

**PRODUCTION OF 500 TONS PER DAY OF PURE HYDROGEN GAS
FROM REFINERY OFF-GAS STREAM**

A PROJECT REPORT SUBMITTED IN THE PARTIAL FULFILLMENT
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OF

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2013**



National Institute of Technology

Rourkela

CERTIFICATE

This is to certify that the thesis entitled, "**PRODUCTION OF 500 TONS PER DAY OF PURE HYDROGEN GAS FROM REFINERY OFF-GAS STREAM**" submitted by **Pramod Kumar Bal** in partial fulfillments for the requirement for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology Rourkela (Deemed University) is an authentic work carried out by him under supervision and guidance.

To best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institution for the award of any Degree.

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NOMENCLATURE

E_1 - steam generator

E_2 - preheater for boiler feed water

HC - hydrocarbon

SR - steam reformer

F_{H_2}, F_{stm} - mass flow rate of hydrogen/export steam from the unit

$(H/C)_{in}$ - recycle hydrogen to carbon molar ratio in the feed

Q- Rate of heat flow

C_p - specific heat at constant pressure

V_S - Volume of the reactor

F_{A0} - feed flow rate

G_1 - feed gas rate

Y_1 - feed concentration

G_S - feed gas rate on salute free basis

L_S - Liquid flow rate

U_{sfl} - superficial velocity

C_{sb} - Souder's Brown flooding constant

ρ_G, ρ_L - Vapour and liquid density

σ - Surface tension

F_{lv} - flow parameter

U_S - operating velocity

A_a - active tray area

A_T - tower cross-section

D_c - column diameter

h- Height of tower

H_{tG} - height of gas phase transfer unit

N_{tG} - number of gas phase unit

E- Modulus of elasticity

j- Welding joint efficiency

f- Allowable stress

U- out of roundness in %

t_{sk} - thickness of skirt

W_a - weight of attachment

W_l - weight of liquid content

W_s - weight of shell

W_{ins} - weight of insulation

T- Period of vibration

C- Stress concentration factor

ABSTRACT

Steam methane reforming (SMR) is one of the most promising processes for hydrogen production. Several studies have demonstrated its advantages from the economic viewpoint. Nowadays process development is based on technical and economic aspects, however, in the near future; the environmental impact will play a significant role in the design of such processes. In this paper, an SMR process is studied from the viewpoint of overall environmental impact, using an exergoenvironmental analysis. This analysis presents the combination of exergy analysis and life cycle assessment. Components where chemical reactions occur are the most important plant components from the exergoenvironmental point of view, because, in general, there is a high environmental impact associated with these components. This is mainly caused by the energy destruction within the components, and this in turn is mainly due to the chemical reactions. The obtained results show that the largest potential for reducing the overall environmental impact is associated with the combustion reactor, the steam reformer, the hydrogen separation unit and the major heat exchangers. The environmental impact in these components can mainly be reduced by improving their exergetic efficiency. A sensitivity analysis for some important exergoenvironmental variables is also presented in the paper.

Keywords: Hydrogen production, Steam methane reforming process, Exergy analysis;

Chapter 1

1. Introduction ^[1]:

Hydrogen is a chemical element with symbol H and atomic number 1 with an atomic weight of 1.00794u, hydrogen is the lightest element and its monatomic form (H) is the most abundant chemical substance, constituting roughly 75% of the Universe's baryonic mass. Non-remnant stars are mainly composed of hydrogen in its plasma state. At standard temperature and pressure hydrogen is a colorless, odorless, nontoxic, nonmetallic, highly combustible diatomic gas with the molecular formula H₂. Naturally occurring atomic hydrogen is rare on Earth because hydrogen readily forms covalent compounds with most elements and is present in the water molecule and in most organic compounds. Hydrogen plays a particularly important role in acid-base chemistry with many reactions exchanging protons between soluble molecules. The latter cation is written as though composed of a bare proton, but in reality, hydrogen cations in ionic compounds always occur as more complex species. The most common isotope of hydrogen is protium (name rarely used, symbol ¹H) with a single proton and no neutrons. As the simplest atom known, the hydrogen atom has been of theoretical use. For example, as the only neutral atom with an analytic solution to the Schrödinger equation, the study of the energetics and bonding of the hydrogen atom played a key role in the development of quantum mechanics. Hydrogen gas was first artificially produced in the early 16th century, via the mixing of metals with strong acids. In 1766–81, Henry Cavendish was the first to recognize that hydrogen gas was a discrete substance, and that it produces water when burned, a property which later gave it its name: in Greek, hydrogen means "water-former".

Industrial production is mainly from the steam reforming of natural gas, and less often from more energy-intensive hydrogen production methods like the electrolysis of water. Most hydrogen is employed near its production site, with the two largest uses being fossil fuel processing (e.g., hydrocracking) and ammonia production, mostly for the fertilizer market. Hydrogen is a concern in metallurgy as it can embrittle many metals, complicating the design of pipelines and storage tanks.

Hydrogen can be produced from a variety of feedstocks. These include fossil resources, such as natural gas and coal, as well as renewable resources, such as biomass and water with input from renewable energy sources (*e.g.* sunlight, wind, wave or hydro-power). A variety of process technologies can be used, including chemical, biological, electrolytic, photolytic and thermochemical. Each technology is in a different stage of development, and each offers unique opportunities, benefits and challenges. Local availability of feedstock, the maturity of the technology, market applications and demand, policy issues, and costs will all influence the choice and timing of the various options for hydrogen production. High to ultra-high purity hydrogen may be needed for the durable and efficient operation of fuel cells, consumption in different process plants, in semiconductor industry and as an energy carrier. Impurities are believed to cause various problems in the current state-of-the-art fuel cell designs, including catalyst poisoning and membrane failure. As such, additional process steps may be required to purify the hydrogen to meet industry quality standards.

Chapter 2

Literature Review

2.1 refinery off-gas stream ^[2]

Refinery gas is a mixture of gases generated during refinery processes which are used to process crude oil into various petroleum products which can be traded or sold. The composition of refinery gas varies, depending on the composition of the crude it originates from and the processes it has been subjected to common components include butanes, butylenes, methane and ethylene. Some products found in refinery gas are subject to control as a result of programs which are designed to address climate change.

2.1.1 Refinery off-gas composition ^[2]

Table-1 refinery off-gas composition

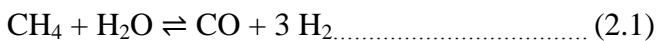
Component	Mol. %	Mol. Wt.
CH ₄	92.48	16
C ₂ H ₆	1.69	30
C ₃ H ₈	0.13	44
i-C ₄ H ₁₀	0	58
n-C ₄ H ₁₀	0	58
CO ₂	5.69	44
N ₂	0.01	28
S	<3ppm	

2.2. Steam reforming ^[3]

Steam reforming, sometimes called Fossil fuel reforming is a method for hydrogen production or other useful products from hydrocarbon fuels such as natural gas. This is achieved in a processing device called a reformer which reacts steam at high temperature with the fossil fuel. The steam methane reformer is widely used in industry to make hydrogen. There is an in development of much smaller units based on similar technology produce hydrogen as a feedstock for fuel cells. Small-scale steam reforming units to supply fuel cells are currently the subject of research and development, typically involving the reforming of methanol or natural gas but other fuels are also being considered as propane, gasoline, auto gas, and ethanol.

2.2.1 Industrial reforming ^[4]

Steam reforming of natural gas or syngas sometimes referred to as steam methane reforming (SMR) is the most common method of producing commercial bulk hydrogen as well as the hydrogen used in the industrial synthesis of ammonia. It is also the least expensive method. At high temperatures (700 – 1100 °C) and in the presence of a metal-based catalyst (nickel), steam reacts with methane to yield carbon monoxide and hydrogen. These two reactions are reversible in nature.



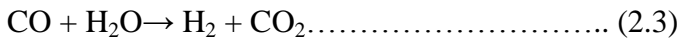
Additional hydrogen can be recovered by a lower-temperature gas-shift reaction with the carbon monoxide produced. The reaction is summarized by



The first reaction is strongly endothermic (consumes heat), the second reaction is mildly exothermic (produces heat). The United States produces nine million tons of hydrogen per year, mostly with steam reforming of natural gas. The worldwide ammonia production, using hydrogen derived from steam reforming, was 109 million metric tons in 2004. This SMR process is quite different from and not to be confused with catalytic reforming of naphtha, an oil refinery process that also produces significant amounts of hydrogen along with high octane gasoline. The efficiency of the process is approximately (65 -75) %.

2.3. shift reactor ^[5]

At the outlet of steam reformers, partial oxidation reactors or coke oven gas units the syngas contains H₂, CO, CO₂, CH₄ and water in chemical equilibrium at high temperatures in the range of 700 to 1400 °C depending on the process pressure and the mixture of feed stock and process steam or water. By means of the CO shift conversion an important portion of the CO content in the cracked gas is used for additional hydrogen generation, which is following the chemical reaction



This process is exothermic and is limited by the chemical equilibrium. There are three different versions of CO shift conversion: High temperature (HT) CO shift conversion at about 300 to 450 °C down to approx. 2.5 % CO on dry basis at the reactor outlet Medium temperature (MT) CO shift conversion or so-called isothermal shift conversion at about 220 to 270 °C down to approx. 0.5 % CO on dry basis at the reactor outlet. Low temperature (LT) CO shift conversion at about 180 to 250 °C down to approx. 0.2 % CO on dry basis at the reactor outlet for every process a special catalyst will be used in a fixed bed reactor to get maximum yield of H₂ product.

The use of HT CO shift conversion is state of the art in almost every hydrogen plant. The application of the low temperature CO shift conversion is normally installed downstream of the HT shift at already reduced CO content in the feed gas. The additional investment is considered for plants having a capacity above approx. 40,000 Nm³/h H₂ product. The catalyst of the LT shift is very sensitive against sulphur, chlorine and liquid water and special attention is required during start up and plant upset conditions. In former concepts the LT shift was important because of the downstream methanisation of CO following the CO₂ removal unit, to meet the product purity at minimum H₂ losses. After the implementation of the Pressure Swing Adsorption (PSA unit) for H₂ purification these process steps have become obsolete. The MT CO shift conversion as isothermal reaction can be approximated in several adiabatic reactors with intercoolers or better in an isothermal reactor with integrated steam generation for cooling of the process gas. The temperature of the shift reaction is controlled easily by setting the pressure of the generated steam.

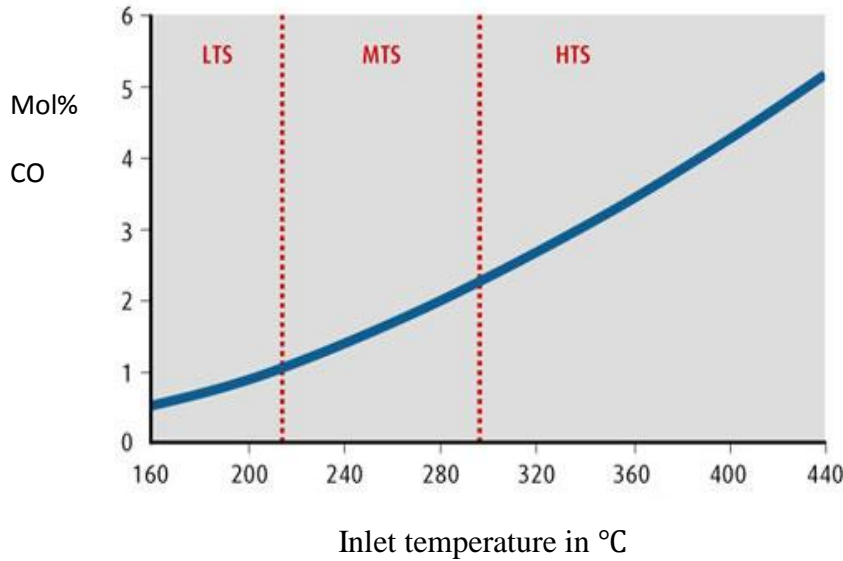


Fig-1 temperature vs. exit carbon monoxide

2.4. pressure swing adsorber ^[6]

Adsorption process is designed in such a way that a gas mixture is fed to adsorber at ambient temperature and increased pressure. At higher temperature, a smaller amount of impurities can be adsorbed on any adsorbent. The regeneration at high temperature level T_2 reduces the loading L_2 of adsorbent at adsorption pressure P_1 and temperature T_2 and reduced pressure P_2 . PSA process works between two pressure levels: (1) Adsorption & (2) Regeneration. In adsorption phase, adsorption of impurities is carried out at high pressure to increase the partial pressure and thus increase loading of impurities on adsorbent. The raw feed gas flows through an adsorber in upward direction and the impurities are selectively adsorbed on the surface of the adsorbent in the order- water, hydrocarbons, CO and N_2 from bottom to top. The purified product gas leaves the adsorber at the outlet and flows to the product line.

The adsorbing capacity of one adsorber being limited, after certain time the impurities break through at the outlet of the adsorber. First the impurities come in traces, but gradually their concentration increases. To avoid this breakthrough, the adsorption step must be interrupted to regenerate the loaded adsorber. For continuous product supply, at least two absorbers are necessary. While the first one is regenerated, a second already regenerated one purifies the raw

feed gas. In the regeneration phase, the process is carried out at low pressure at approximately the same temperature. During this phase, the adsorbed impurities are desorbed. The residual impurities loading are reduced as much as possible in order to achieve high product purity and a high H₂ recovery.

Regeneration phase consist of several steps;

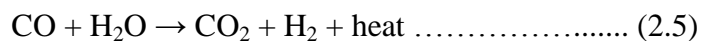
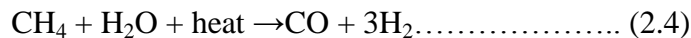
- Expansion to adsorption pressure, where the adsorbed components start to desorb from the adsorbent.
- Purging supports this desorption process with some gas having very low partial pressure of impurities.
- Pressurization to adsorption pressure.

2.5. various methods for hydrogen production ^[7]

- Steam Methane Reforming
- Coal Gasification
- Partial Oxidation of Hydrocarbons
- Biomass Gasification
- Electrolysis
- Thermochemical
- Photo biological

2.5.1. Steam Methane Reforming

Steam reforming involves the endothermic conversion of methane and water vapour into hydrogen and carbon monoxide (2.4). The heat is often supplied from the combustion of some of the methane feed-gas. The process typically occurs at temperatures of 700 to 850 °C and pressures of 3 to 25 bars. The product gas contains approximately 12 % CO, which can be further converted to CO₂ and H₂ through the water-gas shift reaction (2.5).



2.5.2. Coal Gasification

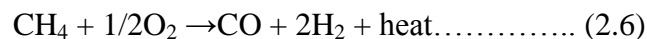
Hydrogen can be produced from coal through a variety of gasification processes (e.g. fixedbed, fluidized bed or entrained flow). In practice, high-temperature entrained flow processes are favored to maximize carbon conversion to gas, thus avoiding the formation of significant amounts of char, tars and phenols. A typical reaction for the process is given in equation (2.4), in which carbon is converted to carbon monoxide and hydrogen



Since this reaction is endothermic, additional heat is required, as with methane reforming. The CO is further converted to CO₂ and H₂ through the water-gas shift reaction, described in equation (2.5). Hydrogen production from coal is commercially mature, but it is more complex than the production of hydrogen from natural gas. The cost of the resulting hydrogen is also higher. But since coal is plentiful in many parts of the world and will probably be used as an energy source regardless, it is worthwhile to explore the development of clean technologies for its use.

2.5.3. Partial Oxidation of Hydrocarbons

Partial oxidation of natural gas is the process whereby hydrogen is produced through the partial combustion of methane with oxygen gas to yield carbon monoxide and hydrogen (2.6). In this process, heat is produced in an exothermic reaction, and hence a more compact design is possible as there is no need for any external heating of the reactor. The CO produced is further converted to H₂ as described in equation (2.5).



2.5.4. Biomass Gasification

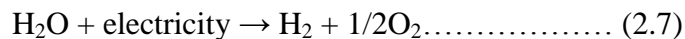
In biomass conversion processes, a hydrogen-containing gas is normally produced in a manner similar to the gasification of coal. However, no commercial plants exist to produce hydrogen from biomass. Currently, the pathways followed are steam gasification (direct or indirect), entrained flow gasification, and more advanced concepts such as gasification in supercritical water, application of thermo-chemical cycles, or the conversion of intermediates (e.g. ethanol,

bio-oil ororrified wood). None of the concepts have reached a demonstration phase for hydrogen production. Biomass gasification is an R&D area shared between H₂ production and biofuels production. Gasification and pyrolysis are considered the most promising medium-term technologies for the commercialization of H₂ production from biomass. A typical flow sheet for the production of hydrogen

In terms of its energy requirements, the drying of biomass might not be justifiable; therefore, other pathways based on wet biomass are being sought as well. Biomass feedstocks are unrefined products with inconsistent quality and poor quality control. The production methods vary according to crop type, location and climatic variations. Erratic fuels have contributed to the difficulties in technological innovation, since less homogenous and low quality fuels need more sophisticated conversion systems. There is a need to rationalize the production and preparation of fuel to produce more consistent, higher-quality fuels that can be described by common standards. Large-scale systems tend to be suitable for cheaper and lower quality fuels, while smaller plants tend to require higher levels of fuel quality and better fuel homogeneity. A better understanding of this relationship, and the specific tolerances that each technology can accommodate, is needed.

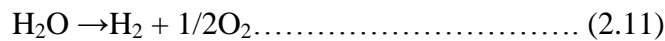
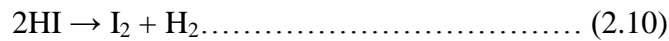
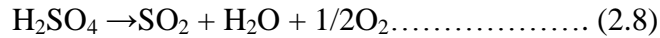
2.5.5. Electrolysis

Water electrolysis is the process whereby water is split into hydrogen and oxygen through the application of electrical energy, as in equation (2.7). The total energy that is needed for water Porous water-filled layer in the earth strata. Electrolysis is increasing slightly with temperature, while the required electrical energy decreases. A high-temperature electrolysis process might, therefore, be preferable when high-temperature heat is available as waste heat from other processes. This is especially important globally, as most of the electricity produced is based on fossil energy sources with relatively low efficiencies.



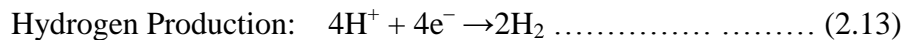
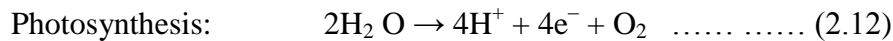
2.5.6. Thermochemical

Thermo-chemical water splitting is the conversion of water into hydrogen and oxygen by a series of thermally driven chemical reactions. Thermo-chemical water-splitting cycles have been known for the past 35 years. They were extensively studied in the late 1970s and 1980s, but have been of little interest in the past 10 years. While there is no question about the technical feasibility and the potential for high efficiency, cycles with proven low cost and high efficiency have yet to be developed commercially. An example of a thermo-chemical process is the iodine/sulphur cycle. For this process, the research and development needs are to capture the thermally split H₂, to avoid side reactions and to eliminate the use of noxious substances. The corrosion problems associated with the handling of such materials are likely to be extremely serious.



2.5.7. Photobiological

Photo-biological production of hydrogen is based on two steps: photosynthesis (2.12) and hydrogen production catalyzed by hydrogenases (2.13) in, for example, green algae and cyanobacteria. Long term basic and applied research is needed in this area, but if successful, a long-term solution for renewable hydrogen production will result. It is of vital importance to understand the natural processes and the genetic regulations of H₂ production. Metabolic and genetic engineering maybe used to demonstrate the process in larger bioreactors. Another option is to reproduce the two steps using artificial photosynthesis.



Chapter 3

Process description

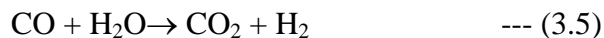
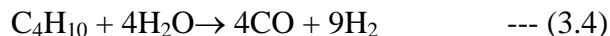
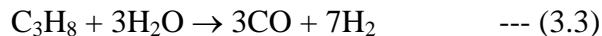
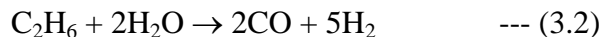
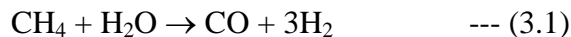
3.1 Introduction ^[8, 9]

Steam reforming of hydrocarbons has established itself as the most economic and preferred process for the production of hydrogen and synthesis gas. In view of the large value addition involved in the process and its high energy consumption coupled with increasing energy cost, the optimal operation of such units is of utmost concern to the industry. The choice of feedstock for steam reforming is largely determined by location, availability, and the local energy policy. Two Common feedstocks range from natural gas to heavy naphtha. Because even the simplest of these feedstocks contains many components (natural gas contains mainly methane but also ethane, propane, butane, and other higher hydrocarbons), a multitude of chemical reactions occur in the steam reformer, making it impractical to account for all of them. Reformation experiments carried out with hydrocarbons such as propane, butane, hexane, and benzene suggest methane to be the primary product of the reaction. Based on this observation, many published works³⁻⁵ on steam reforming with heavier hydrocarbons assume that all hydrocarbons heavier than methane hydrocrack to methane instantaneously at the reformer inlet. As a result, the reaction system within the reformer can be reduced to that for the steam-methane reaction regardless of the feedstock used. This simplifying assumption gained wide acceptance because it was found to be satisfactory for predicting the gas composition at the reformer outlet. This is primarily because the reforming reactions are thermodynamically and not kinetically controlled. However, axial conversion profiles in an ammonia plant steam reformer suggest that methanation is completed between 2 and 6 m from the reformer.

3.2 Process Description

Figure 2 shows a simplified flow diagram of the industrial hydrogen unit considered in this study. The feed to the reformer furnace is comprised of refinery off gas, mixed with suitable quantities of recycle H₂ and steam, which are required to maintain the reformer catalyst in its active state and to prevent carbon formation, respectively. The reactions occurring in the reformer are steam-methane reforming reactions. The four reforming reactions (eqs 3.1-3.4) occur mainly in the steam reformer, while thermodynamics favor the shift reaction (eq 3.5) in the high-temperature (HT) shift converter. (An additional low-temperature shift converter may be present in some plants to achieve additional CO conversion, but it is absent in the industrial unit modeled.) The surplus heat in the process gas at the reformer outlet is recovered (in E₁) and used to generate very high pressure (VHP) steam. Part of this steam is mixed with feed, while the remainder is exported outside the unit. The shift reaction (eq 3.5) occurring in the HT shift converter produces additional H₂. The hot syngas leaving the shift converter is used to preheat boiler feed water (in E₂) before it is further cooled and flashed to remove entrained steam as condensate, which is recycled back to the process. The H₂-rich stream then enters a pressure-swing adsorber (PSA), which separates H₂ from off-gases. The PSA off gas is used to supplement external fuel for combustion in the reformer furnace. The general equations are given below:

For the methane reforming the following reaction take place



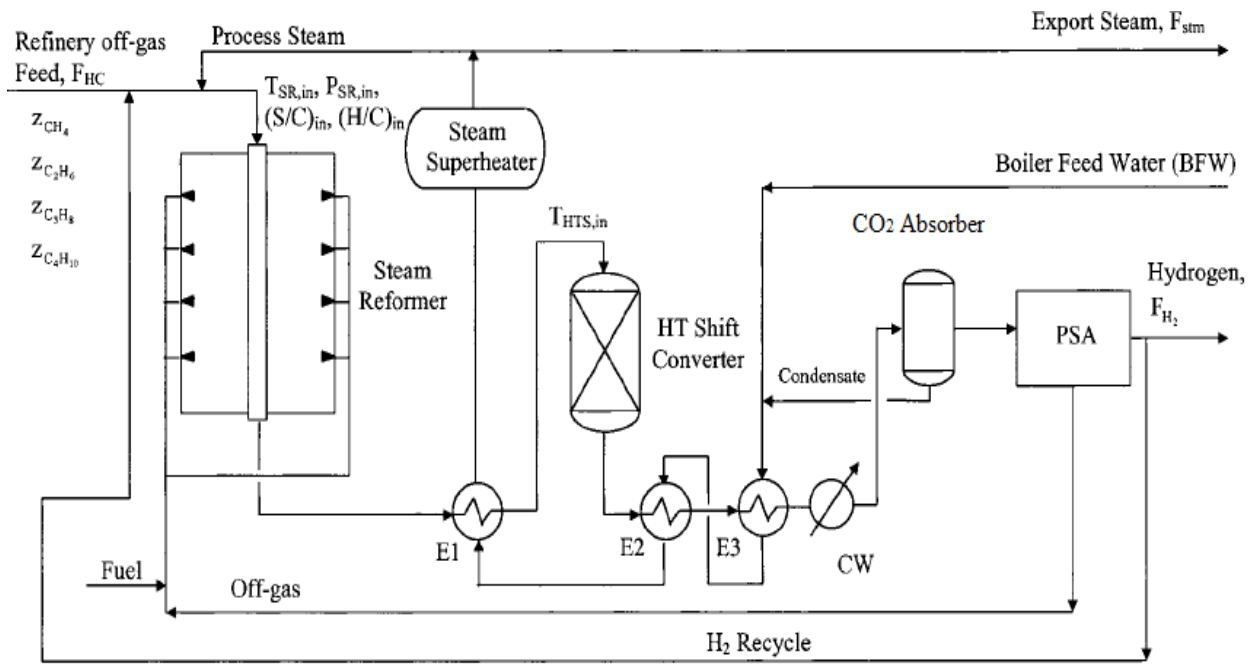


Fig-2 simplified process diagram of H₂ production

Chapter 4

Material balance ^[10]

Material balances are the basis of process design. A material balance taken over complete process will determine the quantities of raw materials required and products produced. Balances over Individual process until set the process stream flows and compositions. The general conservation equation for any process can be written as;

Material out = material in + accumulation

For a steady state process the accumulation term is zero. If a chemical reaction is taking place a particular chemical species may be formed or consumed. But if there is no chemical reaction, the steady state balance reduces to:

Material out = Material in

A balance equation can be written for each separately identifiable species present, elements, compounds and for total material

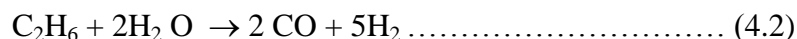
4.1 basis

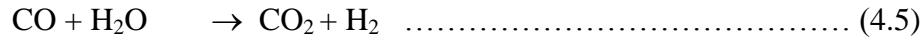
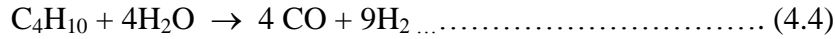
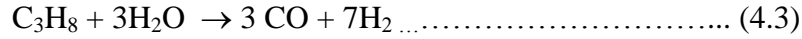
500 T/days of hydrogen gas produced

$(500 \times 1000) / (24 \times 2) = 10,500 \text{ kg mol/hr}$ hydrogen produced

4.2 refinery off-gases required

The reactions involved are as followed:





IF x kg mol / hr of refinery off-gas be supplied then the H₂ content as based on the refinery off-gas composition is given by:

$$= (3*0.9248 + 5*0.0169 + 7*0.0013) * X$$

$$= 2.8121X$$

Hence,

$$2.8121 X = 10,500 \text{ kg mol/hr}$$

$$\therefore X = 3733.86 \text{ kg-mol / hr}$$

Hence, refinery off-gas required = 3733.86 kg-mol / hr.

4.3 material balance of individual equipment

4.3.1 Desulfurizer

In the desulfurizer, there is removal of sulfur, since, the concentration of the sulfur being encountered is less than 3 ppm, we can say that for the desulfurizer.

Input = 3733.86 kg-mol / hr of the refinery off-gas

Output = 3733.86 kg-mol / hr of the refinery off-gas.

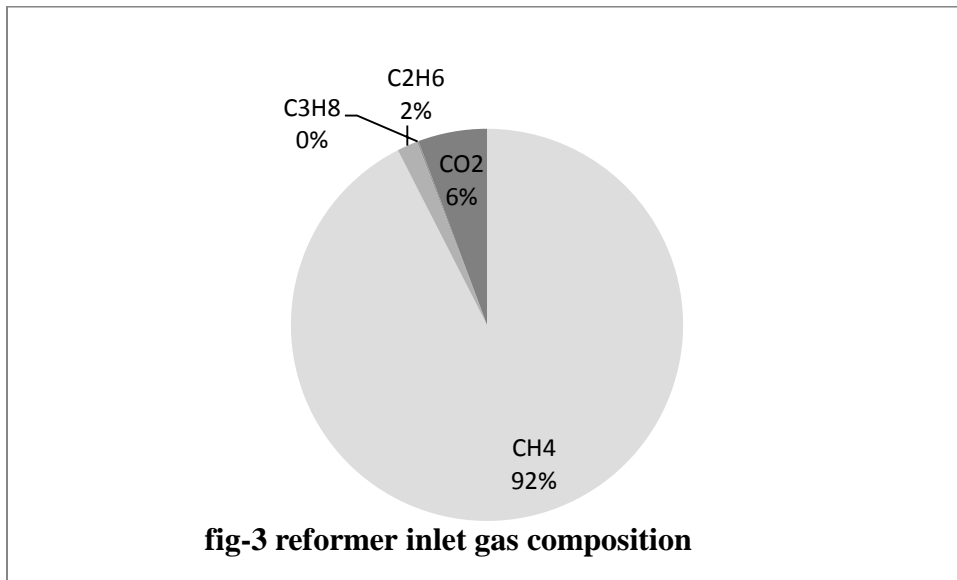
Both the input and output have the same composition and this composition is seen in the table below for feed to the primary reformer

4.3.2 Reformer:

Table-2 refinery off-gas composition at reformer inlet

Refinery off-gas Composition at Reformer Inlet				
Component	Mol%	kg mol / hr	Mol. Wt.	Kg/hr
CH ₄	92.48	3453.07	16	55249.12
C ₂ H ₆	1.69	63.10	30	1893
C ₃ H ₈	0.13	4.85	44	213.4
C ₄ H ₁₀	0	0	58	0
CO ₂	5.69	212.45	44	9347.8
N ₂	0.01	0.37	28	10.36
Total	100	3733.86		66713.68

Now the above data can be plotted in pie chart given below



$$\text{Total carbon in ROG} = (0.9248 * 1) + (0.0169 * 2) + (0.0013 * 3) + (0.0569 * 1) = 1.0194$$

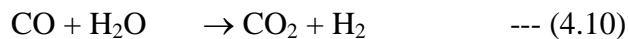
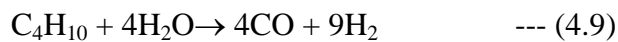
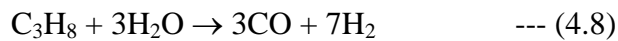
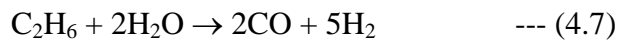
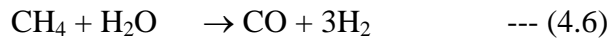
Here taking the steam to carbon mole ratio is 3:1 we have.

$$\text{Steam} = 3 * 1.0194 * 3733.86 = 11418.89 \text{ kg mol / hr} = 205540.03 \text{ Kg / hr}$$

Total feed to reformer = ROG+ steam

$$= 3733.86 + 11418.89 = 15152.75 \text{ kgmol / hr}$$

For the methane reforming the following reaction take place



Assume: (1) 80% conversion of the first reaction.

(2) 100% conversion of 4.7, 4.8 and 4.9 reaction.

(3) 65% conversion of reaction 4.10

From the reaction -1

$$\text{CH}_4 \text{ consumed} = 0.8 * 3453.07 = 2762.456 \text{ kg mol / hr}$$

$$\text{CH}_4 \text{ unconverted} = 3453.07 - 2762.456 = 690.614 \text{ kg mol / hr}$$

$$\text{H}_2\text{O consumed} = 2762.456 \text{ kg mol / hr}$$

$$\text{H}_2 \text{ produced} = 3 * 2762.456 = 8287.368 \text{ kg mol / hr}$$

$$\text{CO produced} = 2762.456 \text{ kg mol / hr}$$

From the reaction-2

$$\text{C}_2\text{H}_6 \text{ consumed} = 63.10 \text{ kg mol / hr}$$

$$\text{H}_2\text{O Consumed} = 2 * 63.10 = 126.2 \text{ kg mol / hr}$$

$$\text{CO produced} = 126.2 \text{ kg mol / hr}$$

$$\text{H}_2 \text{ produced} = 5 * 63.10 = 315 \text{ kg mol / hr}$$

From reaction -3

$$\text{C}_3\text{H}_8 \text{ consumed} = 4.85 \text{ kg mol / hr}$$

$$\text{H}_2\text{O consumed} = 3 * 4.85 = 14.55 \text{ kg mol / hr}$$

$$\text{CO produced} = 14.55 \text{ kg mol / hr}$$

$$\text{H}_2 \text{ produced} = 7 * 4.85 = 33.95 \text{ kg mol / hr}$$

From reaction -4

All components are zero in reaction-4

Total CO produced from the first four reactions

$$2762.456 + 126.2 + 14.55 + 0$$

$$= 2903.206 \text{ kg mol/hr}$$

Total H₂ produced

$$8287.368 + 315 + 33.95 + 0$$

$$= 8636.318 \text{ kg mol/hr}$$

Total H₂O consumed

$$= 2762.456 + 126.2 + 14.55 + 0$$

$$= 2903.206 \text{ kg mol / hr}$$

H₂O remaining

=11418.89– 2903.206

= 8515.684 kg mol / hr

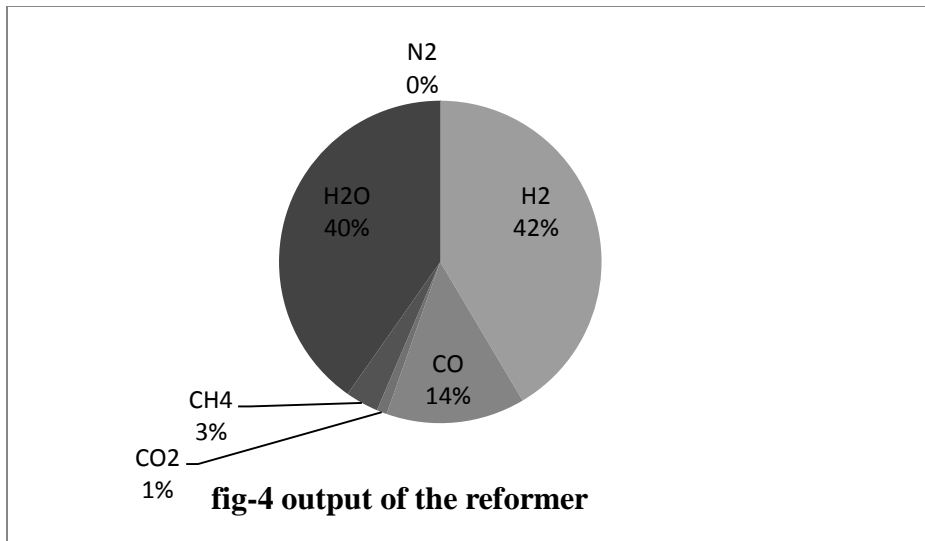
N₂ is used as an inert gas

So, N₂ Input = N₂ Output=0.37 kg mol/ hr

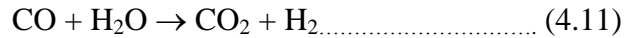
Table-3 output of the reformer

Output from Reformer				
Component	kg mol / hr	Mol%	Mol. Wt.	Kg/hr
N ₂	0.37	0.0018	28	10.36
H ₂	8636.318	41.20	2	17272.636
CO	2903.206	13.85	28	81289.768
CO ₂	212.45	1.013	44	9347.8
CH ₄	690.614	3.295	16	11049.824
H ₂ O	8515.684	40	18	153282.312
Total	20958.642	100		272252.7

The above data are plotted in pie chart given below



4.3.3 Shift Reactor:



CO inlet = 2903.206 kg mol/hr.

.CO consume = 0.65 * 2903.206 = 1916.115 kg mol/hr.

CO outlet = 2903.206 –1116.115= 987.69 kg mol/hr.

H₂O consumed = 1916.115 kg mol/ hr.

H₂O outlet =8515.684–1916.115= 6479.44 kg mol/ hr

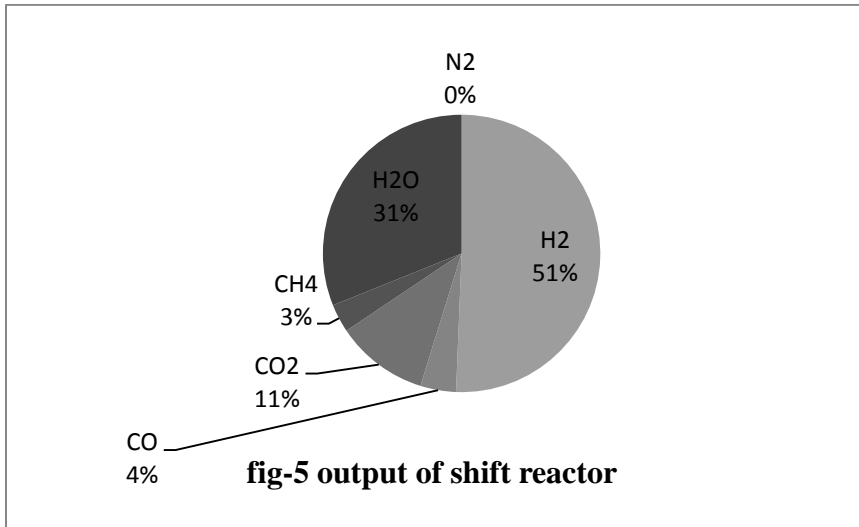
H₂ produced = 1916.115kg mol/hr.

CO₂ produced =1916.115 kg mol/hr

Table-4 output of shift reactor

Output from shift reactor				
Component	kg mol / hr	Mol%	Mol. Wt.	Kg/hr
N ₂	0.37	0.00176	28	10.36
H ₂	10552.433	50.348	2	21104.866
CO	866.962	4.136	28	24274.936
CO ₂	2248.694	10.729	44	98942.536
CH ₄	690.614	3.295	16	11049.824
H ₂ O	6479.44	30.915	18	116629.92
Total	20958.642	100		272012.442

The above data can be plotted in pie chart given below



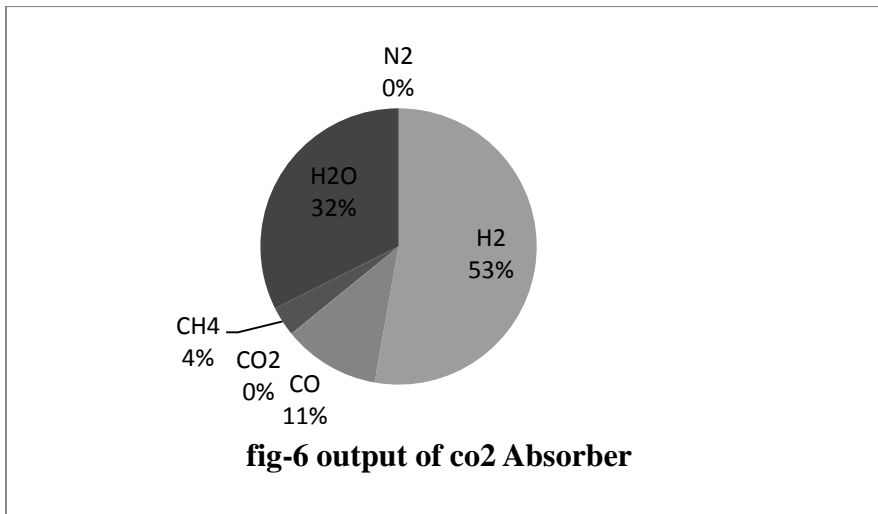
4.3.4 CO₂ Absorber

The absorption of CO₂ is done by MDEA solution.

CO₂ inlet = 2248.694kg mol/ hr

Assume efficiency of CO₂ absorber is 99%.

CO₂ outlet (remaining) = (0.01 * 2248.694) = 22.486kg mol/hr.



4.3.5 Pressure Swing Adsorber

Assume that 99.9% of CO, CO₂ & CH₄ are get adsorbed.

Assume that 100% H₂O & 0.5% H₂ get adsorbed in PSA unit.

CO outlet = 0.001 * 866.962 = 0.866 kg mol/ hr.

CO₂ outlet = 0.001 * 22.486= 0.022 kg mol/ hr.

CH₄ outlet = 0.001 * 690.614= 0.690 kg mol/ hr.

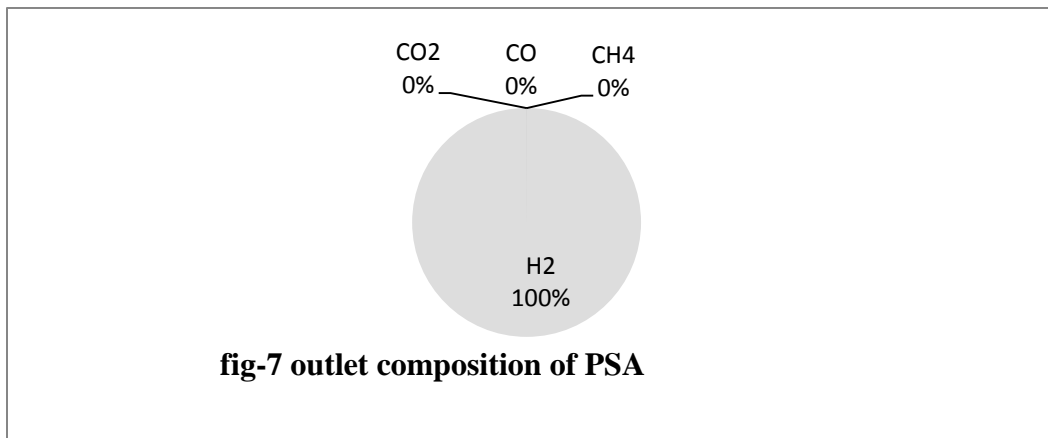
H₂O outlet = 0 kg mol/ hr.

H₂ outlet = 0.995 * 10552.433 = 10499.671kg mol/ hr=10500 kg mol/hr.

Table-5 outlet composition of PSA

Composition at PSA Outlet				
Component	Kg mol / hr	Mol %	Mol. Wt.	Kg/hr
H ₂	10500	99.984	2	21000
CO	0.866	0.0082	28	24.248
CO ₂	0.022	0.00020	44	0.968
CH ₄	0.690	0.0065	16	11.04
Total	10501.578	100		21036.256

The above data are plotted in pie chart given below



Overall material balance flow sheet for H₂ production

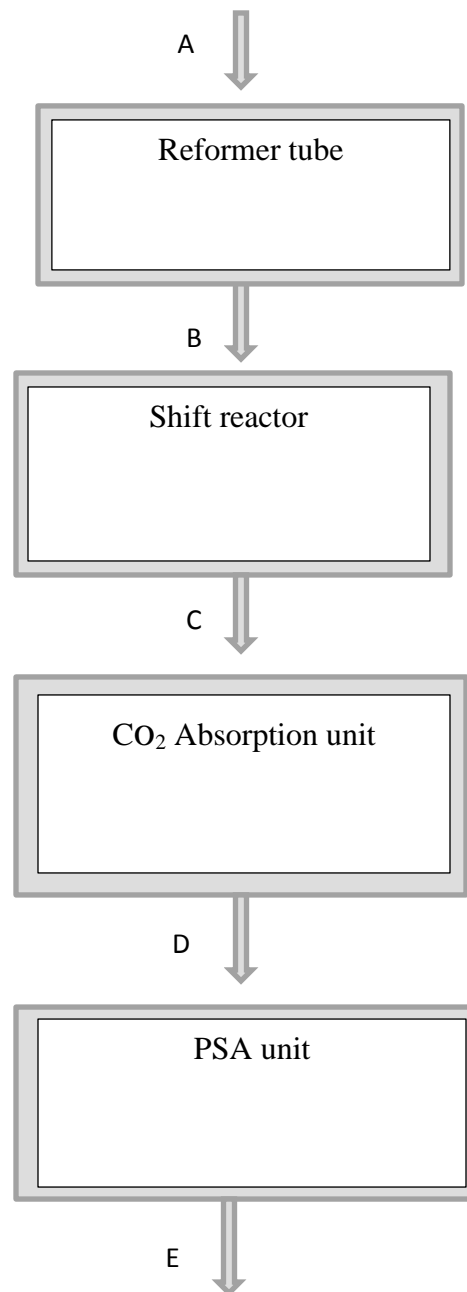


Fig-8 Material balance flow sheet of hydrogen production

Table-6 Material balance of hydrogen production

Stream	component	Mole%	Kgmol/hr
A	CH ₄	92.48	3453.07
	C ₂ H ₆	1.69	63.10
	C ₃ H ₈	0.13	4.85
	C ₄ H ₁₀	0	0
	CO ₂	5.69	212.45
	N ₂	0.01	0.37
B	N ₂	0.0018	0.37
	H ₂	41.20	8636.318
	CO	13.85	2903.206
	CO ₂	1.013	212.45
	CH ₄	3.296	690.614
	H ₂ O	40	8515.684
C	N ₂	0.00176	0.37
	H ₂	50.348	10552.433
	CO	4.136	866.962
	CO ₂	10.729	2248.694
	CH ₄	3.295	690.614
	H ₂ O	30.915	6479.44
D	N ₂	0.0019	0.37
	H ₂	56.696	10552.433
	CO	4.658	866.962
	CO ₂	0.120	22.468
	CH ₄	3.71	690.614
	H ₂ O	34.81	6479.44
E	H ₂	99.99	10500
	CO ₂	0.0001	0.02

Chapter 5

Energy balance ^[10]

5.1 Energy balance at individual equipment

5.1.1 Energy balance at steam reformer

Table-7 Inlet gas properties of reformer

Component	Flow rate (kg/hr)	C _p at 475k (kJ/kg.k)
CH ₄	55249.12	2.483
C ₂ H ₆	1893	1.616
C ₃ H ₈	213.4	1.645
CO ₂	9347.8	0.858
N ₂	10.36	1.034

$$Q_{in} = MC_p\Delta T$$

$$= \{(55249.12 \cdot 2.483) + (1893 \cdot 1.616) + (213.4 \cdot 1.645) + (9347.8 \cdot 0.858) + (10.36 \cdot 1.034)\} (457 - 298)$$

$$= 23.63 \cdot 10^6 \text{ kJ/hr}$$

Table-8 outlet gas properties of reformer

Component	Flow rate (kg/hr)	C _p at 698k (kJ/kg.k)
H ₂	17272.636	14.57
N ₂	10.36	1.064
CO	81289.768	1.017
CO ₂	9347.8	1.126
CH ₄	11049.824	3.602
H ₂ O	153282.312	2.080

$$Q_{out} = MC_p \Delta T$$

$$= \{(17272.636 * 14.57) + (10.36 * 1.064) + (81289.768 * 1.017) + (9347.8 * 1.126) + (11049.8 * 3.602) + (153282.3 * 20)\} (698 - 298)$$

$$= 281.42 * 10^6 \text{ kJ/hr}$$

$$\Delta Q = Q_{out} - Q_{in}$$

$$= 257.79 * 10^6 \text{ kJ/hr}$$

5.1.2 Energy balance at steam generator

$$Q = MC_p \Delta T \quad \text{where, } T_1 = 373\text{k}$$

$$\Rightarrow M = Q / C_p \Delta T \quad T_2 = 298\text{k}$$

$$= (257.79 * 10^6) / (38.73 * 75) \quad C_p = 38.73 \text{ kJ/kmol.k}$$

$$= 88747.740 \text{ kgmol/hr}$$

$$\text{Export stream} = (88747.740 - 11418.89)$$

$$= 77328.850 \text{ kmol/hr}$$

5.1.3 Energy balance at shift converter

Table-9 Inlet gas properties of shift converter

Component	Flow rate (kg/hr)	C _p at 623k (kJ/kg.k)
H ₂	17272.636	7.197
N ₂	10.36	7.008
CO	81289.768	7.276
CO ₂	9347.8	11.311
CH ₄	11049.824	12.546
H ₂ O	153282.312	8.677

$$Q_{in} = MC_p \Delta T$$

$$= \{(10.36 * 7.197) + (17272.636 * 7.008) + (81289.768 * 7.2) + (9347.8 * 11.311) + (11049.824 * 12.546) + (153282.312 * 8.677)\} (623 - 298)$$

$$= 743.26 * 10^6 \text{ kJ/hr}$$

Table-10 outlet gas properties of shift converter

Component	Flow rate (kg/hr)	C _p at 700k (kJ/kg.k)
H ₂	21104.866	7.035
N ₂	10.36	7.351
CO	24274.936	7.451
CO ₂	98942.536	11.489
CH ₄	11049.829	11.88
H ₂ O	116629.92	8.951

$$Q_{\text{out}} = MC_p \Delta T$$

$$= \{(10.36 * 7.351) + (21104.866 * 7.035) + (24274.936 * 7.451) + (11.489 * 98942.536) + (11049.829 * 11.88) + (116629.92 * 8.951)\} (700 - 298)$$

$$= 1070.72 * 10^6 \text{ kJ/hr}$$

$$\Delta Q = Q_{\text{out}} - Q_{\text{in}}$$

$$= (1070.72 - 743.26) * 10^6 \text{ kJ/hr}$$

$$= 327.46 * 10^6 \text{ kJ/hr}$$

5.1.4 Energy balance at CO₂ Absorber

Table-11 Inlet gas properties of CO₂ Absorber

Component	Flow rate (kg/hr)	C _p at 366k (kJ/kg.k)
H ₂	21104.866	6.974
N ₂	10.36	6.991
CO	24274.936	7.013
CO ₂	98942.536	9.871
CH ₄	11049.824	9.736
H ₂ O	116629.92	9.185

$$Q_{in}=MC_p\Delta T$$

$$= \{(10.36*6.991) + (21104.868*6.974) + (24274.936*7.013) + (98942.536*9.871)+ \\ (11049.824*9.736) + (116629.92*9.185)\} (366-298) \\ = 168.16*10^6 \text{ kJ/hr}$$

Table-12 outlet gas properties of CO₂ Absorber

Component	Flow rate (kg/hr)	C _p at 466k (kJ/kg.k)
H ₂	21104.866	6.895
N ₂	10.36	6.961
CO	24274.936	6.965
CO ₂	988.592	8.890
CH ₄	11049.824	8.552
H ₂ O	116629.92	8.026

$$Q_{out}= MC_p\Delta T$$

$$= \{(21104.868*6.895)+(10.36*6.961)+(24274.936*6.965)+(988.592*8.890)+ \\ (11049.824*8.552)+(116629.92*8.026)\}(466-298) \\ = 227.29*10^6 \text{ kJ/hr}$$

$$\Delta Q= Q_{out}-Q_{in}$$

$$= (227.29-168.16)*10^6 \\ = 59.13*10^6 \text{ kJ/hr}$$

5.1.5 Energy balance at PSA

Table-13 Inlet gas properties of PSA

Component	Flow rate (kg/hr)	C _p at 373k (kJ/kg.k)
H ₂	21104.868	6.972
N ₂	10.36	6.921
CO	24274.936	6.015
CO ₂	988.592	9.723
CH ₄	11049.824	9.736
H ₂ O	116629.92	8.185

$$Q_{in} = MC_p \Delta T$$

$$= \{(10.36 \times 6.921) + (21104.868 \times 6.972) + (24274.936 \times 6.015) + (988.592 \times 9.723) + (11049.824 \times 9.736) + (116629.92 \times 8.185)\} (373 - 298)$$

$$= 102.37 \times 10^6 \text{ kJ/hr}$$

Table-14 outlet gas properties

Component	Flow rate (kg/hr)	C _p at 500k (kJ/kg.k)
H ₂	21000	6.993
CO ₂	0.88	10.662
CO	24.248	7.120

$$Q_{out} = MC_p \Delta T$$

$$= \{(21000 \times 6.993) + (0.88 \times 10.662) + (24.248 \times 7.120)\} (500 - 298)$$

$$= 29.48 \times 10^6 \text{ kJ/hr}$$

$$\Delta Q = Q_{out} - Q_{in}$$

$$= -72.88 \times 10^6 \text{ kJ/hr}$$

$$\text{Now } \Delta M = M_{in} - M_{out}$$

$$= 25343.268 \text{ kg/hr}$$

$$\Delta T = 500 - 373$$

$$= 127 \text{ k}$$

$$C_p = \Delta Q / m \Delta T$$

$$= (72.88 \times 10^6) / (25343.268 \times 127)$$

$$= 22.64 \text{ kJ/kg.k}$$

5.1.6 Off-gas temperature calculation

$$\Delta M = 10.36 + 11049.824 + 116629.92$$

$$= 127690.104 \text{ kg/hr}$$

$$Q = MC_p \Delta T$$

$$\Delta T = Q / MC_p$$

$$= (72.88 \times 10^6) / (127690 \times 22.64)$$

$$= 25.210 \text{ k}$$

$$T - 298 = 25.210 \text{ k}$$

$$T = 323.210 \text{ k} \quad (\text{Off-gas temperature})$$

Chapter 6

Equipment design

6.1 CO₂ Absorption column design ^[11]

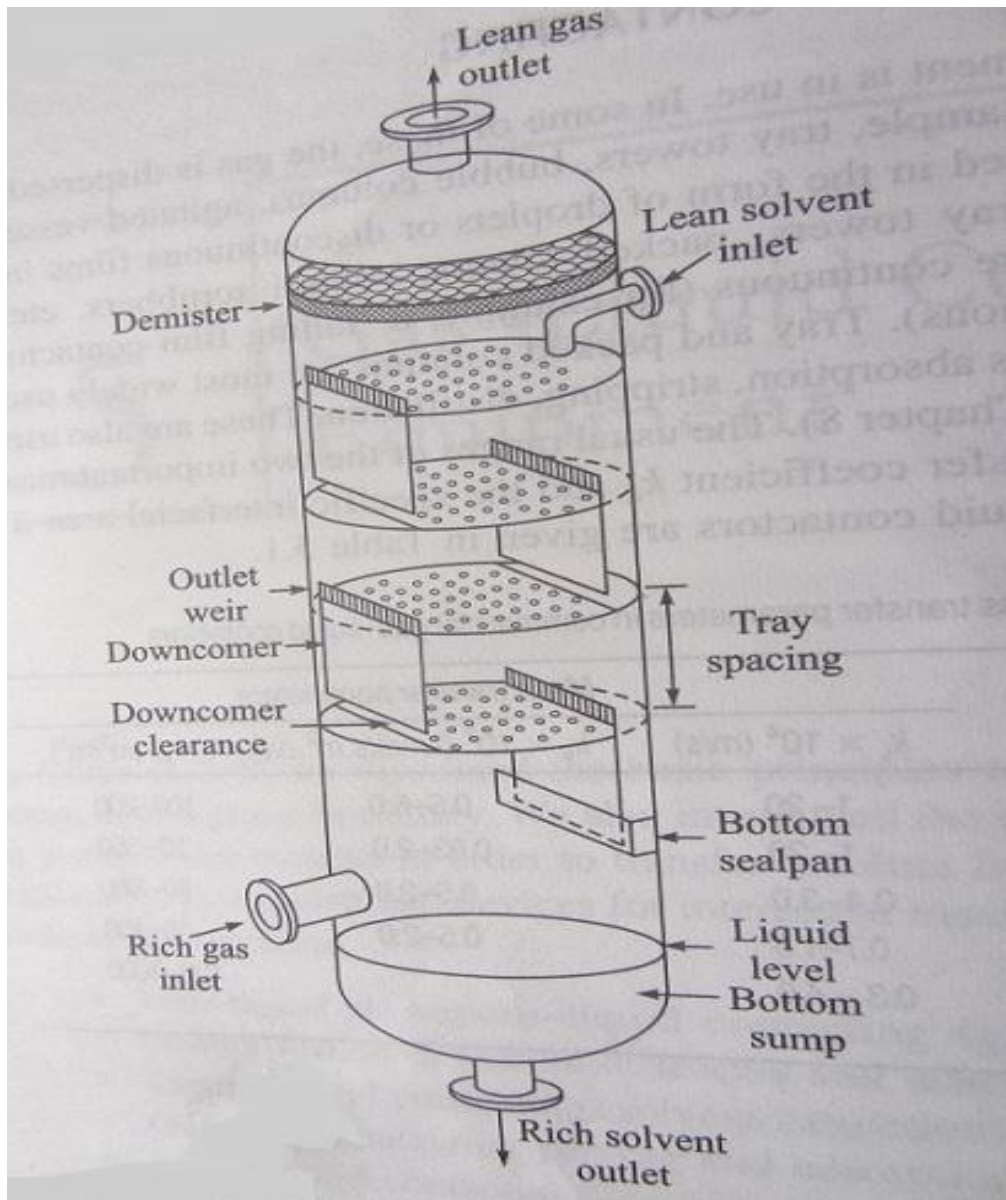


Fig-9 CO₂ Absorption column

Basis: 99% of CO₂ is absorbed

The feed gas rate= 20838.513 kmol/hr

$$G_1 = 20838.513 \text{ kmol/hr}$$

Feed concentration, $y_1 = 0.107$ mole

$$\begin{aligned} Y_1 &= y_1 / (1 - y_1) \\ &= (0.107) / (1 - 0.107) \\ &= 0.119 \text{ mole} \end{aligned}$$

$$\begin{aligned} \text{Feed gas rate on solute free basis } (G_s) &= G_1 * (1 - y_1) \\ &= 20838.5(1 - 0.107) \\ &= 18608.79 \text{ kmol/hr} \end{aligned}$$

$$\begin{aligned} \text{CO}_2 \text{ gas entering} &= G_1 y_1 \\ &= (20838.513) * (0.107) \\ &= 2229.72 \text{ kmol/hr} \end{aligned}$$

$$\begin{aligned} \text{Therefore CO}_2 \text{ absorbed} &= 2229.72 * 0.99 \\ &= 2207.42 \text{ kmol/hr} \end{aligned}$$

CO₂ leaving= 22.3 kmol/hr

$$\begin{aligned} \text{Concentration of } Y_2 &= 22.3 / G_s \\ &= 22.03 / 18608.79 \\ &= 0.0019 \text{ mole} \end{aligned}$$

$$\begin{aligned} \text{Concentration of } y_2 &= Y_2 / (1 + Y_2) \\ &= 0.0019 / (1 + 0.0019) \\ &= 0.0018 \text{ mole} \end{aligned}$$

Equation of equilibrium line $Y = 1.32X$ (6.1)

$$\begin{aligned} X_1 &= Y_1 / 1.32 \\ &= 0.119 / 1.32 \\ &= 0.09 \end{aligned}$$

$$\begin{aligned} \text{Now the material balance equation is } G_s (Y_1 - Y_2) &= L_s (X_1 - X_2) \\ 18608.79(0.119 - 0.0019) &= L_s (0.09 - 0) \\ L_s &= 24212 \text{ kmol/hr} \end{aligned}$$

$$\begin{aligned} \text{Actual liquid rate is 1.25 times the original, } L_s &= 1.25 * 24212 \\ &= 30265.12 \text{ kmol/hr} \end{aligned}$$

$$\begin{aligned}
 \text{The liquid at the bottom of the tower } (L_1) &= L_S + \text{CO}_2 \text{ absorbed} \\
 &= 30265.12 + 2207.42 \\
 &= 32472.54 \text{ kmol/hr}
 \end{aligned}$$

6.1.1 Calculation of tray or column diameter

$$\begin{aligned}
 \text{Data given:- } \rho_G &= 2.82 \text{ kg/m}^3 \\
 &= 0.175 \text{ lb/ft}^3 \\
 \rho_L &= 1038 \text{ kg/m}^3 \\
 &= 64.67 \text{ lb/ft}^3
 \end{aligned}$$

$$\begin{aligned}
 \text{Now flow parameter } (F_{LV}) &= (L_1/G_1) * (\rho_G / \rho_L)^{0.5} \\
 &= (32472.54/20838.513) * (0.175/64.67)^{0.5} \\
 &= 1.558 * 0.052 \\
 &= 0.081 \text{ unit}
 \end{aligned}$$

Now calculate $C_{SB} = 0.23$ from graph between F_{LV} and tray spacing 18 inch

$$\begin{aligned}
 \text{Superficial velocity } U_{sf} &= C_{SB} * [(\rho_L - \rho_G) / \rho_G]^{0.5} * (\sigma/20)^{0.2} \text{ ft/sec} \\
 &= 0.23 * 1.004 * 19.19 \\
 &= 4.5 \text{ ft/sec}
 \end{aligned}$$

Taking the operating velocity as 70% of the flooding velocity

$$\begin{aligned}
 U_S &= 4.5 * 0.70 \\
 &= 3.15 \text{ ft/sec}
 \end{aligned}$$

$$\begin{aligned}
 \text{Volumetric flow rate of gas} &= 272012.442 / 2.82 \\
 &= 96458.31 \text{ m}^3/\text{hr} \\
 &= 3406393.07 \text{ ft}^3/\text{hr}
 \end{aligned}$$

$$\begin{aligned}
 \text{Active tray area } (A_a) &= \text{volumetric flow rate of gas} / \text{operating velocity} \\
 &= 3406393.07 / (3.15 * 3600) \\
 &= 300 \text{ ft}^2
 \end{aligned}$$

$$\begin{aligned}
 \text{Tower cross section } (A_T) &= A_a / (1 - f_d) \\
 &= 300 / (1 - 0.2) \\
 &= 375 \text{ ft}^2
 \end{aligned}$$

$$\begin{aligned}
 \text{Tower diameter } (D_C) &= (375 * 4 / 3.14)^{0.5} \\
 &= 21 \text{ ft} \\
 &= 6.4 \text{ m}
 \end{aligned}$$

6.1.2 Calculation of column height

Data given:-

$$G_S = 18608.79 \text{ kmol/hr} \quad y_1 = 0.107$$

$$L_S = 30265.12 \text{ kmol/hr} \quad y_2 = 0.0018$$

$$K_x a = 1.25 \text{ kmol/m}_3 \cdot \text{s} \cdot \Delta x \quad x_2 = 0$$

$$K_y a = 0.075 \text{ kmol/m}_3 \cdot \text{s} \cdot \Delta y$$

Now the vapour-liquid equilibrium data are found from the equation given below

$$y = 1.32x / (1 + 0.32x) \dots \dots \dots (6.2)$$

Table-15 vapour- liquid equilibrium data

x	0	0.01	0.03	0.05	0.07
y= 1.32x/(1+0.32x)	0	0.013	0.039	0.064	0.090

Now plotting the equilibrium data on x-y plane and the operating line also plotted on the same graph for determining the number of theoretical plate required

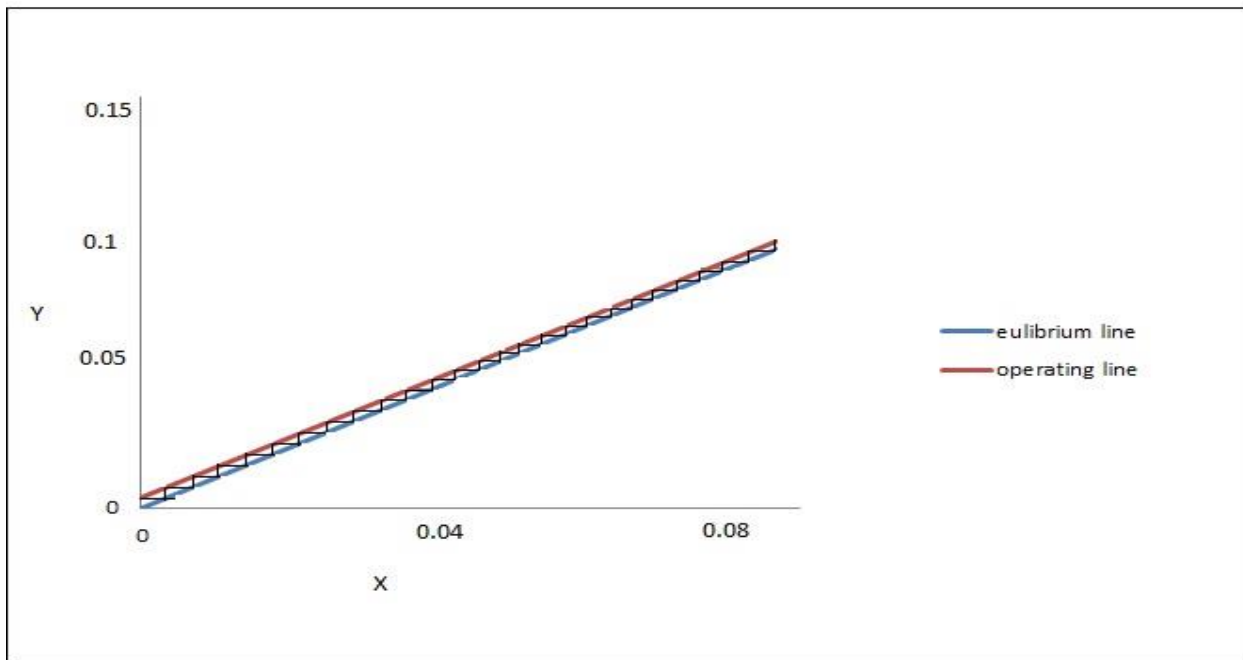


Fig-10 Operating line and Equilibrium line graph

From graph the number of ideal tray found is equal to 26

$$\begin{aligned} \therefore \text{Number of real tray} &= \frac{\text{Number of ideal tray}}{\text{tray efficeancy}} \\ &= 26 / 0.65 \\ &= 40 \end{aligned}$$

$$\begin{aligned} \text{Now the slop } -K_x a / K_y a &= -1.25 / 0.075 \\ &= -16.67 \end{aligned}$$

$$\text{Now } P_1(x, y) = (0.0805, 0.107)$$

$$\text{From graph } P_1(x_i, y_i) = (0.0905, 0.103)$$

$$\text{Slop } -K_x a / K_y a = - (K_x a / K_y a) * (1 - y)_{im} / (1 - x)_{im}$$

$$\text{Now } (1 - y)_{im} = \frac{(1 - y_i) - (1 - y)}{\ln \frac{(1 - y_i)}{(1 - y)}}$$

$$\begin{aligned} (1 - y)_{im} &= \frac{(1 - 0.103) - (1 - 0.107)}{\ln \frac{(1 - 0.103)}{(1 - 0.107)}} \\ &= 0.894 \end{aligned}$$

$$\begin{aligned} (1 - x)_{im} &= \frac{(1 - x) - (1 - x_i)}{\ln \frac{(1 - x)}{(1 - x_i)}} \\ &= \frac{(1 - 0.0805) - (1 - 0.0905)}{\ln \frac{(1 - 0.0805)}{(1 - 0.0905)}} \\ &= 0.914 \end{aligned}$$

$$\begin{aligned} -K_x a / K_y a &= - (K_x a / K_y a) * (1 - y)_{im} / (1 - x)_{im} \\ &= -16.67 * (0.894 / 0.914) \\ &= -16.30 \end{aligned}$$

$$\text{From graph } P_2(x, y) = (0.035, 0.050)$$

$$P_2(x_i, y_i) = (0.0375, 0.048)$$

$$\begin{aligned} (1 - y)_{im} &= \frac{(1 - 0.952) - (1 - 0.95)}{\ln \frac{(1 - 0.952)}{(1 - 0.95)}} \\ &= 0.950 \end{aligned}$$

$$(1 - x)_{im} = \frac{(1 - 0.965) - (1 - 0.9625)}{\ln \frac{(1 - 0.965)}{(1 - 0.9625)}}$$

$$= 0.963$$

$$-K_x a / K_y a = -16.67 * (0.950 / 0.963)$$

$$= -16.44$$

From graph $P_3(x,y) = (0.0275, 0.040)$

$$P_3(x_i, y_i) = (0.03, 0.038)$$

$$(1 - y)_{im} = \frac{0.962 - 0.96}{\ln \frac{0.962}{0.96}}$$

$$= 0.960$$

$$(1 - x)_{im} = \frac{0.9725 - 0.97}{\ln \frac{0.9725}{0.97}}$$

$$= 0.971$$

$$-K_x a / K_y a = -16.67 * (0.960 / 0.971)$$

$$= -16.48$$

$$N_{tG} = \int_{y_2}^{y_1} \frac{(1-y)_{im}}{(1-y) * (y-y_i)} dy$$

$$= \int_{y_2}^{y_1} f(y) dy$$

= Area under the graph

Table-16 Data of y and f(y)

y	0.107	0.050	0.040
y _i	0.103	0.048	0.038
f(y)	250	500	500

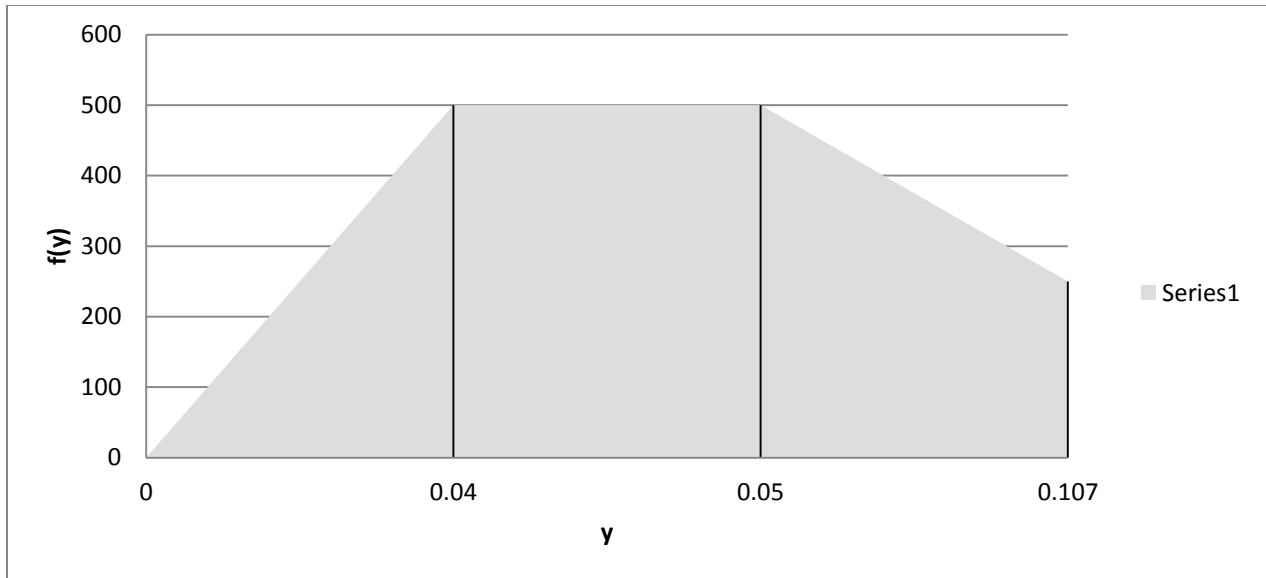


Fig-11 the graph between y and f(y)

Now the graph is plotted between y and f(y)

The number of gas phase transfer unit (N_{tG}) = area under the curve

$$= 34$$

Number of gas phase transfer unit from graph (N_{tG}) = 34

Height of gas phase transfer unit (H_{tG}) = $G/K_y a$

$$G = G_1/A_T$$

$$G_1 = 20838.1513/34 \text{ kmol/h.m}^2$$

$$= 612.8 \text{ kmol/h.m}^2$$

$$G_2 = G_s/(1-y_2) \cdot 1/A_T$$

$$= 18608.79/(0.9982 \cdot 34)$$

$$= 548.304 \text{ kmol/h.m}^2$$

$$G = (G_1 + G_2)/2$$

$$= (612.8 + 548.304)/2$$

$$= 580.55 \text{ kmol/h.m}^2$$

$$H_{tG} = 580.55/(270 \cdot 2.285)$$

$$= 0.941$$

$$\text{Height (h)} = H_{tG} \cdot N_{tG}$$

$$= 0.941 \cdot 34$$

$$= 32 \text{ m}$$

Mechanical design ^[12]

6.1.3 Shell design

Data given:-

Diameter of the column = 6.4m

Height of the column = 32m

Outside pressure is 1atm = 0.1 MN/m²

Design pressure $P_d = 0.1 * 1.05$

$$= 0.105 \text{ MN/m}^2$$

Shell is I.S 2825-1969

Allowable stress $f = 98.1 \text{ MN/m}^2$

Welding joint efficiency $j = 0.85$

Modulus of elasticity $E = 1 * 10^5 \text{ MN/m}^2$

Now $D_o/L = 6.4/32$

$$= 0.2$$

By using D_o/L ratio we can find K and M value from table given in book

Now $K = 0.224$, $M = 2.54$

$$P = K * E * (t/D_o)^M$$

$$0.105 = 0.224 * 10^5 * (t/6.4)^{2.54}$$

$$t = 0.051 \text{ m}$$

$$= 51 \text{ mm}$$

Checking plastic deformation:-

$$P = 2f * (t/D_o) * \frac{1}{1 + [1.5U(1 - 0.2D_o/l) / 100 * (t/D_o)]}$$

Where out of roundness (U) = 1.5% for new vessel

$$P = 2 * 98.1 * (0.051/6.4) * \frac{1}{1 + [1.5 * 1.5(1 - 0.2 * 0.2) / 100 * (0.051/6.4)]}$$

$$= 0.417 \text{ MN/m}^2$$

$$0.417 > 0.105$$

The shell thickness is correct

6.1.4 Head design

Assume Torispherical head

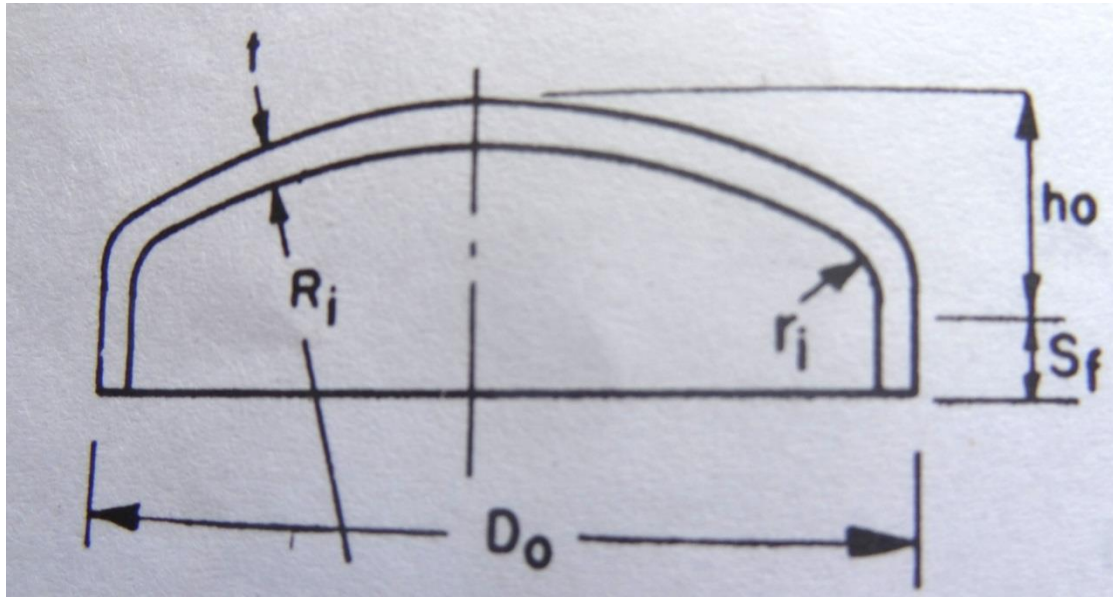


Fig-12 Torispherical head

$$\text{Head thickness } t_h = PD_o C / 2fJ$$

Where $C \rightarrow$ stress concentration factor

“ C ” calculates from h_E/D_o and t/D_o data table given in book

$$h_E = [\text{least of } h_o, D_o^2/4R_o, (D_o r_o/2)]$$

$$D_o = D_i + 2t_s$$

$$= 6.4 + 2 * 0.051$$

$$= 6.502 \text{ m}$$

Assume $R_i = R_o = D_o = 6.502 \text{ m}$

$$r_o = 0.06 D_o$$

$$h_o = R_o - \sqrt{\left(R_o - \frac{D_o}{2}\right) * \left(R_o + \frac{D_o}{2} - 2r_o\right)}$$

$$= 6.502 - \sqrt{(6.502 - 3.251) * (6.502 + 3.251 - 2 * 0.390)}$$

$$= 1.10 \text{ m}$$

$$D_o^2/4R_o = (42.27) / (4 * 6.502)$$

$$= 1.625 \text{ m}$$

$$(D_o r_o / 2)^{1/2} = (6.502 * 0.390 / 2)^{0.5}$$

$$= 1.126 \text{ m}$$

$$h_E = h_o = 1.10$$

$$h_E / D_o = 1.10 / 6.502$$

$$= 0.169$$

$$t / D_o = PC / 2fJ$$

$$= 0.105 * C / (2 * 98.1 * 0.85)$$

$$t / D_o = 0.6 * 10^{-3} C$$

Now C can be found from t / D_o and h_E / D_o table given in book

$$t / D_o = 0.002$$

$$C = 4.1$$

$$t_h = 0.002 * D_o$$

$$= 0.002 * 6.502$$

$$= 0.013 \text{ m}$$

$$= 13 \text{ mm}$$

6.1.5 Support design

Assume the support is skirt support

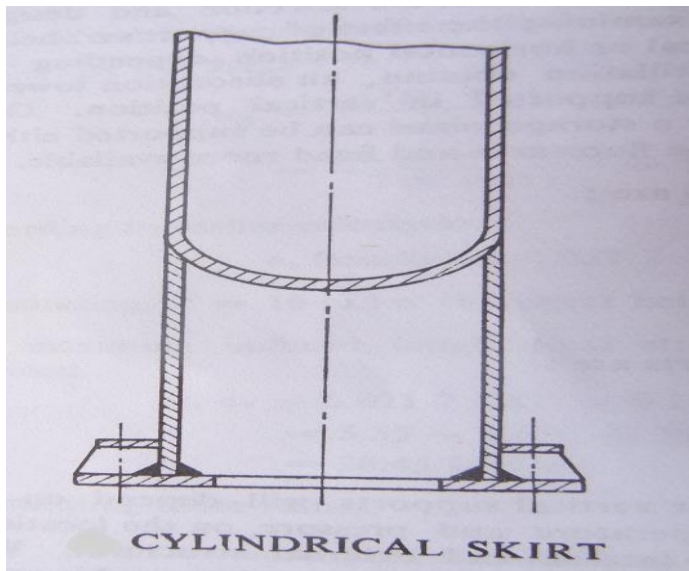


Fig-13 Cylindrical Skirt support

(i) Stress on skirt support due to dead weight of vessel

$$f_{db} = \frac{\sum W}{\pi D_{sk} t_{sk}}$$

$$\text{Now } \sum W_{min} = \pi D t_s L \gamma_{steel} + W_a$$

$$\text{But } t_s = \frac{PD}{2fj} + C$$

$$= 0.8 * 10^{-3} / (2 * 96 * 10^6 * 0.90) + 3 * 10^{-3}$$

$$= 0.003 \text{ m}$$

$$= 3 \text{ mm}$$

$$W_s = \pi D t_s L \gamma_{steel}$$

$$= 3.14 * 6.4 * 0.003 * 32 * 7.7 * 10^4 \text{ N}$$

$$= 148549.632 \text{ N}$$

$$W_a = 18\% \text{ of } W_s$$

$$= 26738.93 \text{ N}$$

$$\sum W_{min} = W_a + W_s$$

$$\sum W_{min} = 175288.565 \text{ N}$$

$$= 175.2 \text{ KN}$$

$$\sum W_{max} = W_a + W_s + W_I + W_{ins} + W_{tray} + W_{loaders}$$

$$\text{Now } W_{ins} = \pi D_{eff} t_{ins} L \gamma_{ins}$$

$$= 3.14 * (6.4 + 2 * 75 * 10^{-3}) * 75 * 10^{-3} * 32 * 5.64 * 10^3$$

$$= 278394.912 \text{ N}$$

$$W_{tray} = 1000 * \left(\frac{\pi}{4} D^2\right) * 26$$

$$= 1000 * 0.785 * 6.4^2 * 26$$

$$= 835993.6 \text{ N}$$

$$W_{loader} = 365 * (32 + 4)$$

$$= 13140 \text{ N}$$

$$W_I = \frac{\pi}{4} D_i^2 * \rho_t * L$$

$$= (3.14/4) * (6.4 - 2 * 75 * 10^{-3})^2 * 1000 * 32$$

$$= 981250 \text{ N}$$

$$\therefore \Sigma W_{max} = 2284067.077 \text{ N}$$

$$= 2284.067 \text{ KN}$$

Now to calculate period of vibration

$$\begin{aligned} T_{min} &= 6.36 \cdot 10^{-5} (H/D)^{3/2} \cdot (W/t_s)^{1/2} \\ &= 6.35 \cdot 10^{-5} (32/6.4)^{3/2} (1754.2/0.003)^{1/2} \\ &= 0.167 < 0.5 \end{aligned}$$

$$\therefore K_2 = 1$$

$$\begin{aligned} T_{max} &= 6.36 \cdot 10^{-5} (H/D)^{3/2} \cdot (W/t_s)^{1/2} \\ &= 6.35 \cdot 10^{-5} (32/6.4)^{3/2} (2284.067/0.003)^{1/2} \\ &= 0.615 > 0.5 \end{aligned}$$

$$\therefore K_2 = 2$$

$$K_1 = 0.7 \text{ (cylindrical)}$$

$$K = K_1 \cdot K_2$$

$$= 0.7 \cdot 2$$

$$= 1.4$$

$$\begin{aligned} \text{Now } f_{db} \text{ (min)} &= \frac{\Sigma W}{\pi D_{sk} t_{sk}} \\ &= \frac{175.2}{\pi \cdot 6.4 \cdot t_{sk}} \\ &= \frac{8.718}{t_{sk}} \text{ KN/m}^2 \end{aligned}$$

$$\begin{aligned} f_{db} \text{ (max)} &= \frac{\Sigma W}{\pi D_{sk} t_{sk}} \\ &= \frac{2284.067}{\pi \cdot 6.4 \cdot t_{sk}} \\ &= \frac{113.65}{t_{sk}} \text{ KN/m}^2 \end{aligned}$$

(ii) Stress due to wind load

$$\begin{aligned}
P_{lw} &= KP_1 h_1 D_{sk} \\
&= 1.4 * 0.8 * 21 * 6.4 * 10^{-3} \\
&= 0.150 \text{ MN}
\end{aligned}$$

$$\begin{aligned}
P_{up} &= K P_2 h_2 D_{sk} \\
&= 1.4 * 0.8 * 11 * 6.4 * 10^{-3} \\
&= 0.07884 \text{ MN}
\end{aligned}$$

$$\begin{aligned}
\therefore \text{Total banding moment } M_{wb} &= P_{lb} \frac{h_1}{2} + P_{up} * \left(\frac{h_1 + h_2}{2} \right) \\
&= 0.150 * (21/2) + 0.07884 * 32/2 \\
&= 2.836 \text{ MN}
\end{aligned}$$

$$\begin{aligned}
\therefore f_{wb} &= \frac{M_{wb}}{Z} = \frac{M_{wb}}{\frac{\pi D_{sk}^2}{4} t_{sk}} \\
&= \frac{4 * 2.836}{3.14 * 6.4^2 t_{sk}} \\
&= \frac{0.08820}{t_{sk}} \text{ MN/m}^2
\end{aligned}$$

(iii) Stress due to seismic load

$$T = 0.167 \text{ to } 0.615$$

$$\begin{aligned}
\therefore C_S (\text{max}) &= 0.02/T \\
&= 0.02/0.615 \\
&= 0.032
\end{aligned}$$

$$\begin{aligned}
C_S (\text{min}) &= 0.02/T \\
&= 0.02/0.167 \\
&= 0.119
\end{aligned}$$

$$\begin{aligned}
\text{Now } f_{sb} (\text{min}) &= \frac{\frac{8}{3} * C_S * W_{min} * H}{\pi * D_{sk}^2 * t_{sk}} \\
&= \frac{\frac{8}{3} * 0.119 * 175.2 * 32}{\pi * 6.4^2 t_{sk}} \\
&= 13.83/t_{sk} \text{ KN/m}^2
\end{aligned}$$

$$\begin{aligned}
 f_{sb}(\max) &= \frac{\frac{8}{3} * C_s * W_{max} * H}{\pi * D_{sk}^2 * t_{sk}} \\
 &= \frac{\frac{8}{3} * 0.032 * 2284.067 * 32}{\pi * 6.4^2 * t_{sk}} \\
 &= 48.493 / t_{sk} \text{ KN/m}^2
 \end{aligned}$$

$$\begin{aligned}
 \text{Resultant tensile stress } (f_t)_R &= (f_{wb} \text{ or } f_{sb})_{\text{greater}} - f_{db} \\
 &= \frac{0.0882}{t_{sk}} - \frac{8.718 * 10^{-3}}{t_{sk}} \\
 &= 0.079 / t_{sk} \text{ MN/m}^2
 \end{aligned}$$

$$\begin{aligned}
 \text{Resultant compressive stress } (f_c)_R &= (f_{wb} \text{ or } f_{sb})_{\text{greater}} + f_{db} \\
 &= \frac{0.0882}{t_{sk}} - \frac{113.65 * 10^{-3}}{t_{sk}} \\
 &= 0.201 / t_{sk} \text{ KN/m}^2
 \end{aligned}$$

$$\text{Now } (f_t)_R \leq f_{tJ}$$

$$0.079 / t_{sk} = 96 * 0.90$$

$$t_{sk} = 0.0009 \text{ m}$$

$$= 0.9 \text{ mm}$$

$$\text{Similarly } (f_c)_R = 0.125 * E * (t_{sk} / D)$$

$$0.201 / t_{sk} = 0.125 * 2 * 10^5 * t_{sk} / 6.4$$

$$t_{sk} = 7.132 * 10^{-3} \text{ m}$$

$$= 7.132 \text{ mm}$$

Bolting plate requirement:-

$$(f_c)_{max} = \frac{\sum W_{max}}{A} + \frac{(M_{sb} \text{ or } M_{wb})_{\text{greater}}}{Z}$$

$$A = \pi D_m l$$

$$D_m = D_o + l$$

$$Z = \frac{\pi}{4} D_m^2 l$$

$$\text{take } l = 100 \text{ mm} = 0.1 \text{ m}$$

$$D_m = 6.4 + 0.1$$

$$= 6.5 \text{ m}$$

$$Z = 3.14 * 6.5^2 * 0.1$$

$$= 3.31 \text{ m}^2$$

$$A = 3.14 * 6.5 * 0.1$$

$$= 2.041 \text{ m}^2$$

$$\sum W_{max} = 2284.067 \text{ KN}$$

$$M_{sb} = 2/3 \text{ CWH}$$

$$= \frac{2}{3} * 0.032 * 2284.067 * 32$$

$$= 1560 \text{ KN}$$

$$= 1.560 \text{ MN}$$

$$(f_c)_{max} = (2284.067 * 10^{-3} / 2.041) + (2.836 / 3.31)$$

$$= 1.975 \text{ MN/m}^2$$

$$(f_c)_{max} < 9.5 \text{ MN/m}^2$$

so all the data are correct and it is suitable for design

$$t_{BP} = 1 * \sqrt{\frac{3 * (f_c)_{max}}{f_{allowable}}}$$

$$= 0.1 * \sqrt{\frac{3 * 1.975}{96}} = 0.024 \text{ m}$$

$$t_{BP} = 24 \text{ mm}$$

if $t_{BP} > 20 \text{ mm}$, then gussets plate be used to reinforce the plate

$$t_{BP} = \sqrt{\frac{6 * M_y}{f_{allowable}}}$$

Assume Breath of bearing plate (b) = 100 mm

$$\text{Number of bearing plate (N)} = \frac{\pi D_m}{b}$$

$$= 3.14 * 6.5 / 0.1$$

$$= 204 \text{ gusset plate}$$

here $l/b = 1$

$$\therefore M (\text{max}) = M_y = -0.119 f_c l^2$$

$$= -0.119 * 1.975 * (0.1)^2$$

$$= 0.0023 \text{ MJ}$$

$$\begin{aligned} \therefore t_{BP} &= \sqrt{\frac{6 * M_y}{f_{allowable}}} \\ &= \sqrt{\frac{6 * 2.35 * 10^{-3}}{96}} \\ &= 0.012 \text{ m} \\ &= 12 \text{ mm} \end{aligned}$$

$$\begin{aligned} \text{Dimension of bearing plate} &= l * b * t_{BP} \\ &= 0.1 * 0.1 * 0.012 \\ &= 1.2 * 10^{-4} \text{ m}^3 \end{aligned}$$

$$\begin{aligned} \text{Stability factor (j)} &= W_{min} * R / M_{wb} \\ &= 175 * 45 / 2836 \\ &= 2.77 > 1.5 \end{aligned}$$

But there is no anchor bolt design because, stability factor (j) > 1.5

Table-17 component required for design

component	number	dimension
Bearing plate	204	0.1*0.1*0.024
Gusset plate	204	0.1*0.1*0.012
Anchor bolt	0	0

Table-18 Specification for CO₂ Absorber Column

PARAMETER	DESCRIPTION
Tower MOC	SS304
Tower ID	6.4 m
Tower OD	6.502 m
Shell thickness	0.051 m
Head thickness	0.013
Height of tower(Without support)	32 m
Type of Head	Torispherical head
Tower Support	Skirt support
Skirt MOC	SS304
Skirt Height	4 m
Skirt thickness	0.0009 m
Type	Pall ring
MOC	Metal (ss)

6.2 Catalytic Reactor Design ^[13, 14]

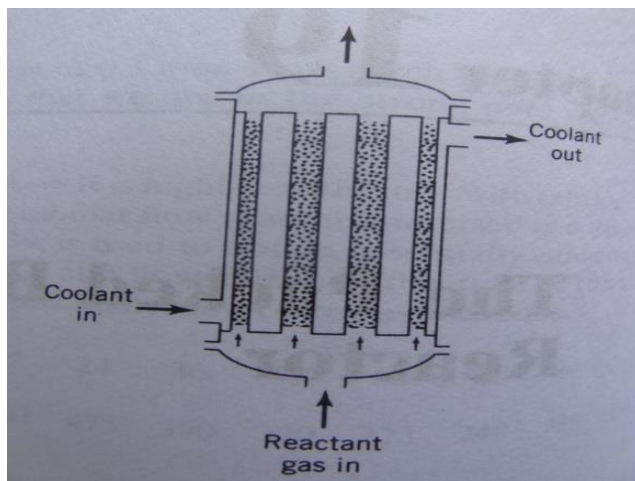


Fig-14 Catalytic reactor

Now based on volume of catalyst pallet the design equation is given below

$$\frac{V_s}{F_{AO}} = \int_0^{X_A} \frac{dX_A}{-r_A}$$

= area under the curve

Table-19 Different value of X_A and finding corresponding rate ($-r_A$)

X_A	0.28	0.15	0.07	0.02
r_A	3.4	5.4	7.6	9.1
$\frac{-1}{r_A}$ ($m^3 \cdot sec/mole$)	0.29	0.18	0.13	0.11

From the above data plotting X_A Vs. $1/r_A$ & finding area under the curve at $X_A = 0.35$

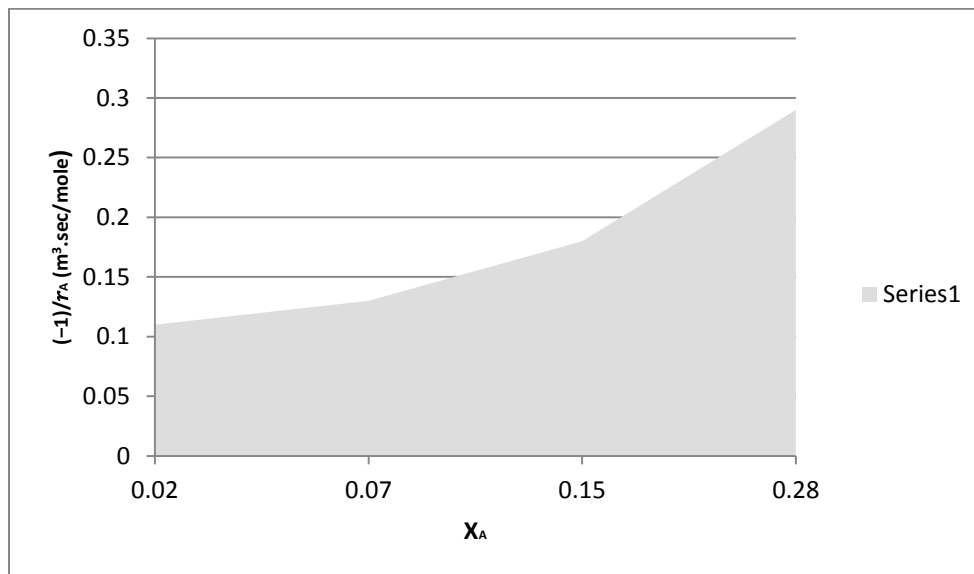


Fig-15 Reactor volume chart

Area under the curve = 0.0675

$$\therefore \frac{V_s}{F_{AO}} = 0.0675$$

$$V_s = F_{AO} * 0.0675$$

$$= 1038.013 * 0.0675 \text{ m}^3$$

$$= 70 \text{ m}^3$$

$$\therefore \text{Volume of catalyst } V_s = 70 \text{ m}^3$$

Assume the dimension of the tube

Length of the tube = 4m

Diameter of the tube = 10 cm

$$\begin{aligned} \therefore \text{Volume of one tube} &= \frac{\pi}{4} D^2 L \\ &= (3.14/4) * 10^{-2} * 4 \\ &= 0.0314 \text{ m}^3 \end{aligned}$$

Take the extra 20% of the volume of the tube

$$\begin{aligned} \therefore \text{The new volume} &= 0.0314 * 1.2 \\ &= 0.037 \text{ m}^3 \end{aligned}$$

$$\begin{aligned} \text{Number of tubes} &= \frac{\text{total volume of the catalyst}}{\text{volume of one tube}} \\ &= 70/0.037 \\ &= 1900 \end{aligned}$$

Now 1900 tubes are arrange in 4-reactor

In one reactor has 475 tubes are arrange

Now the tube diameter of one tube = 0.1m

Length of one tube = 4.8 m

Tubes are arrange in square pitch

$$\therefore \text{The number of square pitch} = 475/4$$

$$= 119$$

Now the equivalent diameter can be calculated from square pitch

$$D_e = \frac{4(P_T^2 - \frac{\pi d_o^2}{4})}{\pi d_o}$$
$$= 4[(10^2 - 3.14 * 3.93^2 / 4)] / (3.14 * 3.93)$$
$$= 72.31 \text{ cm}$$

$$\text{Area of one square pitch} = \frac{\pi}{4} D_e^2$$
$$= (3.14/4) * 72.31^2$$
$$= 4105.30 \text{ cm}^2$$

$$\therefore \text{Area of 119 square pitch} = 119 * 4105.30$$
$$= 488531.46 \text{ cm}^2$$

$$\text{Now the bundle cross flow area } A_s = \frac{D_s * C * B}{P_T}$$

$$D_s = \frac{A_s * P_T}{C * B}$$
$$= (488531.46 * 25.4) / (15.24 * 1920)$$
$$= 424.07 \text{ cm}$$

$$\therefore \text{Diameter of shell } (D_s) = 424.07 \text{ cm}$$

Mechanical design ^[12]

6.2.1 Shell design

Data given:-

Shell inside diameter = 424.07 cm

Outside pressure is 1atm= 0.1 MN/m²

$$\begin{aligned}\text{Design pressure } P_d &= 0.1 * 1.05 \\ &= 0.105 \text{ MN/m}^2\end{aligned}$$

Shell is I.S 2825-1969

Allowable stress $f = 98.1 \text{ MN/m}^2$

Welding joint efficiency $j = 0.85$

$$\begin{aligned}\text{Thickness of shell, } t_s &= \frac{Pd}{2fj} \\ &= (0.105 * 4.24) / (2 * 98.1 * 0.85) \\ &= 0.002 \text{ m} \\ &= 2 \text{ mm}\end{aligned}$$

$$\begin{aligned}\therefore \text{Shell outside diameter} &= 4.24 + 0.004 \\ &= 4.244 \text{ m}\end{aligned}$$

6.2.2 Head design

Assume Torispherical head shown in fig-12

Head thickness $t_h = PD_oC/2fJ$

Where $C \rightarrow$ stress concentration factor

“C” calculates from h_E/D_o and t/D_o data table given in book

$$h_E = [\text{least of } h_o, D_o^2/4R_o, (D_o r_o/2)^{1/2}]$$

$$D_o = 4.244 \text{ m}$$

Assume $R_i = R_o = D_o = 4.224 \text{ m}$

$$r_o = 0.06D_o$$

$$\begin{aligned}h_o &= R_o - \sqrt{\left(R_o - \frac{D_o}{2}\right) * \left(R_o + \frac{D_o}{2} - 2r_o\right)} \\ &= 4.224 - \sqrt{(4.224 - 2.112) * (4.224 + 2.112 - 2 * 0.253)} \\ &= 0.715 \text{ m}\end{aligned}$$

$$\begin{aligned}D_o^2/4R_o &= (17.84) / (4 * 4.224) \\ &= 1.055 \text{ m}\end{aligned}$$

$$\begin{aligned}(D_o r_o/2)^{1/2} &= (4.224 * 0.253/2)^{0.5} \\ &= 0.730 \text{ m}\end{aligned}$$

$$h_E = h_o = 0.715 \text{ m}$$

$$h_E/D_o = 0.715/4.224$$

$$= 0.169$$

$$t/D_o = PC/2fJ$$

$$= 0.105 * C / (2 * 98.1 * 0.85)$$

$$t/D_o = 0.6 * 10^{-3} C$$

Now C can be found from t/D_o and h_E/D_o table given in book

$$t/D_o = 0.002$$

$$C = 4.1$$

$$t_h = 0.002 * D_o$$

$$= 0.002 * 4.224$$

$$= 0.008 \text{ m}$$

$$= 8 \text{ mm}$$

Table-20 Specification for Catalytic reactor

PARAMETER	DESCRIPTION
Number of reactor	4
Number of tubes	1900
Number square pitch	475
Diameter of tube	0.1m
Length of the tube	4.8 m
Catalyst type	Ni
Volume of catalyst	70 m ³
Shell thickness	0.002m
Type of Head	Torispherical head
Head thickness	0.008m

Chapter 7

Piping design and Instrumentation diagrams

7.1 Piping Design ^[15]

Operating velocity = Volumetric flow rate / Area of cross section

From the area of cross section diameter can be calculated.

The design velocity depends on the operating pressure.

Table-21 Operating velocity for fluids

Fluid	Operating pressure Kg/cm ²	Optimum operating velocity m/s
Gases	<1.05	3-20
	1.05-2	5-25
	>2	20-60
Steam	10-40	20-40
	>40	30-60

Table-22 Inside diameter of pipes

From	To	T °C	P Kg/cm ²	n Kmol/s	V m ³ /s	u m/s	D _i m
Feed gas	Control valve	202	4	1.037	10.44	40	0.576
Control valve	Reformer inlet	202	40	4.209	4.237	35	0.392
Reformer outlet	Steam generator	425	35	5.821	9.84	25	0.708
Steam generator	HTS inlet	350	32	4.221	6.966	50	0.421
HTS outlet	Preheater	427	30	5.78	11.433	36	0.636
Cooler	CO ₂ Absorber	93	45	5.1	3.51	39	0.338
CO ₂ Absorber	PSA	193	35	4.6	5.19	30	0.469

The volumetric flow rate is calculated by assuming ideal behavior of gas. From the area of cross section diameter of tube is calculated. The thickness of tubes can be calculated from the schedule number.

Schedule number = $1000 P/S$

P is the design pressure which is 10% more than operating pressure.

S is the allowable stress at working temperature

Schedule number = $2000t/D_m$

D_m is the mean diameter of the pipe = $D_i + t$

Table- 23 Outside diameter of pipes

From	To	S MPa	t mm	NPS	Type	D ₀ m	D _i m
Feed gas	Control valve	72	1.50	23	40S	0.579	0.576
Control valve	Reformer inlet	72	10.2	16	60N	0.412	0.392
Reformer outlet	Steam generator	101.6	11.6	28	30N	0.731	0.708
Steam generator	HTS inlet	79	8.51	17	10N	0.438	0.421
HTS outlet	Preheater	104.6	9.02	25	50N	0.654	0.636
Cooler	CO ₂ Absorber	110.4	6.88	14	28N	0.351	0.338
CO ₂ Absorber	PSA	110.4	7.36	19	30N	0.483	0.469

7.2 Instrumentation Diagram

In instrumentation diagram there are so many parameters are use these are defined below

- (1) Pressure controller (PC) :- It is use to regulate pressure
- (2) Temperature controller (TC):- temperature controller is an instrument used to control temperature. The temperature controller takes an input from a temperature sensor and has an output that is connected to a control element such as a heater or fan.
- (3) Control valve (CV) :- Control valve are valves used to control flow rate, pressure, temperature and liquid level by fully or partially opening.
- (4) Concentration controller (CC) :- it is used to control the concentration of gas and liquid flow rate.
- (5) Level controller (LC) :- used to control the liquid level

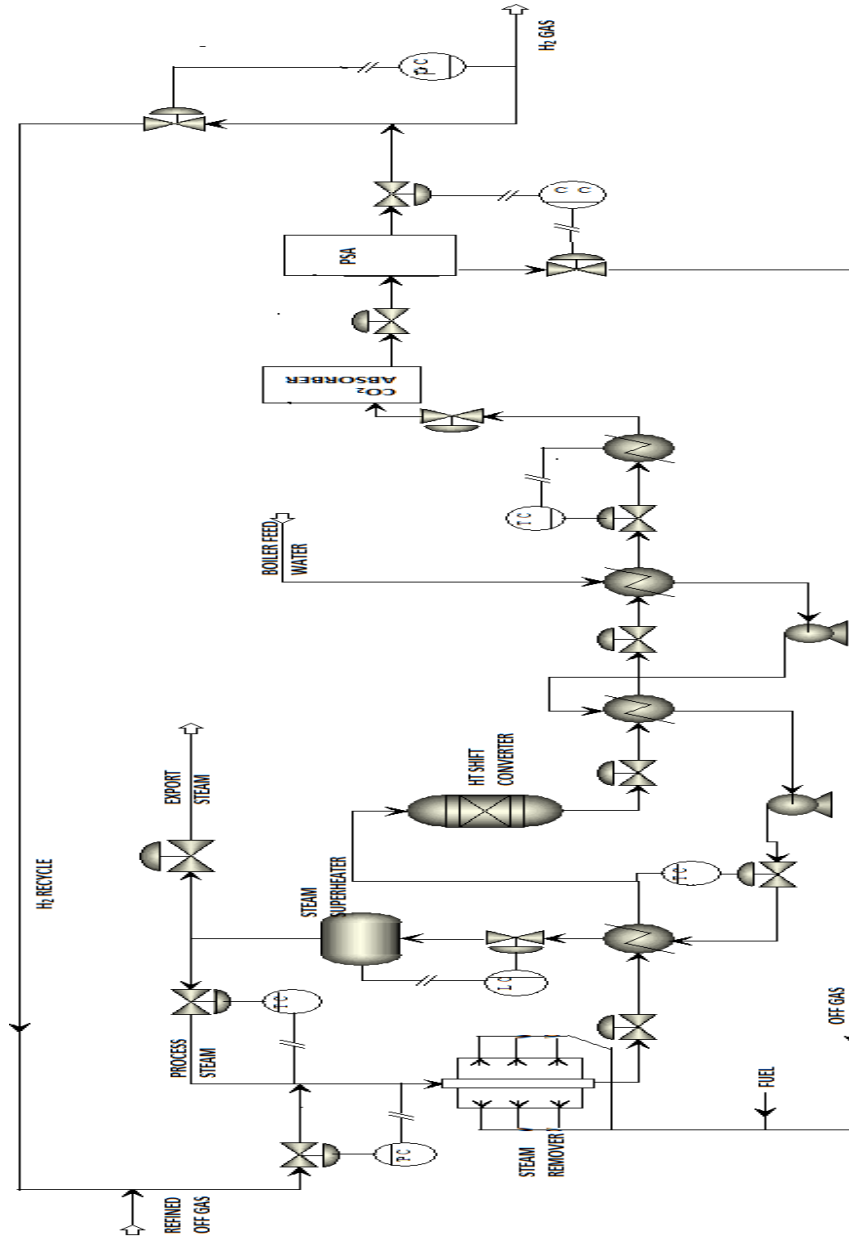


Fig-16 Instrumentation Diagram

Chapter 8

Plant layout

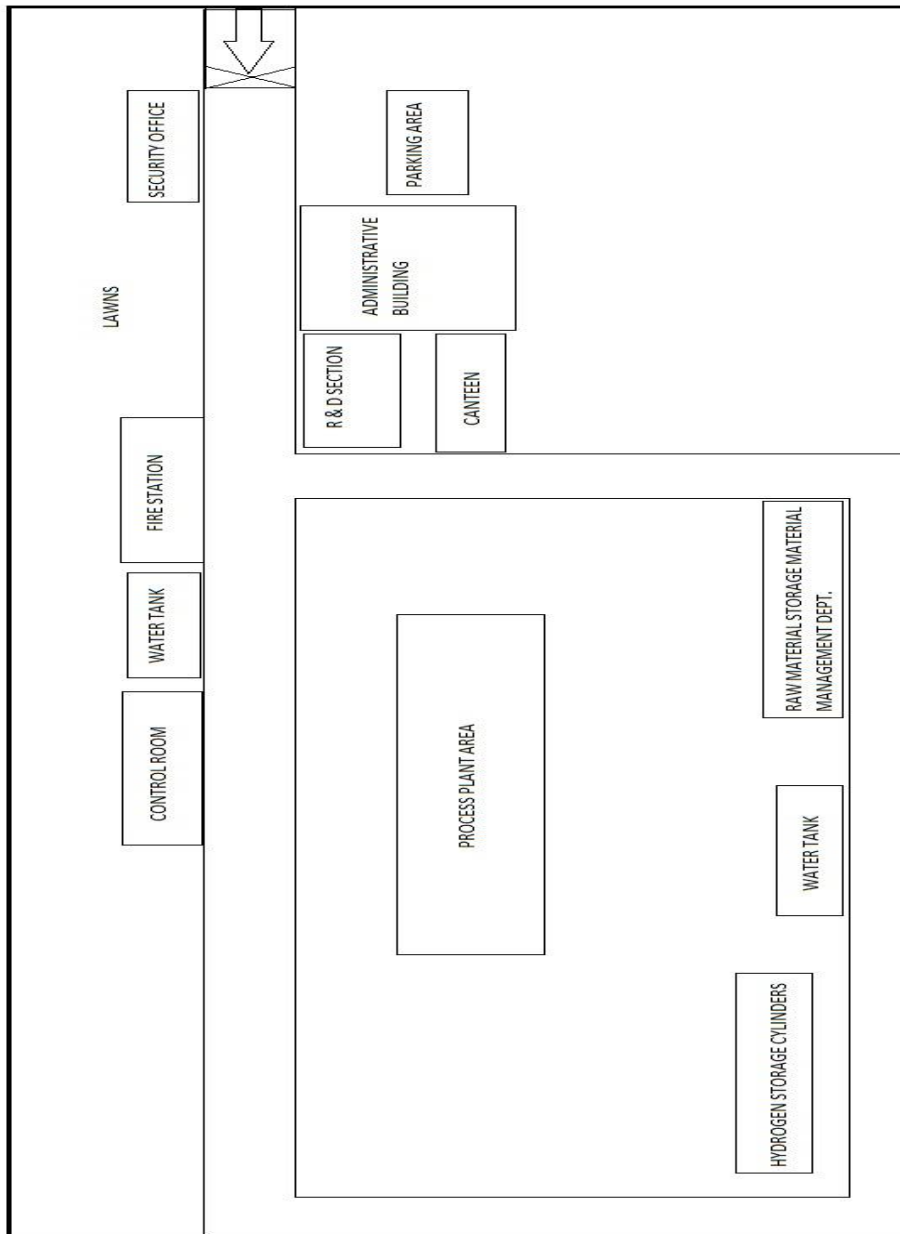


Fig-17 PLANT LAYOUT

Chapter 9

Conclusion

A plant for producing 500 tons/day of H₂ gas using refinery off gas is the scope of the present work. In this regard complete material balance, energy balance, design of a few equipment's (CO₂ Absorber and catalytic reactor), piping design and instrumentation diagram and plant layout has been done, however due to lack of appropriate information and data cost estimation of the process could not be done. Hydrogen being a very important gaseous product, finds its application in the refinery itself as a fuel. Processing of off gas to produce hydrogen is a very successful and profitable proposition. The process adapted is a highly developed and efficient are compared to the entire process followed. Further work in this project can be carried out to complete the design and economic analysis of this project.

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