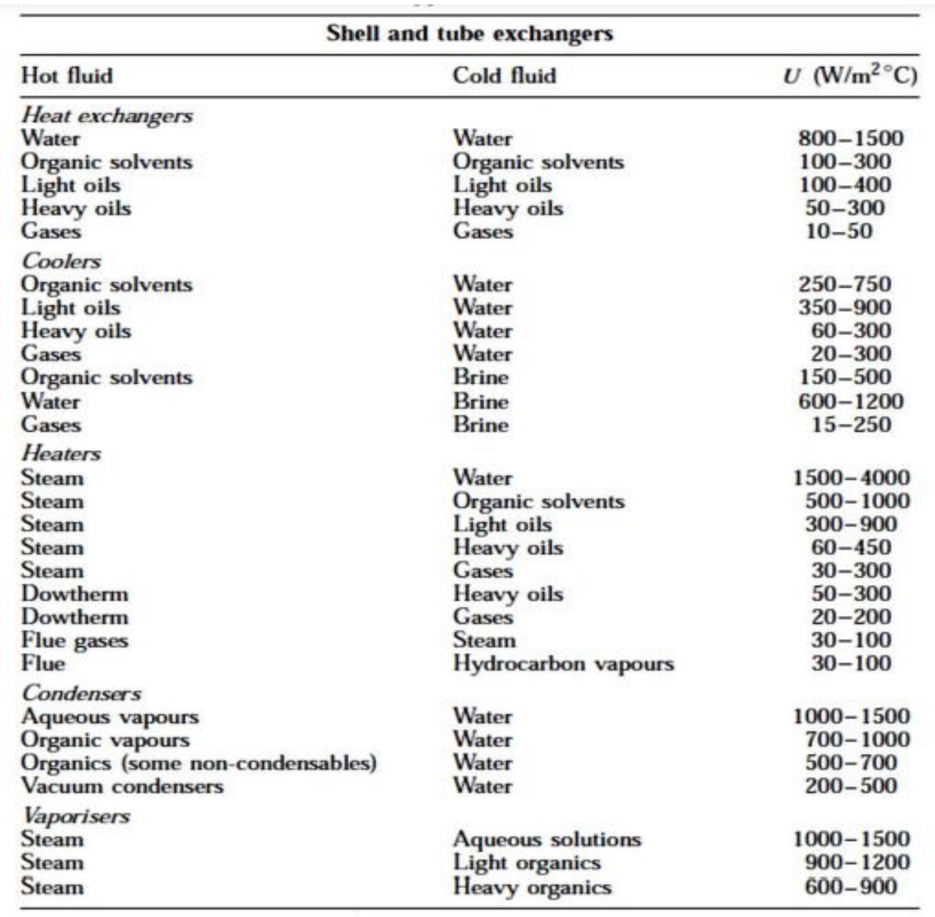
$$= 1.05e7\ {}^{kJ}/_{hr}$$

6.2.3. Logarithmic Mean Temperature Difference (LMTD):

$$LMTD = \frac{\theta_2 - \theta_1}{\ln\left(\frac{\theta_2}{\theta_1}\right)}$$

$$= 303°\text{C}$$

Table 22 – Overall Heat Transfer Coefficient



Shell and tube exchangers

Hot fluid	Cold fluid	U (W/m^2°C)
Heat exchangers		
Water	Water	800–1500
Organic solvents	Organic solvents	100–300
Light oils	Light oils	100–400
Heavy oils	Heavy oils	50–300
Gases	Gases	10–50
Coolers		
Organic solvents	Water	250–750
Light oils	Water	350–900
Heavy oils	Water	60–300
Gases	Water	20–300
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
Steam	Light organics	900–1200
Steam	Heavy organics	600–900

$U = 257\ {}^{W}\!/_{m^2C}$ from above table

Area

$$A = \frac{Q}{U\Delta T}$$

$$A = \frac{2{,}916{,}666}{257 \times 303} = 37.4m^2$$

$$Length\ of\ tube = L = 3.66\ m$$

$$Area\ of\ tube = a = \ \pi \times l \times d_o$$

$$a = \pi \times 3.66 \times 0.03 = 0.334m^2$$

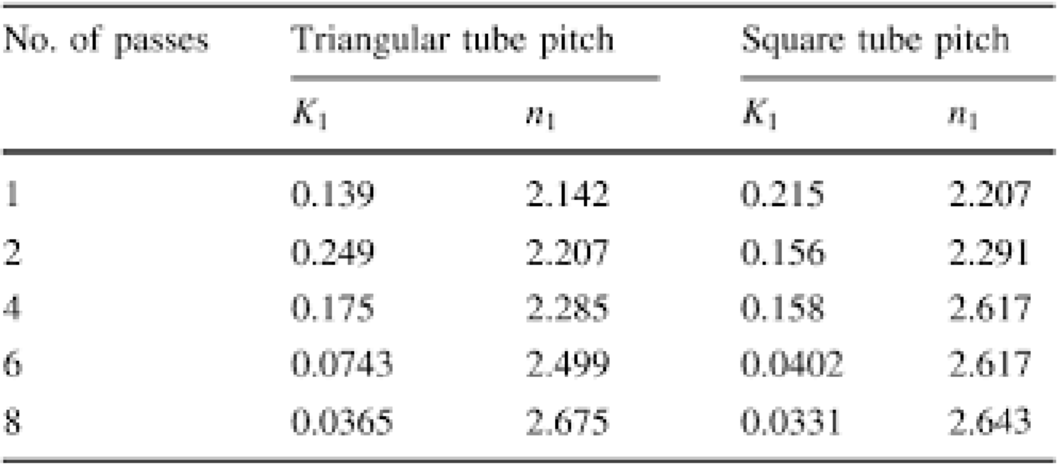
$$Number\ of\ tubes = N_t = \frac{A}{a} = 128\ tubes$$

For one tube passes, we find bundle diameter using table below:

$$Bundle\ Diameter = D_b = d_o\left(\frac{N_t}{K}\right)^{1/n_1}$$

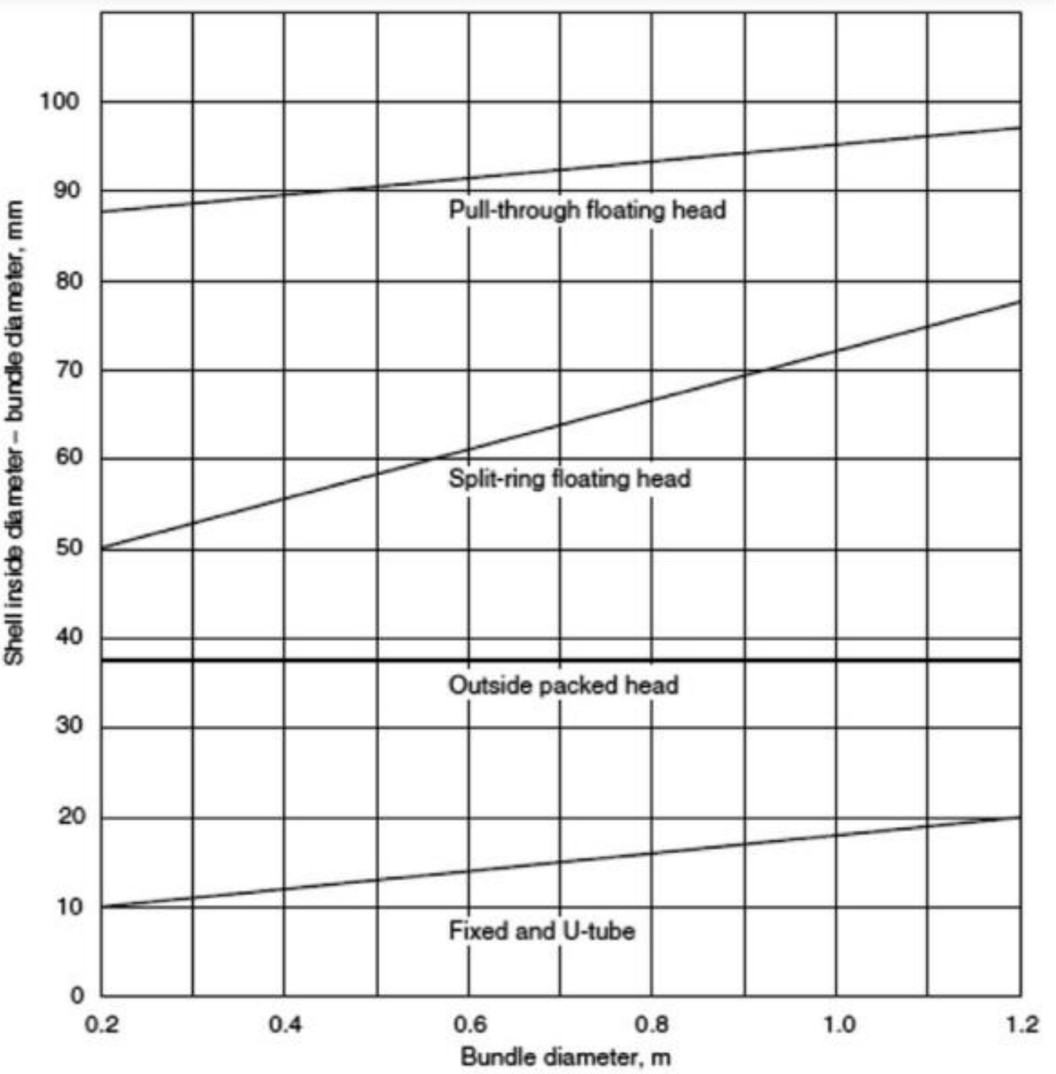
$$D_b = 0.03\left(\frac{128}{0.319}\right)^{1/2.142} = 0.36m$$

Table 23 – Pitch



No. of passes	Triangular tube pitch		Square tube pitch	
	K_1	n_1	K_1	n_1
1	0.139	2.142	0.215	2.207
2	0.249	2.207	0.156	2.291
4	0.175	2.285	0.158	2.617
6	0.0743	2.499	0.0402	2.617
8	0.0365	2.675	0.0331	2.643

Figure 11 – Clearance vs Bundle Dia



$Clearance\ =\ 0.093\ m$

6.2.4. Shell side co-efficient:

$$Baffle\ spacing\ (Ib)\ =\ 0.5\ \times\ ds\ =\ 0.343\ m$$

$$P_t\ =\ 1.25d_o = 0.0375m$$

$$A_s = \frac{(P_t - d_o) \times D_s}{P_t} = 0.137\ m^2$$

$$Mass\ Velocity = \frac{89{,}667}{0.137} = 6.54e5\ {}^{kg}/_{m^2 s}$$

$$D_e = \frac{1.10}{d_o}(P_t^2 - 0.917d_o^2) = 0.021\ m$$

$$R_e = 3959.2$$

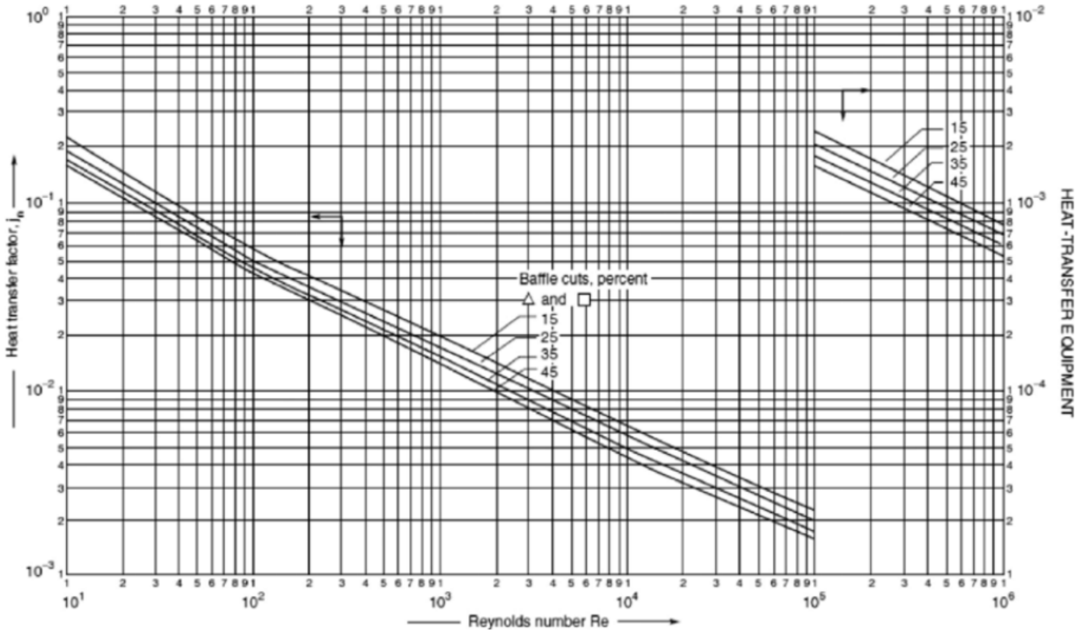


Figure 12 – Heat Transfer Factor for Shell

$$J_h = 0.008$$

$$P_r = \frac{\mu \times C_p}{k} = 8.57$$

$$\frac{h_o}{\theta_s} = \frac{j_h \times R_e \times Pr^{0.33} \times K_f}{De} = 1245\, {}^{W}/_{m^2{}^\circ\mathrm{C}} \quad ; \; \theta_s = 1$$

$$h_o = 1245\, {}^{W}/_{m^2{}^\circ\mathrm{C}}$$

6.2.5. Tube side Coefficient:

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

$$= 0.0005\, m^2$$

$$No.of\ tubes = 128$$

$$Total\ flow\ area = 128 \times 0{,}0005 = 0.07 m^2$$

$$Mass\ Velocity = \frac{8751}{0.07} = 1.25e5\, {}^{kg}/_{m^2 s}$$

$$R_e = \frac{D_i \times G_a}{\mu} = 72468$$

$$Pr = \frac{\mu \times C_p}{K} = \frac{\mathbf{2.58e - 4 \times 2.54}}{0.148} = 0.434$$

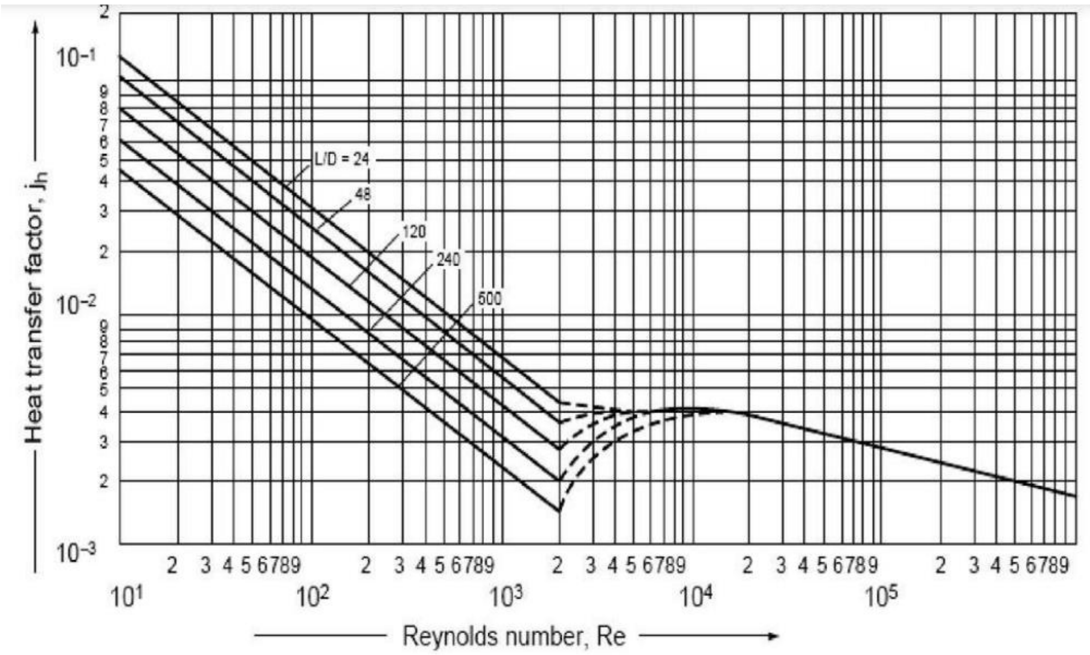


Figure 13 – Heat Transfer Factor for Tube

$$\frac{h_i}{\theta_t} = \frac{J_h \times R_e \times Pr^{0.33} \times K_f}{d_i} = 634 \, {}^{W}\!/_{m^2 {}^\circ\mathrm{C}}$$

6.2.6. Mean Wall Temperature θ_t:

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

$$h_i = 634 \, {}^{W}\!/_{m^2 {}^\circ\mathrm{C}}$$

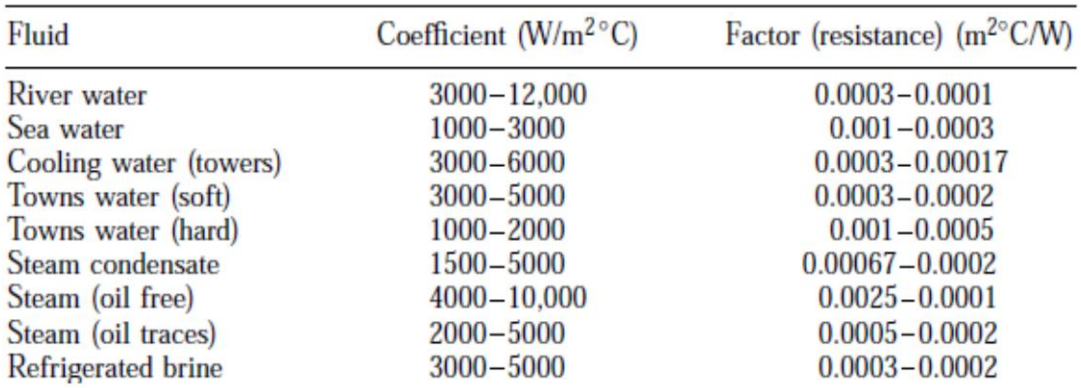
6.2.7. Overall Coefficient:

$$h_{io} = h_i \times \frac{ID}{OD} = 634 \times \frac{0.025}{0.03} = 508 \, {}^{W}\!/_{m^2 {}^\circ\mathrm{C}}$$

$$U_c = \frac{h_{io} \times h_o}{h_{io} + h_o} = 365 \, {}^{W}\!/_{m^2 {}^\circ\mathrm{C}}$$

$$For \; R_d = 0.003$$

Table 24 – Fouling Resistance



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

$$R_d = \frac{U_c - U_D}{U_D \times U_c}$$

$$U_D = 257\, {}^{W}\!/_{m^2 {}^\circ\mathrm{C}}$$

Since, in the given range so acceptable design.

6.2.8. Pressure Drop Calculations:

Shell Side:

$$\Delta P_s = 8 \times J_f \times \left(\frac{D_s}{d_e}\right) \times \left(\frac{L}{d_i}\right) \times \left(\frac{\rho\mu^2}{2}\right) \times \left(\frac{\mu}{\mu_w}\right)^{-0.14}$$

$$\Delta P_s = 8 \times 0.003 \times \left(\frac{0.685}{0.021}\right) \times \left(\frac{12.8}{0.025}\right) \times \left(\frac{\mathbf{3.63} \times .258^2}{2}\right) \times 1$$

$$= 9514.7 Pa = 1.38\ Psi$$

Tube Side:

$$\Delta P_t = N_p \left[8 \times J_H \times \frac{L}{d_i} \times \left(\frac{\mu}{\mu_w}\right)^{-m} + 2.5\right] \times \frac{\rho u_t^2}{2} = 16685.3\ Pa = 2.42\ psi$$

6.2.9. Design Summary:

Table 25 – Design Specifications of HYU-WH-104

Design Specifications		
Heat Exchange Type	**Shell & Tube HEX**	
Parameters	**Specs**	**Units**
No. of Tubes	128	Tubes
LMTD	303	℃

Baffle Spacing	1.6	in.
Tube OD	25	mm
Tube Passes	1	-
Shell Passes	2	-
Pitch	50.8	mm(Tri)
BWG	16	-
Duty	2912.5	kW
Design Overall Coefficient	257.37	W/ m^2.℃
Pressure Drop Shell Side	2.42	psi
Pressure Drop Tube Side	1.38	psi

6.3 High Temperature Shift Converter (HYU-V-102)

HTS converter is a packed bed reactor. the major design parameters are calculated below:

6.3.1. Volume of Reactor:

$$\boldsymbol{V_r} = (\boldsymbol{\pi D^2/4}) \times \boldsymbol{H}$$

$$V_r = \frac{\pi \times (1.3)^2 \times 3.3}{4}$$

$$V_r = 5.2\, m^3$$

6.3.2. Volume of Catalyst:

$$Bulk\ Density\ of\ Catalyst = 1105\ {}^{kg}/_{m^3}$$

$$Voidage = \varepsilon = 0.76$$

$$\varepsilon = \frac{V_r - V_c}{V_r}$$

$$0.03 = \frac{5.2 - V_c}{5.2}$$

$$V_c = 3.6\, m^3$$

6.3.3. Weight of Catalyst:

$$Weight\ of\ Catalyst = Bulk\ Density \times Volume\ of\ Catalyst$$

$$Weight\ of\ Catalyst = 1105 \times 3.6$$

$$Weight\ of\ Catalyst = 4000\ kg$$

6.3.4. Gas hourly Space Velocity:

$$Space\ Velocity = \frac{Volumetric\ Feed\ Flow\ Rate}{Volume\ of\ reactor}$$

$$Space\ Velocity = \frac{1892.32}{5.2}$$

$$Space\ Velocity = \ 363\ h^{-1}$$

6.3.5. Pressure drop:

The pressure drop in the packed bed reactor is given by the Ergun Equation as:

$$\frac{\Delta P}{L} = \frac{150\mu v_o}{{D_p}^2} \times \frac{1-\varepsilon^2}{\varepsilon^3} + \frac{1.75\rho_g v_o^2}{D_p} \times \frac{1-\varepsilon}{\varepsilon^2}$$

Where,

L = 3.3 m

μ = 0.02 cp

v_o = 0.4 m/s

D_p = 6 mm

ε = 0.16

ρ_g = 4.625 kg/m3

$$\Delta P = 147\ kPa$$

6.3.6. Design Summary:

Table 26 – Design Specifications HTS Converter

Design Specifications		
Material of Construction	**SS Grade-304**	
Reactor Type	**Tubular Reactor**	
Parameters	Specs	Units
Inlet flow rate	8751	Kh/hr
Weight of Catalyst	4000	kg
Bulk Density of Catalyst	1105	kg/hr
Volume of Catalyst	3.6	m^3

Bed volume	4.3	m^3
Voidage	0.76	-
Volume of Reactor	5.2	m^3
Height	3.3	m
Diameter	1.3	m
Space Velocity	363	h^{-1}
Pressure drop	147	kPa

6.3.6. Design of Monolithic HTS:

The monolithic HTS reactor is designed using the software called COMSOL Multiphysics 5.6.

Model specifications are as follow:

- Single Channel Model
- Cylindrical tube as channel
- Symmetric 2D geometry is assumed
- Catalyst as washcoat is deposited on walls of channels

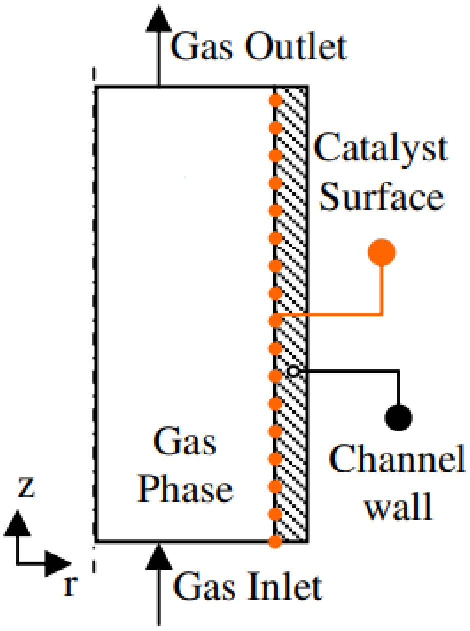


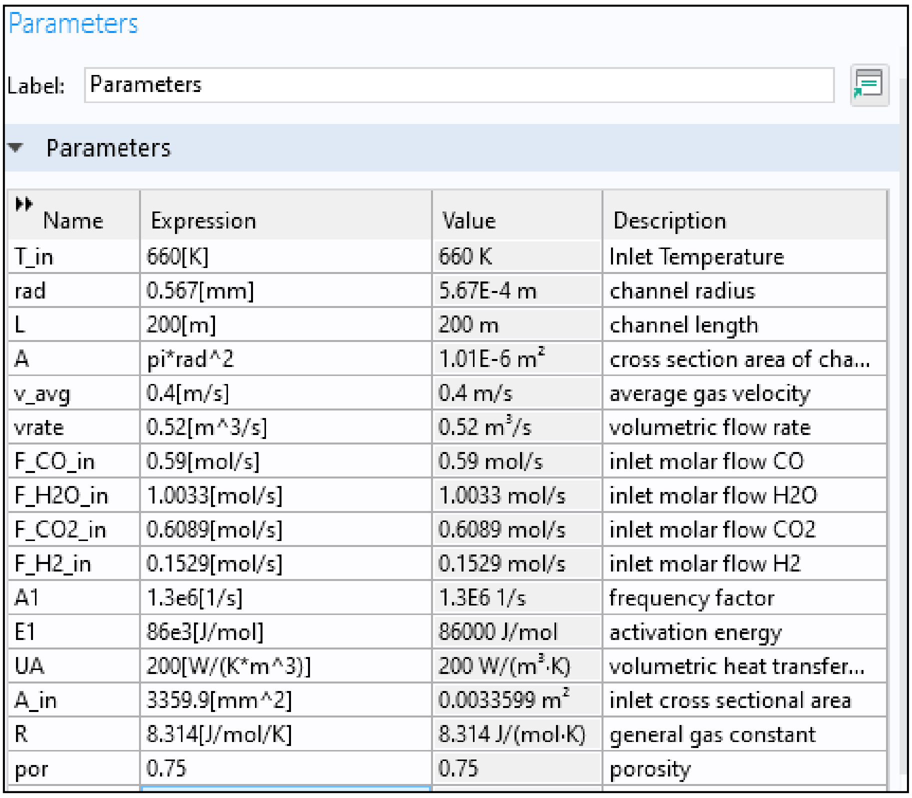
Figure 14 - Model Schematics

Parameter	Value
Channel Radius	0.567 mm
Washcoat Thickness	0.056 mm
Length	200 mm

Table 27 - Geometric Parameters

Following are some of the snap shots showing the development of model in COMSOL.

Figure 14 - Global Parameters



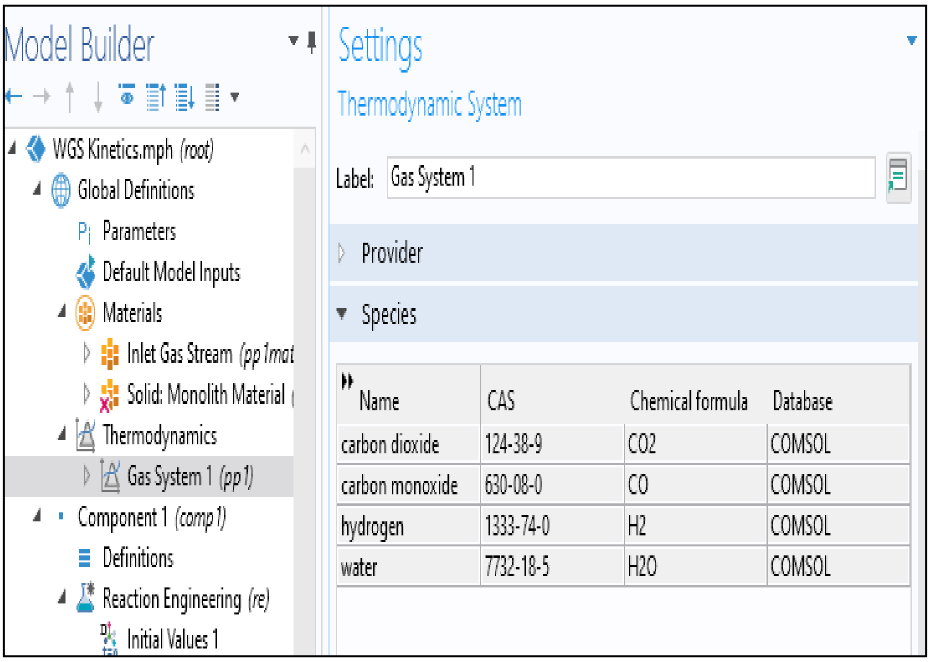
Parameters

Label: Parameters

Parameters

Name	Expression	Value	Description
T_in	660[K]	660 K	Inlet Temperature
rad	0.567[mm]	5.67E-4 m	channel radius
L	200[m]	200 m	channel length
A	pi*rad^2	1.01E-6 m^2	cross section area of cha...
v_avg	0.4[m/s]	0.4 m/s	average gas velocity
vrate	0.52[m^3/s]	0.52 m^3/s	volumetric flow rate
F_CO_in	0.59[mol/s]	0.59 mol/s	inlet molar flow CO
F_H2O_in	1.0033[mol/s]	1.0033 mol/s	inlet molar flow H2O
F_CO2_in	0.6089[mol/s]	0.6089 mol/s	inlet molar flow CO2
F_H2_in	0.1529[mol/s]	0.1529 mol/s	inlet molar flow H2
A1	1.3e6[1/s]	1.3E6 1/s	frequency factor
E1	86e3[J/mol]	86000 J/mol	activation energy
UA	200[W/(K*m^3)]	200 $W/(m^3 \cdot K)$	volumetric heat transfer...
A_in	3359.9[mm^2]	0.0033599 m^2	inlet cross sectional area
R	8.314[J/mol/K]	8.314 $J/(mol \cdot K)$	general gas constant
por	0.75	0.75	porosity

Figure 15- Gas System

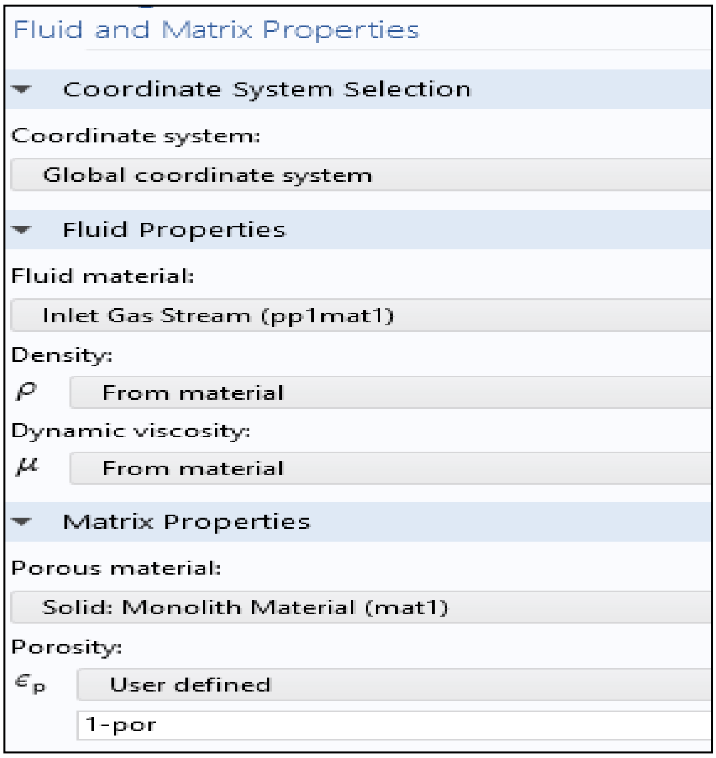


Thermodynamic System

Label: Gas System 1

Name	CAS	Chemical formula	Database
carbon dioxide	124-38-9	CO2	COMSOL
carbon monoxide	630-08-0	CO	COMSOL
hydrogen	1333-74-0	H2	COMSOL
water	7732-18-5	H2O	COMSOL

Figure 16- Fluid and Matrix properties



Coordinate system: Global coordinate system

Fluid material: Inlet Gas Stream (pp1mat1)

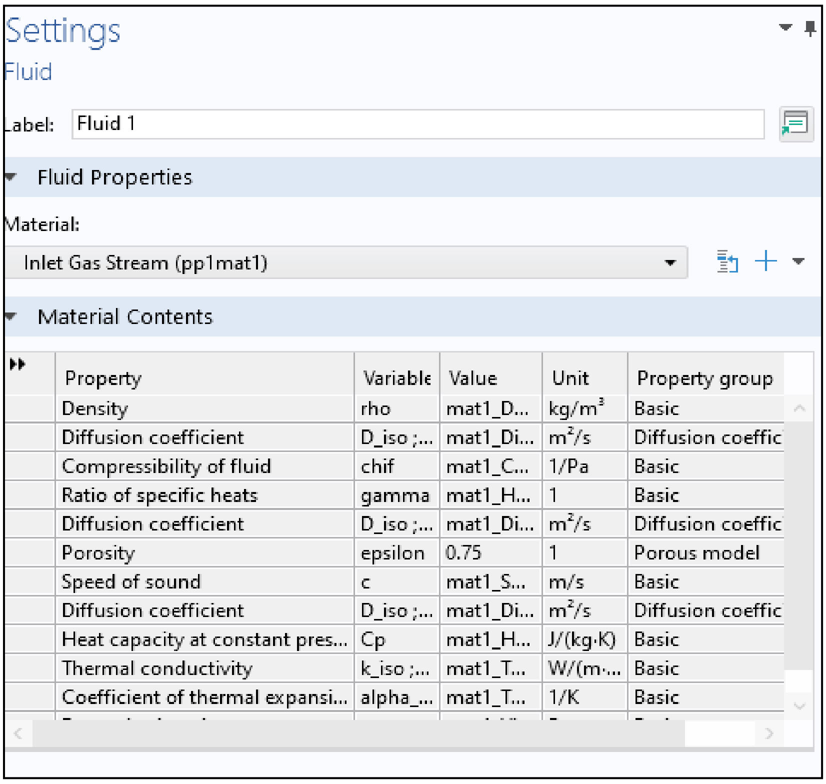
Density: ρ From material

Dynamic viscosity: μ From material

Porous material: Solid: Monolith Material (mat1)

Porosity: ϵ_p User defined 1-por

Figure 17 - Fluid Properties



Settings

Fluid

Label: Fluid 1

Fluid Properties

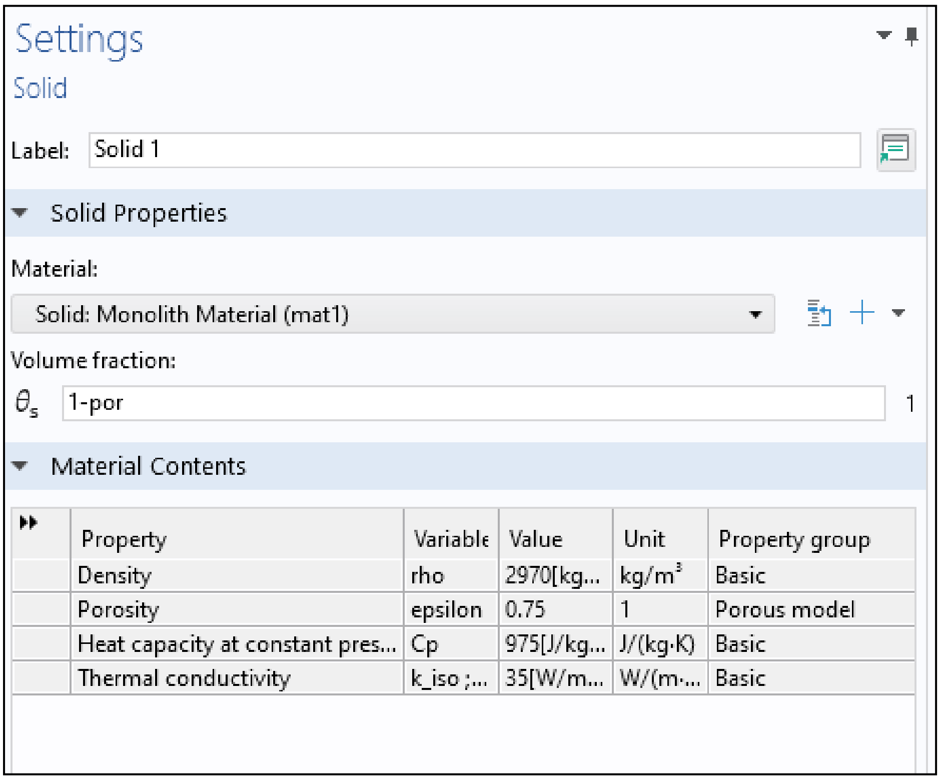
Material:

Inlet Gas Stream (pp1mat1)

Material Contents

Property	Variable	Value	Unit	Property group
Density	rho	mat1_D...	kg/m³	Basic
Diffusion coefficient	D_iso ;...	mat1_Di...	m²/s	Diffusion coeffic
Compressibility of fluid	chif	mat1_C...	1/Pa	Basic
Ratio of specific heats	gamma	mat1_H...	1	Basic
Diffusion coefficient	D_iso ;...	mat1_Di...	m²/s	Diffusion coeffic
Porosity	epsilon	0.75	1	Porous model
Speed of sound	c	mat1_S...	m/s	Basic
Diffusion coefficient	D_iso ;...	mat1_Di...	m²/s	Diffusion coeffic
Heat capacity at constant pres...	Cp	mat1_H...	J/(kg·K)	Basic
Thermal conductivity	k_iso ;...	mat1_T...	W/(m·...	Basic
Coefficient of thermal expansi...	alpha_...	mat1_T...	1/K	Basic

Figure 18 - Solid Properties



Settings

Solid

Label: Solid 1

Solid Properties

Material:

Solid: Monolith Material (mat1)

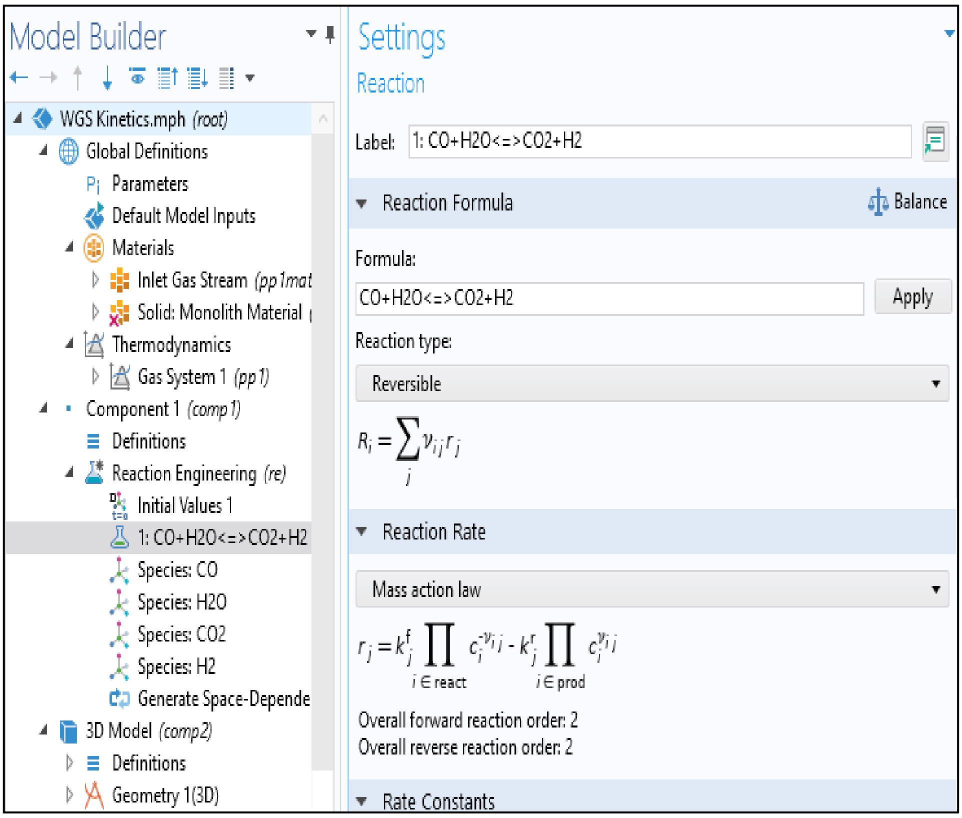
Volume fraction:

θ_s 1-por 1

Material Contents

Property	Variable	Value	Unit	Property group
Density	rho	2970[kg...	kg/m³	Basic
Porosity	epsilon	0.75	1	Porous model
Heat capacity at constant pres...	Cp	975[J/kg...	J/(kg·K)	Basic
Thermal conductivity	k_iso ;...	35[W/m...	W/(m·...	Basic

Figure 19 -Reaction kinetics



Label: 1: CO+H2O<=>CO2+H2

Formula: CO+H2O<=>CO2+H2

Reaction type: Reversible

$$R_i = \sum_j \nu_{ij} r_j$$

Mass action law

$$r_j = k_j^f \prod_{i \in \mathrm{react}} c_i^{-\nu_{ij}} - k_j^r \prod_{i \in \mathrm{prod}} c_i^{\nu_{ij}}$$

Overall forward reaction order: 2
Overall reverse reaction order: 2

Figure 20 - Physics Interfaces

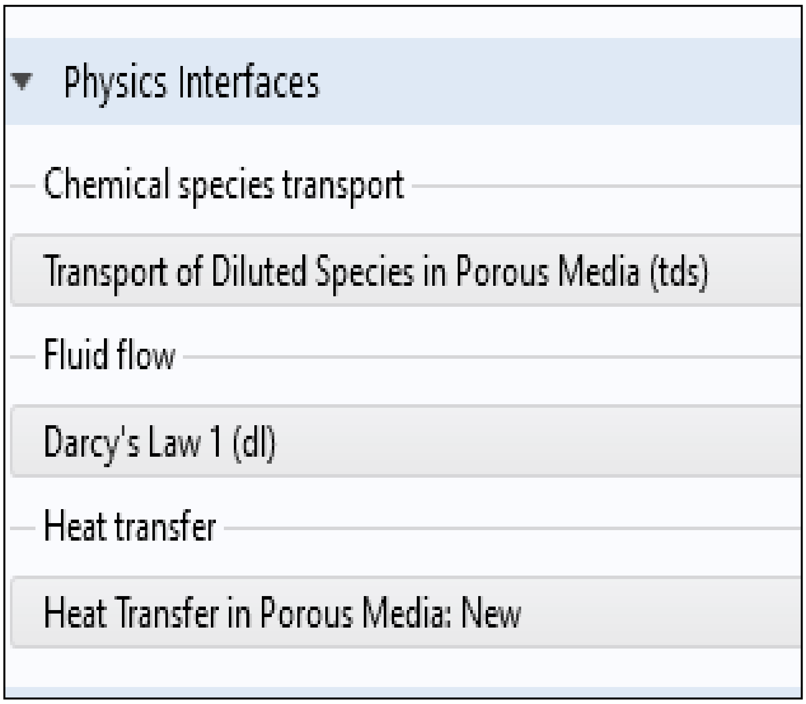


Figure 21 - Geometry Schematics

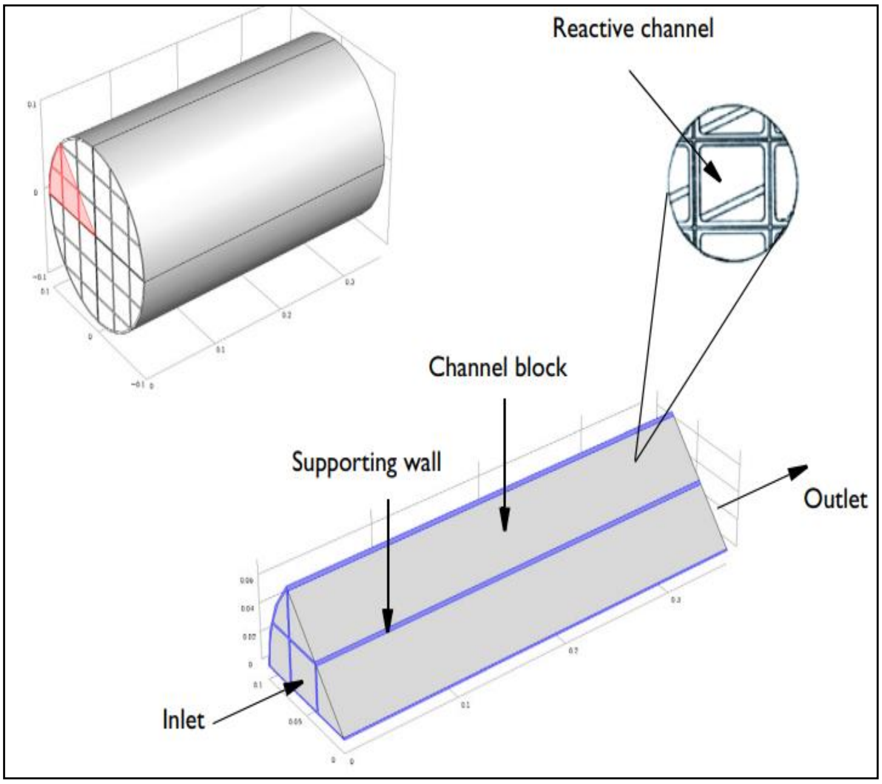


Figure 22 - Pressure Profile across single channel

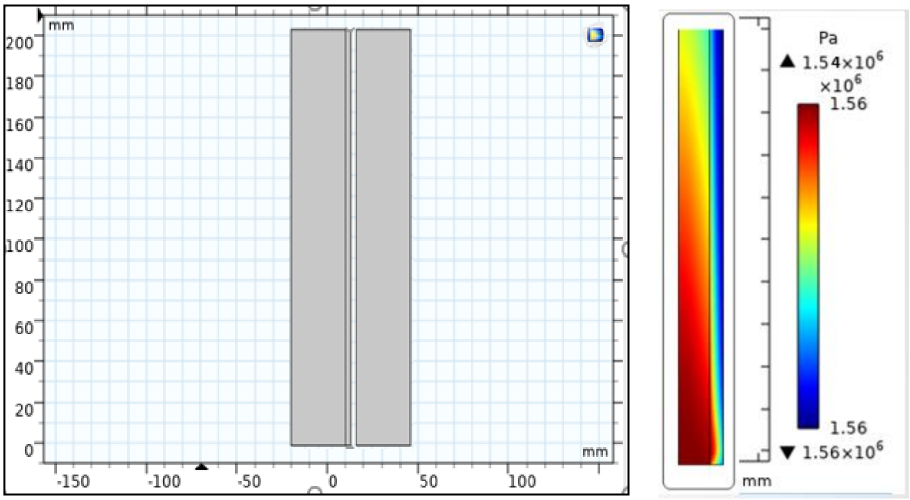


Table 28 - Design Specifications of Monolithic HTS

Design Specifications		
Material of Construction	Ceramics (cordierite)	
Reactor Type	Monolithic Reactor	
Parameters	**Specs**	**Units**
Inlet Flow Rate	8751	Kg/hr
Bulk Density	0.53	g/cm^3
Cells per square inch	200	$cpsi$
Inlet Temperature	387	℃
Steam/C Ratio	2	-
GHSV	5227	h^{-1}
Volume	3.8	m^3
Height	3.1	m
Diameter	1.24	m
GHSV	5227	h^{-1}
ΔP	29	kPa

CHAPTER 7

SIMULATION

The hydrogen plant was simulated with the help of Aspen HYSYS. The simulated Process Flow Diagram is shown below with temperature and pressure values at selected locations highlighted in numbers and their values tabulated in the diagram.

The results obtained were pretty close with the values which were calculated through material and energy balance and equipment design. The fluid package used in this simulation was the PRSV property package employing the Peng-Robinson equation model as referred from the literature, and the other main reason was the presence of sulphur compounds, employing other suitable fluid package resulted in loss of properties of compounds like thiolane etc. Conversion reactor was used and conversions were employed to reactions which were previously determined by the CoMo/Al2O3 catalyst.

7.1. Simulated Process Flow Diagram:

Figure 23 – Simulated Process Flow Diagram

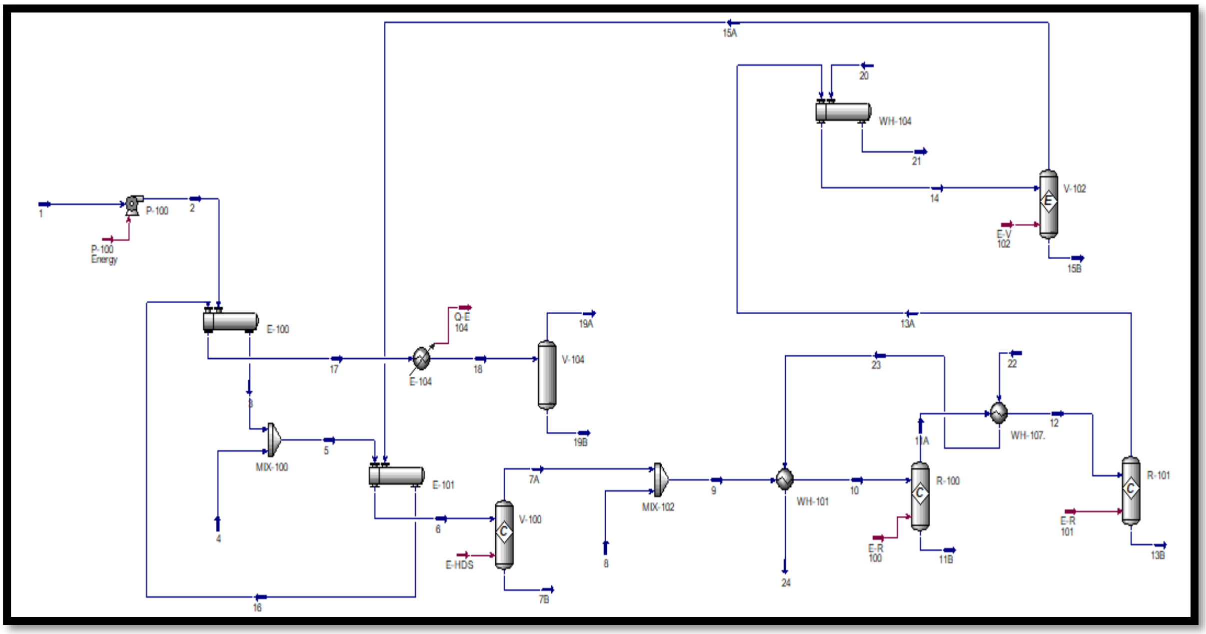
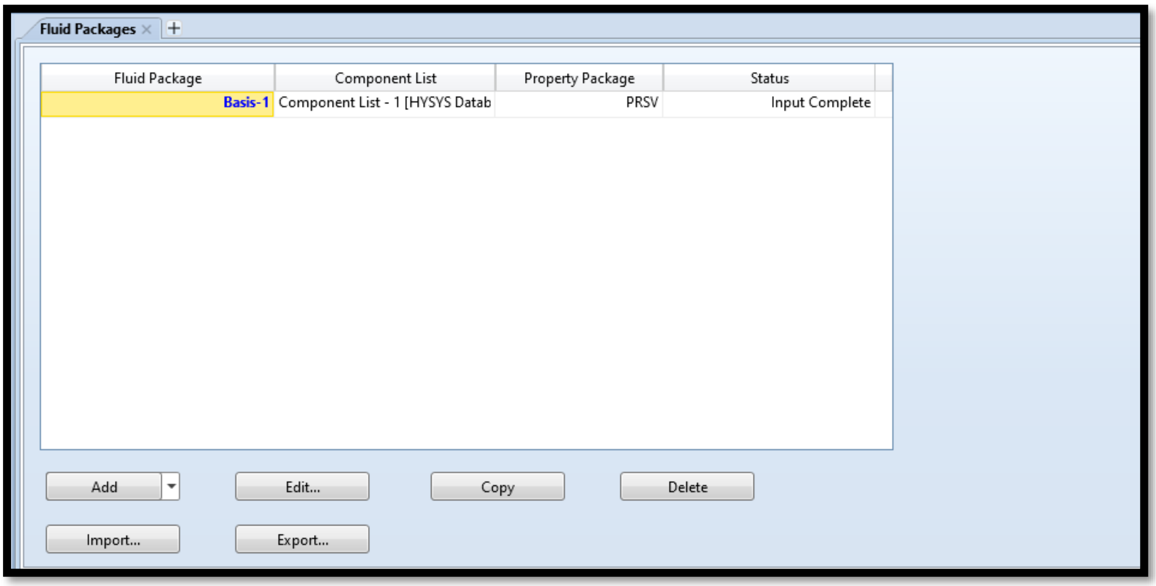
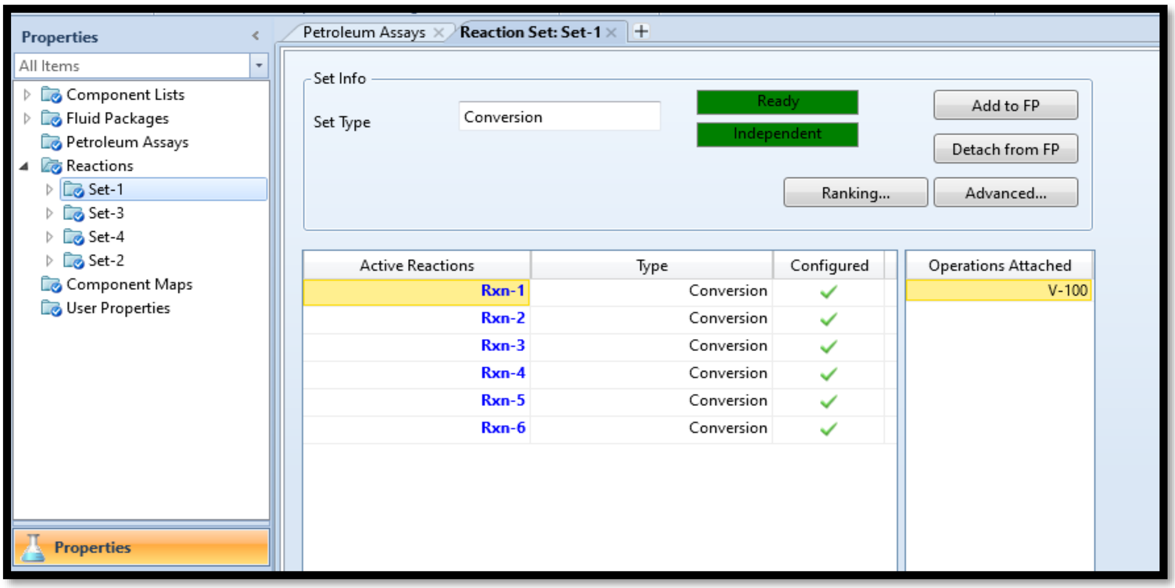


Figure 24 – Fluid Package



Fluid Package	Component List	Property Package	Status
Basis-1	Component List - 1 [HYSYS Datab	PRSV	Input Complete

Figure 25 – Reaction Set



Set Type: Conversion

Ready

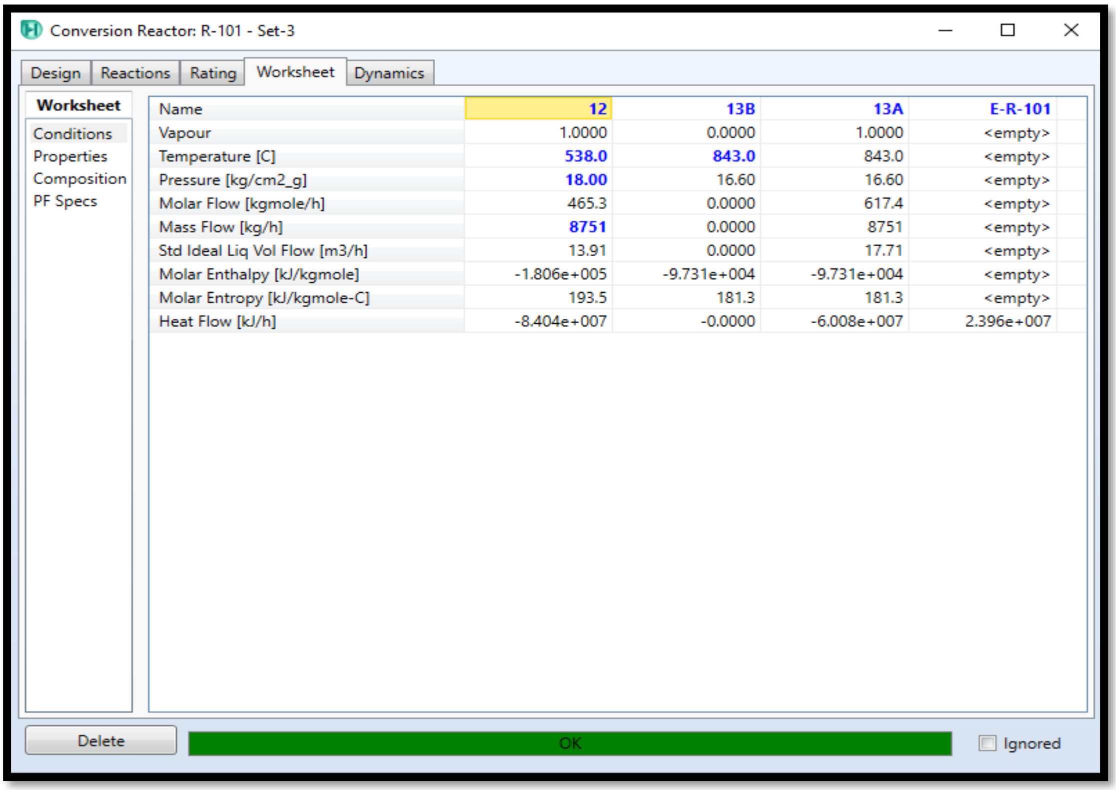
Independent

Active Reactions	Type	Configured
Rxn-1	Conversion	✓
Rxn-2	Conversion	✓
Rxn-3	Conversion	✓
Rxn-4	Conversion	✓
Rxn-5	Conversion	✓
Rxn-6	Conversion	✓

Operations Attached
V-100

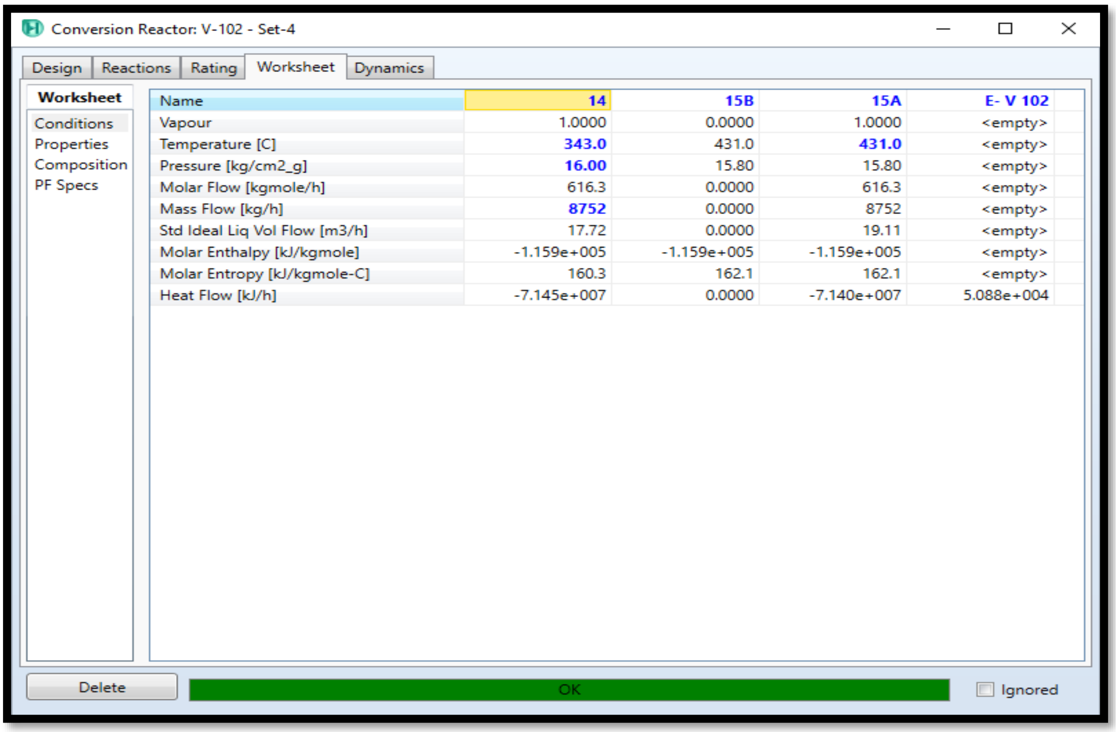
7.2. Reactors Worksheet:

Figure 26 – R-101 Aspen Worksheet



Name	12	13B	13A	E-R-101
Vapour	1.0000	0.0000	1.0000	<empty>
Temperature [C]	538.0	843.0	843.0	<empty>
Pressure [kg/cm2_g]	18.00	16.60	16.60	<empty>
Molar Flow [kgmole/h]	465.3	0.0000	617.4	<empty>
Mass Flow [kg/h]	8751	0.0000	8751	<empty>
Std Ideal Liq Vol Flow [m3/h]	13.91	0.0000	17.71	<empty>
Molar Enthalpy [kJ/kgmole]	-1.806e+005	-9.731e+004	-9.731e+004	<empty>
Molar Entropy [kJ/kgmole-C]	193.5	181.3	181.3	<empty>
Heat Flow [kJ/h]	-8.404e+007	-0.0000	-6.008e+007	2.396e+007

Figure 27 – V-102 Aspen Worksheet



Name	14	15B	15A	E- V 102
Vapour	1.0000	0.0000	1.0000	<empty>
Temperature [C]	343.0	431.0	431.0	<empty>
Pressure [kg/cm2_g]	16.00	15.80	15.80	<empty>
Molar Flow [kgmole/h]	616.3	0.0000	616.3	<empty>
Mass Flow [kg/h]	8752	0.0000	8752	<empty>
Std Ideal Liq Vol Flow [m3/h]	17.72	0.0000	19.11	<empty>
Molar Enthalpy [kJ/kgmole]	-1.159e+005	-1.159e+005	-1.159e+005	<empty>
Molar Entropy [kJ/kgmole-C]	160.3	162.1	162.1	<empty>
Heat Flow [kJ/h]	-7.145e+007	0.0000	-7.140e+007	5.088e+004

CHAPTER 8

ECONOMICS ANALYSIS

For a hydrogen production plant to be established there are several factors to be incorporated before the estimation of financial dependencies. These include, but are not limited to, required production for hydrogen, feed content required, number of necessary equipment's and types, catalytic requirements, utilities needed and many other.

In economic analysis of a chemical plant, first we work out to find fixed capital investment. This is the sum of direct costs and indirect costs. Direct costs include purchased equipment such as reactors, heat exchangers, pumps, etc. They also include installation of said equipment, piping, control and instruments, electrical equipment, buildings, site, facilities, and land. Whereas indirect costs include engineering which include admin, design, inspection etc.

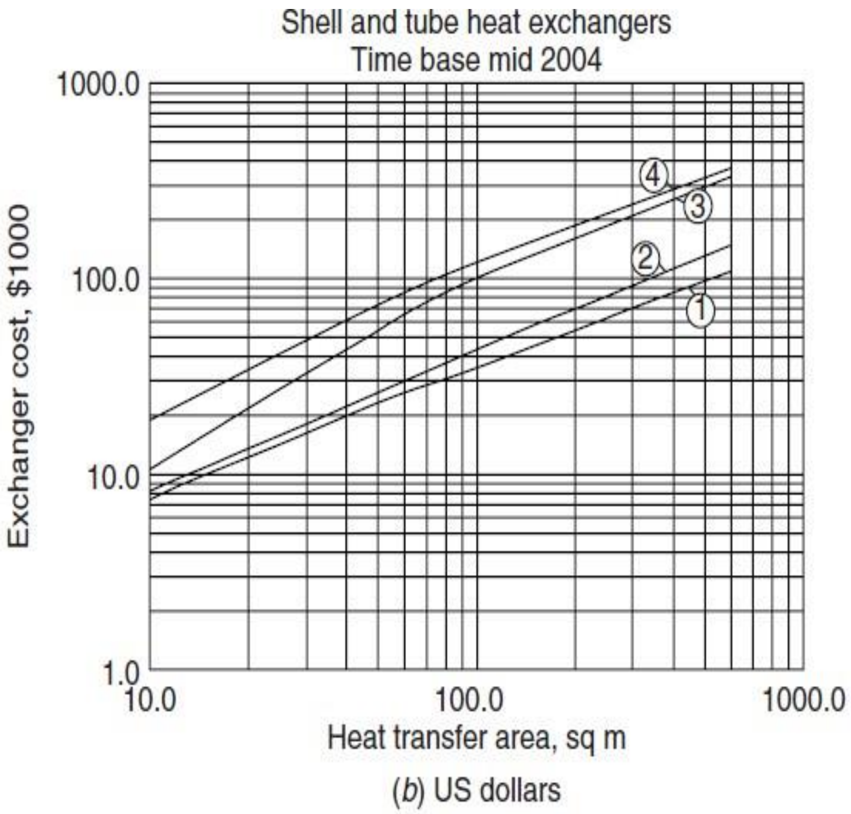
Capital and operating costs are the most essential factors for anyone considering any sort of chemical plant within refinery. An accurate cost estimation is an essential part of a plant foundation. There could be errors in estimation, however its margin can be reduced by a great amount depending on the degree of engineering design

8.1 Cost Estimations of Major Items of Equipment

The cost of major equipment is done from Coulson Richardson's Chemical Engineering Design Volume 6th. Graphs and tables used in cost estimation are attached with each equipment class.

The following graph helps in estimation of costs of Shell and Tube Heat Exchangers:

Figure 28 – Shell and Tube Heat Exchanger PCE



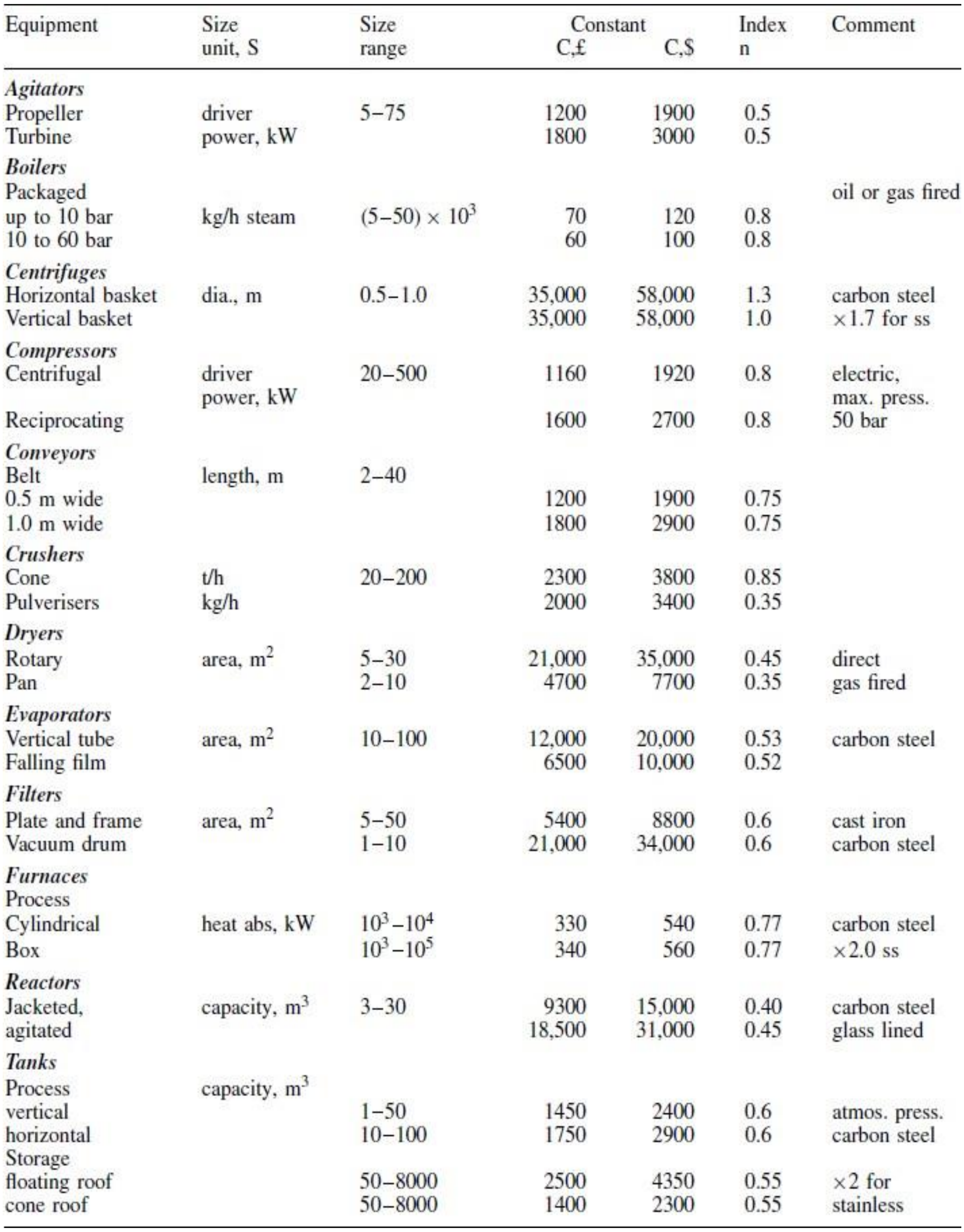
Materials	
Shell	Tubes
① Carbon steel	Carbon steel
② C.S.	Brass
③ C.S.	Stainless steel
④ S.S.	S.S.

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

The following table is used for estimation of cost of proprietary equipment:

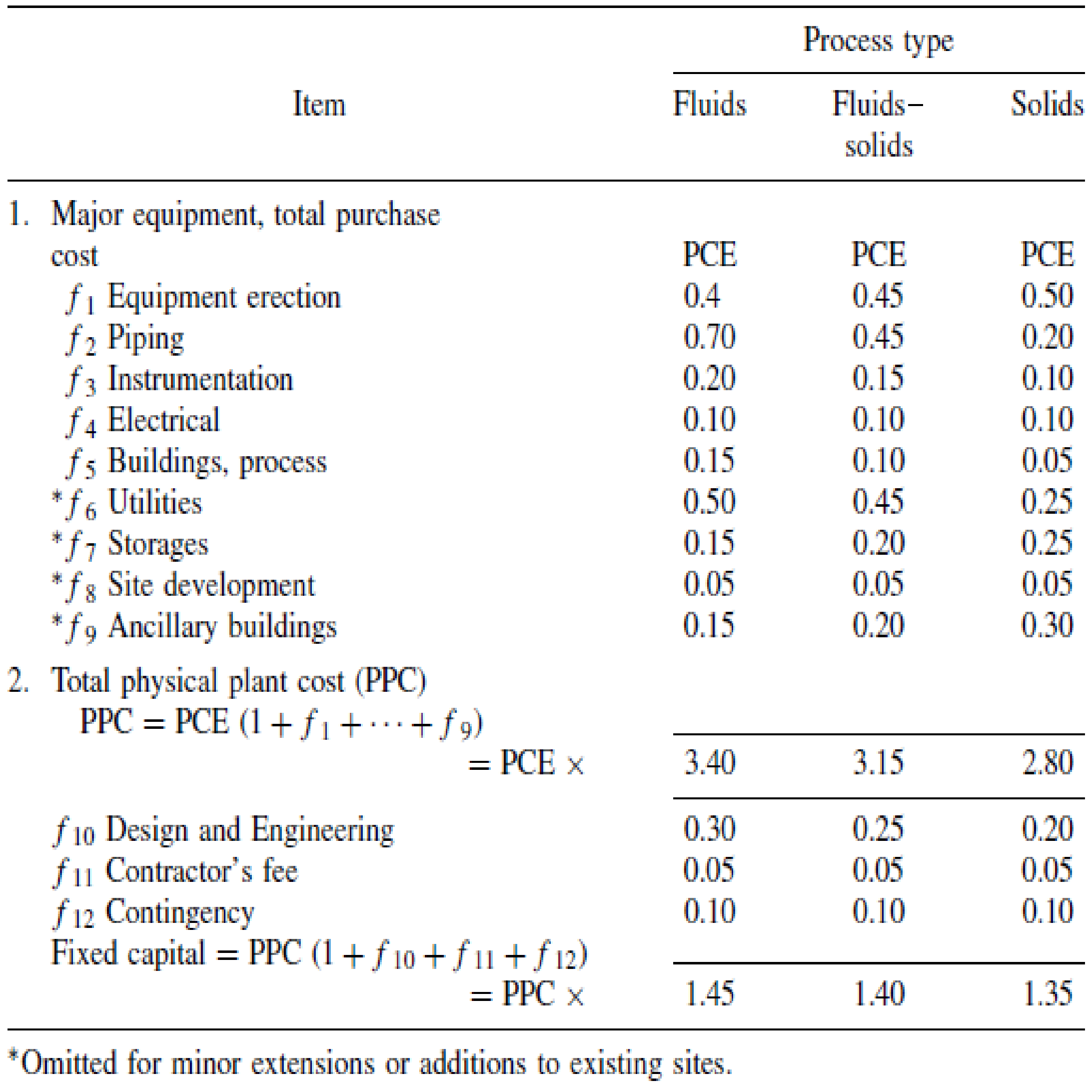
Table 29 – Proprietary Equipment Cost



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	$(5–50) \times 10^3$	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. 50 bar
Reciprocating			1600	2700	0.8	
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

The following table helps in estimation of costs of Project Fixed Capital Costs:

Table 30 – Fixed Capital Cost

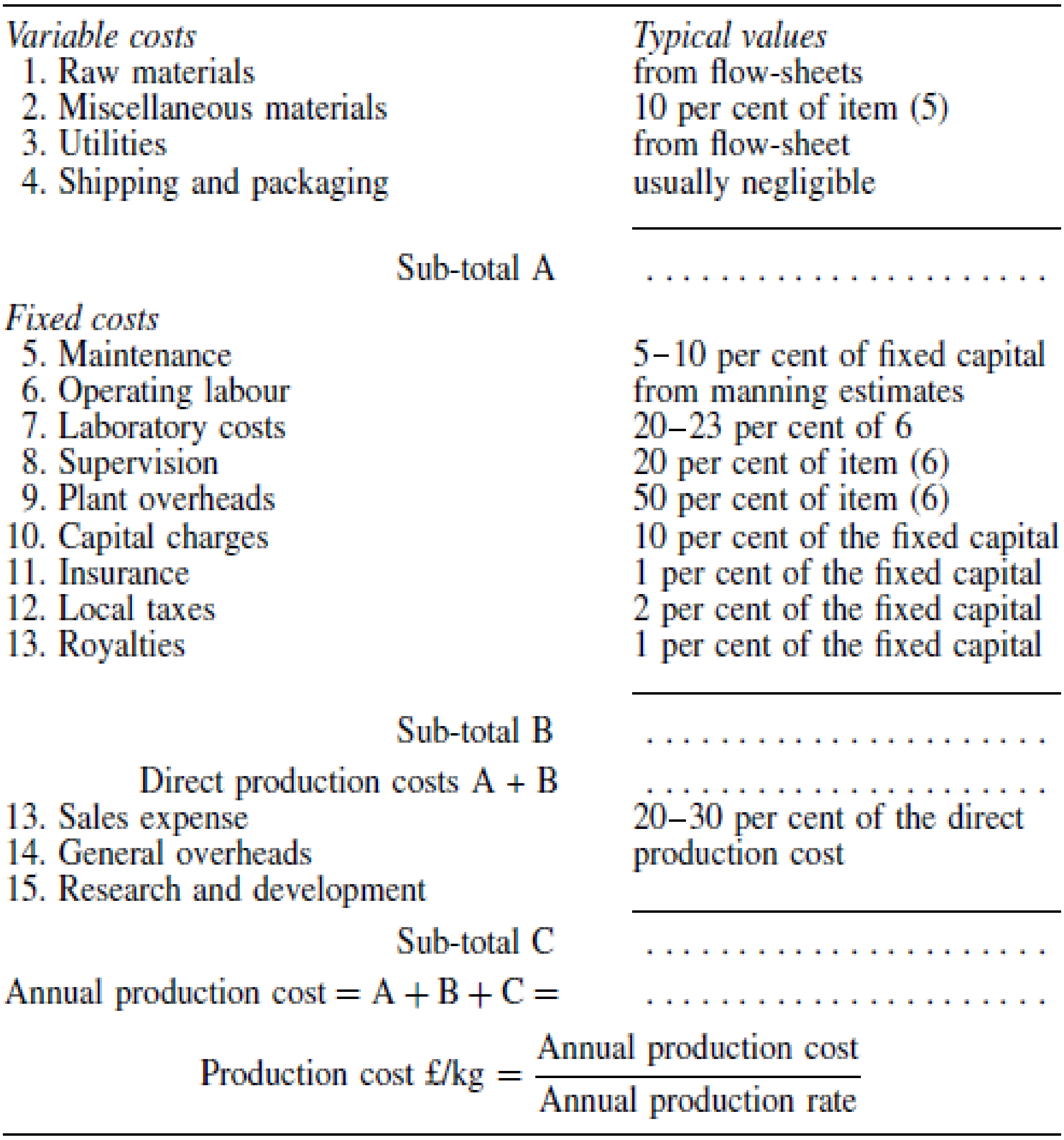


Item	Process type		
	Fluids	Fluids–solids	Solids
1. Major equipment, total purchase cost	PCE	PCE	PCE
f_1 Equipment erection	0.4	0.45	0.50
f_2 Piping	0.70	0.45	0.20
f_3 Instrumentation	0.20	0.15	0.10
f_4 Electrical	0.10	0.10	0.10
f_5 Buildings, process	0.15	0.10	0.05
$^*f_6$ Utilities	0.50	0.45	0.25
$^*f_7$ 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)			
$\text{PPC} = \text{PCE}\ (1 + f_1 + \cdots + f_9)$			
$= \text{PCE} \times$	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
$\text{Fixed capital} = \text{PPC}\ (1 + f_{10} + f_{11} + f_{12})$			
$= \text{PPC} \times$	1.45	1.40	1.35

*Omitted for minor extensions or additions to existing sites.

The following table is a summary of production costs:

Table 31 – Production Costs



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	20–30 per cent of the direct production cost
14. General overheads	
15. Research and development	
Sub-total C	. . . .
Annual production cost = A + B + C =	. . . .

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

8.1.1 Naphtha feed Pump

Centrifugal, carbon steel

characteristic size parameter = 37

cost constant = 1920

index = 0.8

$Ce = CSn$

$Ce = 1920(37)0.4 = \$6139.45$

8.1.2 Naphtha Feed Vaporizer

Shell and tube heat exchanger, carbon steel shell and tube, floating head

Bare Cost = $21,000

Pressure Factor 1.0

Type Factor 1.0

Purchased Cost = $21,000 x 1.0 x 1.0 = $21,000

8.1.3 Feed Heater

Shell and tube heat exchanger, carbon steel shell and tube, floating head

shell diameter = 19.69 in (0.5 m)

number of tubes 128

length 16 ft

Bare Cost = $23,000

Pressure Factor 1.0

Type Factor 1.0

Purchased Cost = $23,000 x 1.0 x 1.0 = $23,00

8.1.4 Reformer Effluent Steam Generator

Shell and tube heat exchanger, carbon steel shell and tube, floating head, shell diameter = 39.37 in (1 m), number of tubes 188, length 19 ft.
Bare Cost = $29,000; Pressure Factor 1.3, Type Factor 1.0 Purchased Cost = $29,000 x 1.3 x 1.0 = $37,700

8.1.5 Hydrotreater (HDS)

Catalyst stainless steel pall ring, carbon steel, diameter 1.5 m, ,NiMo catalyst used.
Ce = CSn

Bare vessel cost = Ce = 12500(18.1)0.3 = $29,799.82 Packing cost = $2300/m3
Volume of packing = (π/4) x 5 = 3.927 m3

Cost of packing = 2 x 3.927 x 2300 = $18,064.95
Total cost = $29,799.82 + $18,064.95 = $47,863.77

8.1.6 Desulfurizer (Vessel)

Vertical pressure vessel, stainless steel, 40 in. (1 m) diameter, 80 in. (2 m) height.
3.5 bar pressure.

Bare vessel = $5,000; Material factor 2.0, Pressure factor 1.0 Purchased cost = $5,000 x 2.0 x 1.0 = $10,000

8.1.7 Steam Generator

Shell and tube heat exchanger, carbon steel shell and tube, floating head, shell diameter = 32.21 in (.89 m), number of tubes 114, length 13 ft.,
Bare Cost = $24,500; Pressure Factor 1.2, Type Factor 1.0 Purchased Cost = $24,500 x 1.2 x 1.0 = $29,400

8.1.8 Reheat Coil

Shell and tube heat exchanger, square pitch, diameter = 28.21 in, number of tubes 104, length 10 ft.,
Bare Cost = $19,500; Pressure Factor 1.2, Type Factor 1.0 Purchased Cost = $19,500 x 1.2 x 1.0 = $23,40

8.1.9 Pre-Reformer

Packed Bed Reactor. Stainless steel pall ring, carbon steel, Ni catalyst used.
2 Beds.
Ce = CSn

Bare cost = Ce = 18000(16.5)0.6 = $96,766.32 Packing cost = $8900/m3
Volume of packing = (π/4) x 2 = 1.570 m3

Cost of packing = 2 x 1.570 x 8900 = $27,946.95
Total cost = $96,766 + $27,946.95 = $124,712

8.1.10 Reformer

Tubular Reactor. Ni catalyst used.
Number of catalyst Tubes: 40
SS Grade Material.
Ce = CSn

Bare cost = Ce = 22300(12.2)0.7 = $128,456
Per Tube cost = $80

Cost of Tubes = 40x 80 = $3200
Total cost = $128,456 + $3200 = $131,656

8.1.11 High Temperature Shift Converter

Packed Bed Reactor. Carbon steel, Fe-Cr catalyst used.

Ce = CSn

Bare cost = Ce = 12600(13.2)0.7 = $76,695

Packing cost = $4560/m3

Volume of packing = (π/4) x8 = 6.283 m3

Cost of packing = 6.283 x4560 = $28,650

Total cost = $28,650+$76,695=$105,345

8.1.12 BFW Exchanger

Shell and tube heat exchanger, shell diameter = 27in, number of tubes 83, length 7ft.

Bare Cost = $16,000; Pressure Factor 1.0, Type Factor 1.0 Purchased Cost = $16,000 x 1.0x 1.0 = $16,000

8.1.13 BFW Pumps

Centrifugal, 31 kW power, carbon steel, cost constant = 1240, index = 0.5

Ce = CSn

Ce = 1240(37)0.5 = $7542

For 2nd Pump.

Centrifugal, 4 kW power, carbon steel, cost constant = 980, index = 0.8

Ce = CSn

Ce = 980(4)0.8 = $2970

8.1.14 Cold Condensate Separator

Vertical pressure vessel, stainless steel, 5 m height

diameter 30 in.

Bare vessel cost = $16,000

Material factor 2.0, Pressure factor 1.0

Purchased cost = $16,000 x 2.0 x 1.0

= $32,000

Table 32 – Total Purchase Cost of Equipment

Equipment	Cost
Naphtha Feed Pump	$6,139
Naphtha Feed Vaporizer	$21,000
Feed heater (Exchanger)	$23,000
Reformer Effluent Steam Generator (Exchanger)	$37,700
Hydrotreater (HDS reactor)	$47,863
Desulfurizer Vessel	$10,000
Steam Generator 2	$29,400
Reheat Coil (Exchanger)	$23,400
Pre-Reformer (PBR)	$124,712
Reformer (TBR)	$131,656
High Temperature Shift Converter (PBR)	$105,345
BFW Heat Exchanger	$16,000
BFW Pumps	$7,542
Cold Condensate Separator	$32,000
Total	**$615,758**

Table 33 - Estimation of Fixed Capital Cost

PCE	$615,758
f1 Equipment erection	0.40
f2 Piping	0.70
f3 Instrumentation	0.20
f4 Electrical	0.10
f5 Buildings	0.15
f6 Utilities	0.50
f7 Storages	0.15
f8 Site development	0.05
f9 Ancillary buildings	0.15

8.2 Total physical plant cost (PPC)

Total physical plant cost (PPC) = 615,758 (1 + 0.40 + 0.70 + 0.20 + 0.10 + 0.50+0.15+0.50+0.15+0.05+0.15)
=$2,401,456

8.3 Fixed Capital

f10 Design and Engineering	0.3
f11 Contractor's fees	0.05
f12 Contingencies	0.10

Fixed capital = 2401456(1 + 0.3 + 0.05 + 0.10) = $3,482,111

8.4 Working Capital

Working capital, allow 5% of fixed capital to cover the cost of start-up. Working capital = 3,482,111 x 0.05 = $171,410

8.5 Total Investment

Total investment required for the project = $3,482,111 + $171,410 = $3,653,521

8.6 Annual Operating Cost

8.6.1 Operating Time

Operating time, allowing for plant attainment = 365 x 0.95 = 347 d/y, 347 x 24 = 8328 h/y.

8.6.2 Fixed Cost

Maintenance 5% of fixed capital = $3,482,111 x 0.05 = $174,105 Operating labor = $30,000
Plant overheads, 40% of operating labor = 0.4 x $30,000 = $12,000 Laboratory, 25% of operating labor = 0.25 x $30,000 = $7,500 Capital Charges, 5% of fixed capital = $3,482,111 x 0.05 = $174,100 Insurance, 2% of fixed capital = 0.02 x $3,482,111 = $69,642
Total Fixed Cost = $174,105+ $30,000 + $12,000 + $7,500 + $174,100 + $69,642
= $467,347

8.6.3 Variable Cost

Miscellaneous materials, maintenance 10% of maintenance cost = $17,410 Utilities:
Power $0.05/M = 0.05 x 3000 x 347 =$52,050 Water $0.03/t = 0.03 x 98000 = $2940
Catalysts Maintenance Cost: 4 x 7500= 30,000
Steam $8/t = 8*175.2 = $1401
Total Variable Cost = $17,410 + $52,050 + 2940+30,000 +1401 =$103,801

8.6.4 Direct Production Cost

Direct Production Cost = \$467,347+ \$103,801 = \$571,148

8.6.5 Annual Operating Cost

Annual Operating Cost, rounded = \$572,000

8.7 Revenue Generated

Hydrogen production per day =490tonnes/d
Hydrogen Market Price
= 9.5 USD/1 ton
Hence, annual revenue = \$1,615,285

8.8 Profit

Profit per Year = $1,615,300 - $572,000= $1,043,300

8.9 Payback Period

Payback Period = Total investment/Profit Payback Period = 3.5 years
It means that in the period of 3 and a half years, if the plant is successfully being operated at 347 days a year capacity with, all investment will be recovered.

CHAPTER 9

INSTRUMENTATION AND PROCESS CONTROL

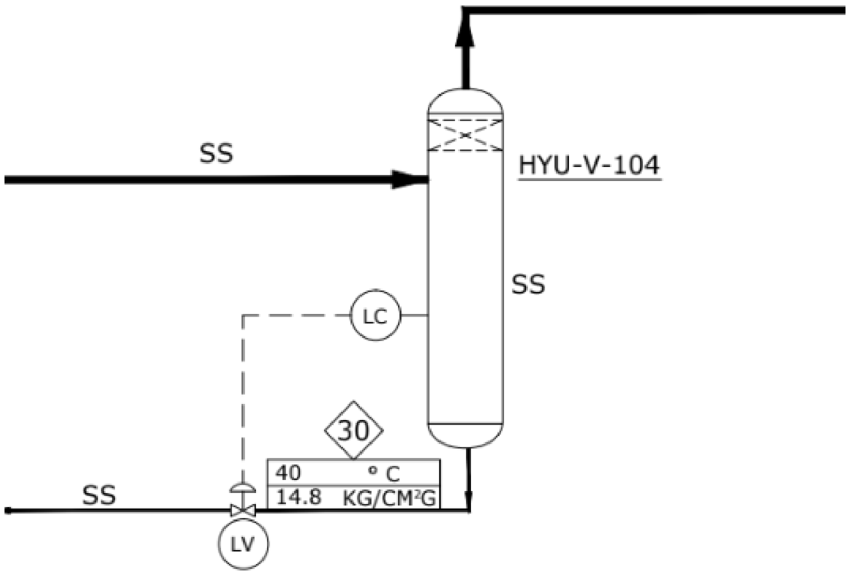
One of the most important elements for any large-scale chemical or a process industry to have complete safety controls without compromising on the required production is how well its instrumentation and controlling of the process is being monitored. Instrumentation and Process Control adds to safety of the process by not only automating several functionalities but also gives more stability and productivity to a designed process. The basic aim is to deal with measurement and control of process variables to ensure the optimum and safe range. Examples of process variables include temperature, pressure, flow, level, pH, speed etc.

Control loops are the fundamental part of any industrial control system. It consists of a group of components working together which maintains a measured variable to its desired set point. Two types of control loops: Open control and Closed control loop. One where the controller actions are independent of the process outputs while in closed control loop, also called feedback control loop, the controller responds to changes in the output process variable is Open Control Loop

Generally, there are three main types of controllers: P (proportional), PI (proportional integral) and PID (proportional integral derivative). P controllers give an output proportional to the error, PI give an output to sum of proportional and integral part of error while PID have an added response to the derivative of the error as well. P controllers always give an output with a slight set-off. PI have fluctuations and gradually eliminate the error while PID have a very fast response. Following are examples of how IPC is applied to our system.

9.1 Level Controller

Figure 29 – Level Control Loop



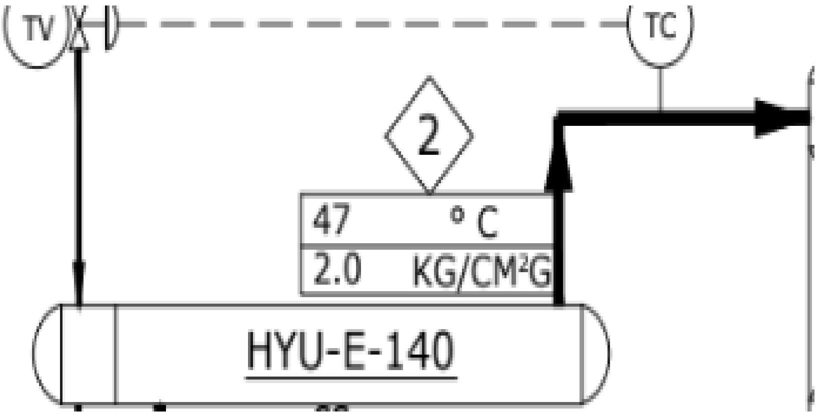
This is the Cold Condensate Separator. In this separator, before entering the hydrogen to adsorption system, the primary objective is to remove content of condensates so that the percentage purity of hydrogen is maximized following to adsorption.

For efficient separation of condensates, it is necessary that a certain level set point is met in the separator vessel. Basically, the cold condensate which gets separated is then sent to deaerator under this level controller

A control system or loop is installed to maintain that level inside the separator. Here the control system is shown by LC. Firstly, there is a measuring element known as level indicator which measures the level of liquid condensates inside the separator. This sends a signal to controller which then performs the necessary actions. Controller maintains the level inside the separator by controlling the outlet flow rates of. If the level drops below the set point (level), LC will decrease the outlet flow rates to maintain the level inside. And if the level increases inside the separator, LC will increase outlet flow rates to maintain the level inside the separator.

9.2 Temperature Controller

Figure 30 – Temperature Control Loop

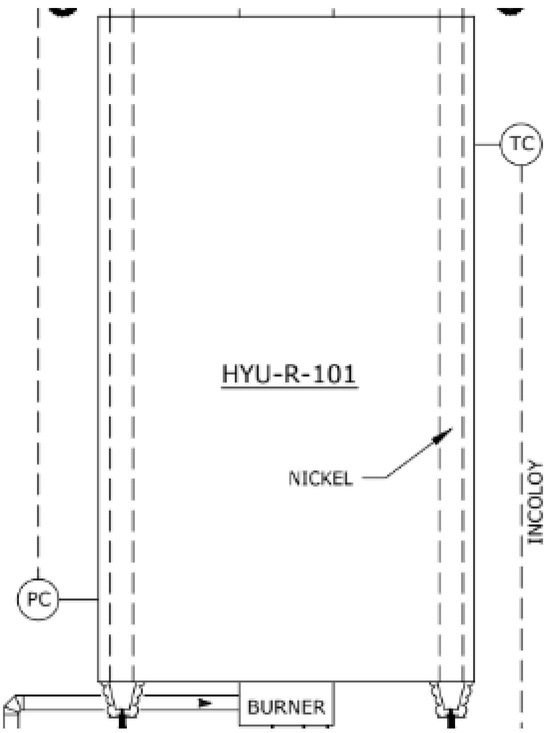


This is the naphtha heater in our process which is installed before the vaporizer. Heater raises the temperature of incoming naphtha stream prior to entering in vaporizer. Process steam is used as a heat source in this. The purposeof this heater is to raise the temperature of our naphtha feed stream to a certain level so efficient that in vaporizer a phase change can occur without any additional requirement. Thus, to maintain the required temperature, temperature control loop is developed.

TC consist of an indicator, and controller. Temperature indicator measures the temperature of outlet stream of heater which is then fed to vaporizer. Indicator sends the measured value to controller then provide signal to TV. TV then takes the necessary action by adjusting the flow rate of incoming steam. If the measured temperature is higher than the set value, controller will decrease the steam flow rate so less heating of naphtha feed will be done. If the measured temperature is lowerthan the set value, controller will increase the flow rate of steam coming to heater.

9.3 Pressure – Temperature – Flow Controller

Figure 31 – Pressure Temperature Flow Controller



Reformer is the most important part of our process. The reforming reaction converts our 20 plus naphtha component feed via reactions involved. So, it is important to monitor the reformer's parameter carefully. It is necessary that the feed enters at a certain pressure so that no decomposition or side reactions take place. Similarly, catalyst tubes temperature is important to ensure proper and efficient reactions. For this reason, two loops, i.e., pressure control loop, and temperature control loop are developed on the reactor. PC loop consists of an indicator, and controller. Indicator measures the pressure of inlet stream and sends signal to controller. Controller take the necessary action by controlling pressure relief valve. If the pressure of inlet stream exceeds the desired or set value, it willopen the relief valve to reduce the pressure of inlet stream. TC loop consists of indicator and a controller. This Indicator keep measuring the temperature for the outlet and keep sending signals to the controller which then performs the necessary actions. If the temperature exceeds the set value, it will increase the cooling waterflowrate and vice versa.

CHAPTER 10

HAZOP ANALYSIS

HAZOP is one of the main techniques used in chemical and process industries globally in order to find the potential possibilities of hazards using the scenarios which can lead to hazard (guide words). The reason for performing HAZOP analysis in hydrogen production plant, since it involves reactions including exothermic reactions, high heat transfers via number of exchangers, presence of Sulphur in plant environment there is a high possibility that a small trigger can initiate the likelihood of a potential hazard which could lead to destruction to environment or pose a lethal threat to human nature as well. This contains several hazards either before, or after its treatment. Therefore, proper analysis must be done using different risk assessment tools.

Risk assessment is performed throughout the application of several suitable methods of study. Two main methods are Quantitative and Qualitative Risk Assessment. The latter is preliminary risk assessment. On the other hand, Quantitative Risk Analysis is HAZOP, and it is what majority of industries utilize.

In summarized way, HAZOP is complete, systematic way to applytechnique for analyzing deviations.

Once a detailed study of HAZOP is performed, and a worksheet result containing lists of identified deviations, recommendations, and suggestions is created, a Safety Analysis is done. Guidewords such as NO, LESS, HIGH,LOW,AS WELL AS,OTHER THAN, INCREASED, DECREASED are mostly used on number of operational parameters such as flow, pressure, temperature. Unfortunately, unexpected events are not included in detailed HAZOP. In this study of hazard and operability analysis, we will cover the important process vessels by taking one process line to find all possible deviations, their potential consequences and will be proposing the solution regarding how to mitigate that specific deviation. Our process vessels will be Reactor (High temperature Shift converter) and a Heat Exchanger

10.1 Vessel: Heat Exchanger

Node: HYU-E-101 Exchanger outlet line

Table 34 – HAZOP Analysis Heat Exchanger

Deviation	Possible Causes	Consequences	Actions to be Taken
No Flow	• Failure in Naphtha Supply • Inlet Valve Closed • Naphtha line plugged • Break in exchanger tube	• No naphtha flow - upset in downstream process • Liquid Naphtha can mix with process gas	• Installing a flow meter and low flow alarm. • Clear the blockage from the line. • Add a lock procedure for valve. • Add a concentration analyzer.
Less Flow	• Inlet valve partially closed • Fouling in feed line • Possible leakage in some tubes of heat exchanger	• Less naphtha flow – possible upset in downstream process • Liquid naphtha mixed with process gas. • Temperature increase more than required	• Installing a flow meter with flow controller and low flow alarm. • Perform the service of the line. • Add a concentration analyzer. • Install a temperature

			sensor.
More Flow	• High Pressure than the operating condition • Malfunctioned Control Valve	Required temperature not achieved can affect downstream process.	• Installation of High flow Alarm with flow meter and flow controller. • Install a temperature sensor.
As well as	Leaks through the heat exchanger tubes.	Naphtha feed mixed with process gas disturbing the downstream process.	Install a concentration analyzer in the line.
Reverse Flow	HDS (hydro-desulfurizer) inlet choked or valve before HDS inlet closed	• Backflow into the heat exchanger, • increased temperature • Decreased heat transfer.	• Installing a check valve. • Installing a high-pressure alarm to detect backflow.

10.2 Vessel: High Temperature Shift Converter (HTS)

Node: Inlet Line of HTS

Table 35 – HAZOP Study HTS

Deviations	**Causes**	**Consequences**	**Actions to be taken**
No Flow	Inlet valve closed.	• Loss of feed to the reactor. • No reaction takes place.	Install a flow meter attached with a flow controller.
More Flow	Control Valve Malfunctioned.	Higher chances of channeling across HTS bed thus less conversion of desired product.	• Inspection of valves. • Installation of high flow alarm.
Less Flow	Line from WH-104 have leakage or partial blockage.	Overall Production loss due to less catalytic activity.	• Immediate Inspection of transfer line from heater to HTS. • Installing flow alarms to detect low flow.
More Temperature	WH-104 not achieving the required the cooling.	Increased temperature leading to excessive coking, less conversion and more pressure drop.	• Installing high temperature shutdown system. • Regular inspection of plant log sheets.
Less Temperature	Possible Damage in tubes of WH-104	Less reaction rate leading to decreased hydrogen production rate.	Installation of temperature controls on inlet line.

High Pressure	Malfunctioning of the valve for instream	Possible explosion of the reactor	Immediate installation of rupture disc across reactor
Low Pressure	Leakage in heat exchanger leading to less flow.	Less catalytic activity and less conversion to H_2	PRV installation using differential control

10.3 Naphtha Feed Pump

Centrifugal Pump

Table 36 – HAZOP Naphtha Feed Pump

Guide Word	**Deviation**	**Cause**	**Consequences and actions**
No	Flow	Shaft failure due to corrosion overload	No flow and increased vibrations: Open and clean the pump.
No	Pressure	Pump failure	No flow causing halting of unit: Checking NPSHA>NPSHR
Low	Flow	Shaft deformation due to work overload	Overheating of pump: Check shaft seal.
		Valve partially closed	Overheating of pump: Open valve.

CONCLUSIONS

The pressure drop was addressed through the following two ways:

- Addressing the inherent
- Addressing the fouling source

Packed bed was replaced by the monolith reactor to have a reduced pressure drop. At the same time the coke formation was reduced by optimization of critical parameters to eliminate pressure drop.

Table 37 – Optimization with Critical Parameters

Parameter	**Value**
Gas-hourly space velocity	50,000 h^{-1}
Temperature	375 – 400 ℃
Inlet steam/CO ratio	2

In this way the following objectives were attained:

- Pressure drop reduced from 147 kPa to 29 kPa
- Reduced coke formation and enhanced catalytic activity
- Hence reduced plant down time

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