NATURAL GAS AS FEEDSTOCK FOR FERTILIZER

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
In
Chemical Engineering

By
K.V.Srinivasan
&
Deepak Kumar Dash

Department of Chemical Engineering
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Under the guidance of
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CERTIFICATE

This is to certify that the thesis entitled **“Natural gas as feedstock for fertilizer’’** submitted by **K.V.Srinivasan, Roll No: 10300040** and **Deepak Kumar Dash, Roll No: 10400041D** in the partial fulfillment of the requirement for the award of **Bachelor of Technology** in **Chemical Engineering**, National Institute of Technology, Rourkela, is being carried out under my supervision.

To the best of my knowledge the matter embodied in the thesis has not been submitted to any other university/institute for the award of any degree or diploma.

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Date:

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ABSTRACT

Separation of the hydrogen needed for the ammonia synthesis reaction, from its source is difficult. Hydrogen production method is the main source of distinction between the various ammonia production routes. Most of the improvements in the technology regarding the ammonia synthesis were concerned with the hydrogen production step. Hydrogen can be produced by steam reforming, partial oxidation and water electrolysis. The bulk of the world ammonia production is based on steam reforming. The major hydrogen sources are natural gas, naphtha and coal. In this project different methods available for hydrogen separation from its source are analyzed and the best possible way to produce synthesis gas (which will form ammonia) from natural gas is found out. The number of reforming stages required for a plant capacity of 1500 tons per day of ammonia production is found out. The mass balance and energy balance calculations for the above said plant capacity is presented in this work. Then the conventional carbon dioxide removal process and methanation process are replaced by the advanced, economical pressure swing adsorption process. It was also found that two stages of shift converters required for this plant capacity. The number of reforming stages required is only one and nitrogen is obtained from oxygen pressure swing absorption units. The oxygen separated is also used as a fuel with natural gas for reforming. The carbon dioxide is separated in another PSA which can be used for the production of urea.

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1. INTRODUCTION

In the ammonia synthesis, nitrogen is combined with hydrogen in a stoichiometric ratio of 1:3 to give ammonia with no by-products. Ammonia itself is used as a fertilizer. About 85% of ammonia consumption is used for the manufacture of fertilizer. Air contains 79 % (volume) of nitrogen. So, nitrogen needed for the reaction can be obtained from air. Now the difficulty lies in separating the hydrogen needed for the reaction from its source. Hydrogen production method is the main source of distinction between the various ammonia production routes. Most of the improvements in the technology regarding the ammonia synthesis over the past four decades were concerned with the hydrogen production step. Hydrogen can be produced by steam reforming, partial oxidation and water electrolysis. The bulk of the world ammonia production is based on steam reforming. The major hydrogen sources are natural gas, naphtha and coal. Most of the steam reforming plants use natural gas as feed stock. Natural gas contains fewer impurities, high hydrogen to carbon ratio and less percentage of higher hydrocarbons. So natural gas is superior when compared with other feed stocks. The scope of this project is to analyze different methods available for hydrogen separation from its source and to find an economical way to produce synthesis gas (which will form ammonia) from natural gas. In this various methods of synthesis gas production are discussed and the best way to produced synthesis gas is found out. The detailed design of the some process equipments is also carried out in this work. This includes the PSA system for air separation, tubular packed bed reactor for methane steam reforming.

2. HISTORICAL DEVELOPMENT

Priestly, first produced ammonia by heating “Sal ammoniac” (ammonium chloride) with Lime in 1754.During 1850-1900, general development of physical chemistry with new concepts of mass action and chemical equilibrium paved the way for ammonia synthesis. It became clear that reaction of nitrogen and hydrogen to from ammonia is reversible. The manufacture of ammonia by passing nitrogen and hydrogen, or gaseous mixture of nitrogen and hydrogen over a catalytic substance at high temperature and removing, at a lower temperature, a part or the whole, of the ammonia contained in gases leaving the catalytic substance, and afterwards passing the gases from which ammonia has been removed over a catalytic substance, the process being carried out on under pressure and nitrogen and hydrogen, or gases containing them, being supplied in accordance with the quantity of ammonia removed from the gases. This is called Haber’s process. In the 20th century, various research and development led to the economical production of synthesis gas. The major steps involved in the production of synthesis gas are

1. Purification of natural gas (desulphurization)
2. Hydrogen production (reforming or partial oxidation)
3. Conversion of CO to CO_2 (shift conversion)
4. Purification of hydrogen (CO_2 removal)
5. Methanation

2.1) PURIFICATION OF NATURAL GAS:

2.1.1) DESULFURISATION:

The main impurities in natural gas are few percentages of higher hydrocarbons, sulfur compounds and negligible CO_2.The sulfur compounds may be H_2S, mercaptans or thiophenic compounds. The sulfur compounds are poisonous to the catalyst used in successive stages, therefore it has to be removed. The processes available for sulfur removal from feed stock are

a) adsorption by activated carbon
b) Removal by chemical reaction with ZnO
c) Hydrogenation of organic sulfur compounds and then removal by using ZnO
d) Molecular sieves

Adsorption by activated carbon, removal by chemical reaction with ZnO are efficient in removing compounds like mercaptans and H_2S but in order to remove organic sulfur compounds, the sulfur compounds must be first converted to H_2S and then removed by using ZnO. Therefore hydrogenation must be carried out.

2.1.2) HYDROGENATION:

Hydrogenation is carried out to convert organic sulfur compounds to H_2S and then absorbed by ZnO. The catalyst used for hydrogenation is cobalt molybdate. Cobalt molybdate is a mixture of cobalt oxide and molybdenum oxide supported on alumina. The reaction temperature is maintained below 400^0C in order to minimize cracking of hydrocarbon feedstock.

The reactions involved are

$$RSH + H_2 \rightleftharpoons RH + H_2S$$

$$ZnO + H_2S \rightleftharpoons ZnS + H_2O$$

After the hydrogenation the H_2S is absorbed using zinc oxide as absorbent. Iron oxide can also be used as absorbent because of its low cost and its potential for regeneration. The partial pressure of H_2S in the gas stream emerging from the iron oxide bed is affected by operating conditions. Therefore control of conditions is difficult. The difference in these two absorbents is related to the effect of water vapor on sulfur adsorption equilibrium. In case of ZnO the equilibrium partial pressure of H_2S remains very low even for wide range of water concentration. The reaction is kinetically controllable, but this is not as in case of iron oxide. Further iron oxide is associated with relative ease of reduction of sulfides, when compared with ZnO. So ZnO is preferred

2.2) HYDROGEN PRODUCTION:

Reforming and partial oxidation are the processes used for hydrogen production from the natural gas. In reforming reaction between steam and natural gas is carried out under pressure to form carbon oxides and hydrogen. These reactions are endothermic. In partial oxidation process oxygen separated from air is reacted with natural gas to form carbon oxides and hydrogen. These reactions are exothermic.

REACTIONS:

A) REFORMING:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H= 206\ KJ/mol$$

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \qquad \Delta H= 165\ KJ/mol$$

B) PARTIAL OXIDATION:

$$CH_4 + 1/2\ O_2 \rightleftharpoons CO + 2\ H_2 \qquad \Delta H = -332\ KJ/mol$$

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O \qquad \Delta H = -802\ KJ/mol$$

From the reactions, it becomes clear that reforming is advantageous than partial oxidation because of the production of more hydrogen. Since reforming is endothermic, energy has to be supplied. In most of the cases, natural gas is used as an energy source. To reduce the heat required, reforming is done in two stages. Around 80% of natural gas is reformed in one stage and then a calculated quantity of air is sent to produce some energy by methane oxygen reactions. By this nitrogen required for ammonia synthesis is also added. The exit gas from reformer contains hydrogen, carbon oxides steam and nitrogen. The catalyst used in reforming is nickel supported on alumina.

2.3) SHIFT CONVERSION:

Carbon monoxide is poisonous to the ammonia synthesis catalyst. So it has to be removed. But instead of removing carbon monoxide it is converted to carbon dioxide and then removed. This is known as shift conversion. This not only converts the carbon monoxide but also produces hydrogen. This is exothermic reaction.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H = -41{,}169\ KJ/Kmol$$

The shift conversion reaction is independent of pressure. Shift conversion can be carried out in single stage or in number of stages. If the shift conversion is carried out at high temperature, it is called high temperature shift (HTS) conversion. If it is at low temperature then it is called low temperature shift (LTS) conversion. The catalysts used for HTS conversion and LTS conversion are chromia promoted iron oxide and ZnO, Al_2O_3, CuO mixture supported on alumina. Since these reactions are exothermic, heat produced must be removed after the reaction. The carbon monoxide conversion is more when employed in multiple stages rather than a single stage. Isothermal shift conversion is one, where the heat produced due to the reactions is removed within the reactor by passing water through the tubes.

2.4) HYDROGEN PURIFICATION:

The gas coming out of the shift converters contain hydrogen, carbon dioxide, steam, nitrogen and some carbon monoxide. Carbon dioxide and carbon monoxide should be removed before sending the gas to the ammonia synthesis reactor. Carbon dioxide can be removed by

a) BENFIELD PROCESS:

This process is also called as hot carbonate process. This process is quite effective in bringing down CO_2 concentration to 2%. Stage wise scrubbing is required to reduce CO_2 concentration further. The solution contains activators added to potassium carbonate to increase rate of absorption of CO_2.

b) CATACARB PROCESS:

This is a catalytic hot potassium salt process in which a catalyst or a promoter is used. The process utilizes an aqueous potassium salt solution containing both catalyst and a corrosion inhibitor. The catalyst increases the reaction rate of both CO_2 absorption and regeneration steps.

c) GIAMMARCO-VETROCOKE PROCESS:

It is based on use of an activated potassium carbonate or sodium carbonate solution. Activators such as boric acid, glycine and many other amino acids increase the absorption efficiency. Boric acid is least effective but shows resistance to thermal decomposition. Glycine is cheap and it can be used in impure state. The activating power of glycine is increased by adding boric acid.

d) AMINE WASH:

Amines are organic bases defined as derivatives of ammonia in which one or more hydrogen atom is replaced by organic group. Mono ethanol amine is the more commonly used one.

$$2(HOCH_2CH_2N_2) + CO_2 + H_2O \rightleftharpoons (HOCH_2CH_2NH_3)_2CO_3$$

$$HOCH_2CH_2NH_2 + CO_2 + H_2O \rightleftharpoons HOCH_2CH_2NH^+_3HCO^-_3$$

$$2(HOCH_2CH_2N_2) + CO_2 \rightleftharpoons CH_2NHCOONH_3CH_2$$

e) PRESSURE SWING ADSORPTION:

Pressure swing adsorption is a gas separation process in which the adsorbent is regenerated by rapidly reducing the partial pressure of adsorbed component, either by lowering the total pressure or by using a purge gas. In the original PSA process two steps i.e. adsorption and regeneration are carried out in two absorbent beds operated in tandem, enabling the processing of continuous feed. In the modern PSA process three or more beds are used to synchronize and accommodate steps in additional such as co current depressurization and pressure equalization. Other variations include the “vacuum swing adsorption” process in which the pressure is varied between atmospheric and mechanical vacuum pump.

2.5) METHANATION:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad \Delta H = -206\ KJ/mol$$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2\,H_2O \qquad \Delta H = -165\ KJ/mol$$

Methanation is the term used to describe the reaction between carbon oxides and hydrogen to form methane and water. These reactions can be used to remove carbons oxides from hydrogen or any synthesis gas, where residual methane is tolerable in the downstream processes. The catalyst which is active for the methanation reaction is nickel. Iron catalysts can also be use but they have excessive carbon deposition leading to blockage of pores. Nickel has good selectivity and there is no carbon deposition or hydrocarbon formation. Catalysts are supported on alumina, kaolin or calcium aluminate cement with magnesia or chromia as promoter.

The first four processes for CO_2 removal are very old one and entire removal of carbon dioxide is not possible. Carbon dioxide concentration of 0.1 % will be there. But concentrations should be around 5-10 ppm. So Methanation is carried out. Here CH_4 formed is inert in ammonia synthesis reaction. But if CO, CO_2 concentrations are high more H_2 is required. Methanation reactions are exothermic. So the heat formed must be removed. Even very low concentrations (50 ppm) of CO and CO_2 are poisonous to ammonia synthesis catalyst. But, when pressure swing adsorption is done pure hydrogen is obtained, so that no impurities will be there. So methanation is not required when pressure swing adsorption is carried out for CO_2 removal.

3. MASS & ENERGY BALANCE

3.1) DETERMINATION OF NUMBER OF STAGES IN REFORMING:

From the literature “kinetics and modeling study of methane-steam reforming over sulfide nickel catalyst on gamma alumina support” by D.L.Hoaxy, S.H.Chan, O.L.Diny, the details regarding the conversion rates of methane are taken. Sulfide nickel catalyst on gamma alumina support is a new, cheap and highly active commercial catalyst (Ni 0309S), which can be used for industrial hydrogen production from hydrocarbon fuels. In the conventional reforming, the reformer temperature is maintained around 800^0C for 80% conversion of methane for a steam methane ratio of 4. But using the sulfide nickel catalyst on gamma alumina support for steam methane ratio of 4 and 800^0C the conversion is 96%. Steam methane ratio of 4 is maintained because at high ratios reforming reactions may reach equilibrium and at low ratios shift conversion will be less. The residence time for this is 3.59 Kg catalyst/ (mol of CH_4/s).At higher residence time CH_4 conversion reaches equilibrium and at lower residence time CH_4 conversion is less. This is the optimum residence time.

At 800^0C CH_4 conversion to CO_2 is 56%. So CH_4 conversion to CO is 40%.

$0.4(CH_4 + H_2O \rightleftharpoons CO + 3H_2)$ $\Delta H = 82{,}400$ KJ

$0.56(CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2)$ $\Delta H = 92{,}404$ KJ

Composition of gas leaving the reformer is given in table 1.

Heat load in reformer = energy required for the reaction + energy required to raise the gas temperature from 520-800^0C

Energy required for the reaction = (0.56 *165,007) + (0.4*206,000)

=174,804 KJ

Energy required to raise the gas temperature = $m*C_p*dT$

Assuming the specific heats of inlet and exit gas are same, the specific heat of inlet gas at 660^0C is

H_2O =31.328 KJ/Kmol ^{0}C

CH_4=60.879 KJ/Kmol ^{0}C

Specific heat = (0.2*60.879) + (0.8*31.238) =37.237 KJ/Kmol ^{0}C

Energy required = 5 *37.237*280=52,132 KJ

Heat Load = 52,132+174,804 =226,936 KJ

Generally, in ammonia production 80% of reforming is done in primary reformer. Using this catalyst, for steam methane ratio of 4, 80% conversion is obtained at 750^0C. CH_4 conversion to CO_2 =52.5%

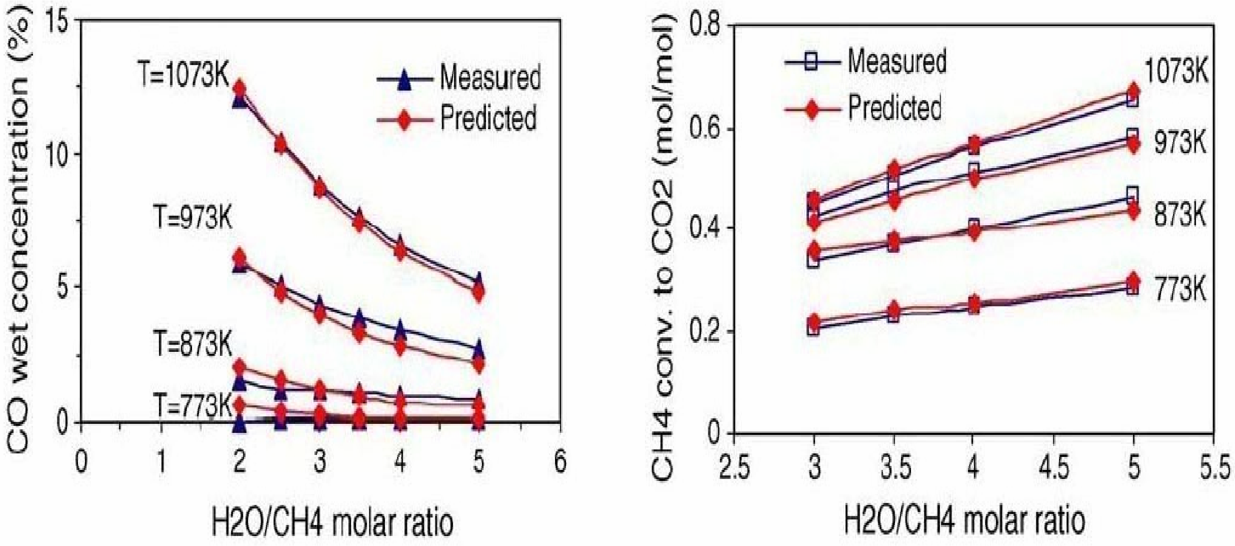
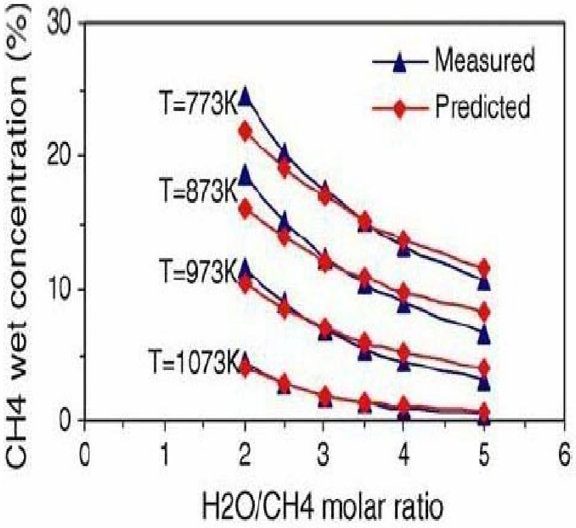


Table 1

Catalyst properties

Nickel content (wt.%)	9.8
S content (wt.%)	4.9
Alumina content (wt.%)	Balance
Surface area (m^2/g)	155
Total pore volume (ml/g)	0.9
Size of the sphere (mm)	1.75
Average crush strength (N)	25



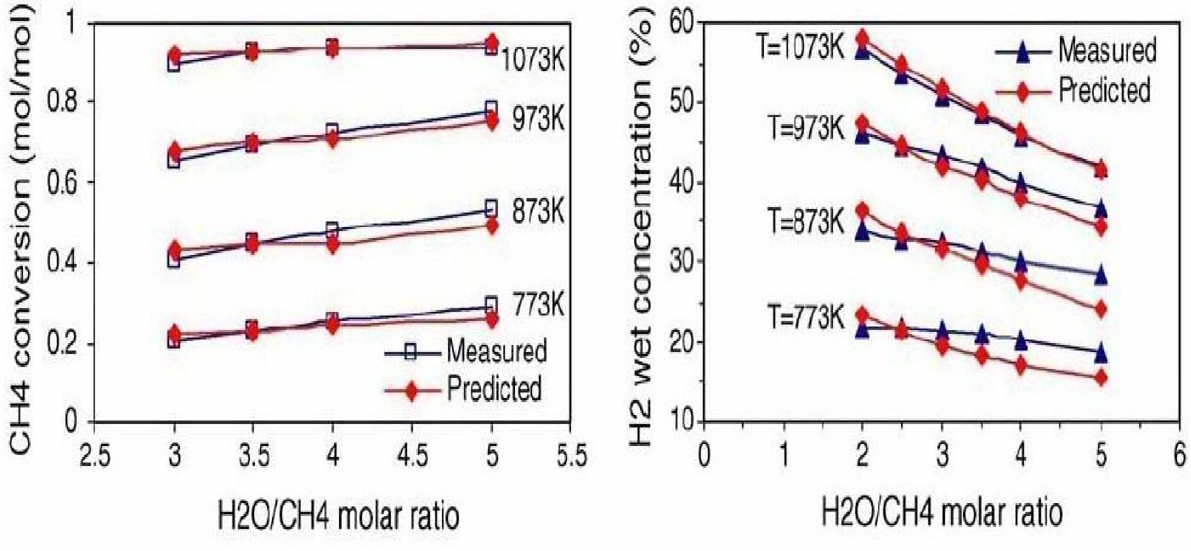


Fig 3.1 Methane steam reforming using sulfide nickel catalyst on gamma alumina support

Table: 3.1 Comparison of composition at reformer outlet for Single Stage and Two Stage reforming

Component	Single stage reforming Kmoles	two stage reforming Kmoles
H_2	3.44	2.925
H_2O	2.48	2.675
CO_2	0.56	0.525
CO	0.4	0.275
CH_4	0.04	0.2

$0.275(CH_4 + H_2O \rightleftharpoons CO + 3H_2)$ ΔH= 56,650 KJ

$0.525(CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2)$ ΔH= 86,629 KJ

Heat required for the reaction= (0.275*206,000) + (0.525*165,007) =143,279 KJ

Heat required to raise the temperature = 5*36.87*230= 42,408 KJ

Heat load = 185,687 KJ

In secondary reformer air is added. Assuming that N_2 is inert, the reactions are

1) $CH_4 + 1.5\ O_2 \rightleftharpoons CO + 2\ H_2O$ ΔH= -519 KJ/mol
2) $CO + 0.5\ H_2 \rightleftharpoons CO_2$ ΔH= -283 KJ/mol
3) $H_2 + 0.5\ O_2 \rightleftharpoons H_2O$ ΔH= -242KJ/mol
4) $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ ΔH= 206KJ/mol
5) $CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$ ΔH= 165 KJ/mol

In the reactions 1, 2 and 3 CH_4, C0, H_2 are lost. One mole CH_4 is approximately equivalent to 4 moles of H_2. One mole of CO is equivalent to one mole of H_2.In the process of adding N_2, H_2 is lost. So reforming can be done in single stage.

Increase in heat load in reformer =226,936-185,687 = 41,149 KJ

= 21.94% by using sulfide nickel catalyst.

If this catalyst is used in an operating plant with conventional reforming, then increase in heat load = 226,936-(185,687+ (5*36.87*50))

=32,031 KJ

5*36.87*50 is added to reformer heat load because in conventional reformers temperature is 800^0C. Rise in temperature is 50 ^{0}c more than what that has been calculated for sulfide nickel catalyst.

Increase in heat load =16.43%

So, single stage reforming can be done, providing suitable material to withstand increase in heat load, thereby increasing hydrogen production and eliminating secondary reformer. But nitrogen has to be separated from air by PSA for ammonia synthesis.

The composition of gases entering the high temperature shift conversion reactors are given in table 1.The gases leave the shift converter at 430^0C. Assuming equilibrium is reached in the shift converter,

K_p at 430 ^{0}C =14

$K_p = (P_{H2}*P_{CO2})/ (P_{CO}*P_{H2O})$

P_{H2}, P_{CO2}, P_{CO}, P_{CO} are partial pressure of H_2, CO_2, CO, H_2O respectively.

If "X" moles of CO is converted then X=0.295 moles.

The composition of gases entering the Low Temperature Shift converter is given in table 2.Assuming equilibrium is reached in the LTS converter, K_p at 190^0C is 280.

If"Y" moles of CO is converted then Y=0.0987 moles.

Table: 3.2. Composition of process streams

Comp	HTS Outlet Mole%	LTS Outlet Mole%	Condenser Outlet Mole% (A)	Recycle Mole% (B)	PSA Inlet Mole% (A-B)
H_2	3.735(53.97%)	3.8337(55%)	3.8337(79%)	0.0853	3.7484
H_2O	2.185(31.58%)	2.0863(30.14%)	nil	Nil	Nil
CO	0.105(1.51%)	0.0063(0.09%)	0.0063(0.13%)	0.0024	0.0039
CO_2	0.855(12.35%)	0.9537(13.78%)	0.9537(19.73%)	0.021	0.9327
CH_4	0.04(0.558%)	0.04(0.558%)	0.04(0.827%)	0.0008	0.0392

The composition of gases leaving the LTS converter is given in table 2. This goes to the condenser where steam is condensed and the condensed steam is stripped off in the condensate stripper.2% by volume of stripper outlet gas is recycled to the hydrogenator. The rest of the gas is sent to the PSA unit for hydrogen separation. The compositions given in table 2 are found out considering only methane. But when feed is natural gas the compositions must be found out.

Natural gas composition:

Methane =93.3% = 1mol

Ethane =3.3% =0.035 mol

Propane =0.9% =0.0096 mol

Nitrogen =2.5% =0.0027mol

For 1 mol of methane (1.072 moles of natural gas)

$0.4(CH_4 + H_2O \rightleftharpoons CO + 3H_2)$

$0.56(CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2)$

$0.035(C_2H_6 + 2H_2O \rightleftharpoons 2CO + 5H_2)$

$0.0096(C_3H_8 + 3H_2O \rightleftharpoons 3CO + 7H_2)$

Assuming that there is no ammonia formation in reformer (nitrogen is inert),recycle gases are inert and all ethane and propane reacts in the reformer, the composition of gases leaving the reformer is the sum of change in composition due to reforming in the reformer and the recycle gas. Since sulfur present is in the order of 50ppm. Hydrogen reacted is 50*2/1000000. Therefore

Unreacted H_2 = H_2 in recycle – H_2 in consumed in hydrogenator

Assuming that the rest of the gases do not take part in any of the reactions in the reformer, the composition must be found out. Taking the recycle gas composition same as that of recycle gas composition considering methane only, the composition of gas leaving the reformer are given in table.3. Following a similar approach done by considering methane alone i.e. equilibrium is attained in the shift reactors, the moles of CO converted in HTS and LTS are 0.3634 and 0.1291. Then the composition of gases coming out of the stripper and recycle are found out. The compositions are tabulated in table 4.The recycle composition for natural gas and methane is almost same. Therefore, one trial is enough. The composition of recycle gas and PSA inlet gas is same as that of the stripper outlet.

3.2) BASIS:

1500 Tons per day of ammonia

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ ΔH= -82,400 KJ/Kmol

1500 tons per day of NH_3 = (1500/17) Kmoles per day of NH_3 = 88,235 Kmoles/day

Hydrogen required = 132,353 Kmoles/day = hydrogen from PSA unit

Assuming 99% recovery of 99.99% pure hydrogen,

H_2 inlet to PSA = 132,353/ (0.99*0.9999)

= 133,703 Kmoles/day =1.547 Kmoles/s

The composition of each and every stream is known. At the PSA inlet percentage of H_2 is known. By back calculations the amount of feed to each of the reactors is found out. The amount of gases passing through each section is given in Table 5. Fig 1 shows the flow of gases, reaction conditions, heat load is each reactor. H_2 percentage in inlet to the PSA is 78.73. So

78.73% is 1.547 Kmoles/s. From this total inlet to PSA is found out. CH_4, N_2 which are inert after the reformer, are known in the PSA inlet. The percentage of CH_4, N_2 are known in the other streams. So the amount of all the other streams is found out.

3.7656moles of H_2 is obtained from 1 mole of CH_4 (in the reformer). Therefore
1.395Kmol/s of H_2 is obtained from 0.370Kmol/s of CH_4
Natural gas required = 0.37/0.933 = 0.3965Kmol/s

TABLE: 3.3 Composition of process streams

comp	Reformer outlet	HTS outlet	LTS outlet	Stripper outlet	PSA outlet	PSA(CO_2) outlet	Flue Gas
H_2	51.6%	56.8%	58.365	78.73%	3.62%	36.2%	3.5%
H_2O	32.65%	27.65%	27.87%	_	_	_	59.9%
CO	6.86%	1.88%	0.119%	0.16%	.715%	7.15%	0.67%
CO_2	7.96%	12.942%	14.71%	19.85%	90%	_	29.9%
CH_4	0.559%	0.559%	0.559%	0.74	3.35%	33.55	_
N_2	0.337%	0.337%	0.337%	0.499%	2.26%	22.6%	2.91%
O_2	_	_	_	_	_	_	2.99%

Table: 3.4: Molar flow rate of components in process streams

Comp	Feed	Reformer Outlet	HTS Outlet	LTS Outlet	Condenser outlet	Recycle	PSA inlet	PSA Outlet
H_2	-	1.395	1.5299	1.579	1.579	0.0316	1.5475	0.0151
H_2O		0.8828	0.7476	0.699	-	-	-	-
CO	-	0.1855	0.0508	0.0032	0.0032	0.00006	0.0031	0.0031
CO_2	-	0.2158	0.3499	0.3981	0.3981	0.008	0.3901	0.3900
N_2	0.01	0.01	0.01	0.01	0.01	0.0002	0.0098	0.0097
CH_4	0.37	0.0148	0.0148	0.0148	0.0148	0.0003	0.0145	0.0144
C_2H_6	0.013	-	-	-	-	-	-	-
C_3H_8	0.0035	-	-	-	-	-	-	-

All compositions are in Kmoles/s

4. ENERGY BALANCE

4.1. OVER LTS CONVERTER

CO converted=0.4764 Kmoles/s

$(\Delta H)_{\text{reaction}}$ =41169*0.4764 = 1,961.29kg/s

Heat added to the stream = m* C_p *dT

$dT = T_0 - T_i$, $T_0 = 190^0C$

$C_p = C_p$ at 180^0C (assuming 20^0C rise)

$2.704*31.536*(190-T_i) = 1961.29$

$T_i=167^0C$. So rise in temperature is 23^0C.

4.2. OVER HTS CONVERTER

CO converted =0.1347 Kmoles/s

$(\Delta H)_{\text{reaction}}$ =0.1347*41169 =5,545.46 KJ/s

$2.704* C_p *(430-T_i)$ = 5,545.46 KJ/s

$C_p = C_p$ at 100^0C (assuming 60^0C rise)

$2.704*30.919*(430-T_i)$ = 5,545.6 KJ/s

$T_i=363.6^0C$.

4.3. HEAT AVAILABLE AT HTS OUTLET

m * C_p* dT =2.704*C_p* (430-167)

C_p is evaluated at 290^0C

=2.704*33.46*263 = 23,796 KJ/s

4.4. HEAT AVAILABLE AT REFORMER OUTLET

m * C_p* dT =2.704 * C_p * (800-363)

C_p is evaluated at 582^0C

=2.704*34.07*437 = 40,259 KJ/s

4.5. HEAT REQUIRED FOR PREHEATING NATURAL GAS

m * C_p* dT =0.3945* C_p *(390-30) C_p is evaluated at 210^0C

=0.3945*32.47*360 = 4,162KJ/s

4.6. HEAT REQUIRED FOR PREHEATING NATURAL GAS AND STEAM

m * C_p* dT =1.9166* C_p *(520-380)

C_p is evaluated at 450^0C

=1.9166*37.8*140 =10,143KJ/s

4.7. HEAT BALANCE OVER REFORMER

802301$(CH_4)_{fuel}$= $(\Delta H)_{reaction}$ + m* C_p *dT

$(\Delta H)_{reaction}$= (0.3552*206,172) + (0.013*347,328) + (0.00357*497,797) =79,524 KJ

m* C_p *dT =33.77*2.925*280 =27,658 KJ

802301$(CH_4)_{fuel}$=79524+27,058

$(CH_4)_{fuel}$=0.1536Kmol/s

$(CH_4)_{recycle}$= (0.4332)*0.0335 = 0.0145Kmol/s

$(CH_4)_{required}$=0.1191Kmol/s =1.9056Kg/s

Natural gas required =1.9056 Kg.

Because, for 3.3% C_2H_4, 0.9% C_3H_8 energy change will be in order of 10^3

$(CH_4)_{fuel}$= (Natural gas) $_{fuel}$

Oxygen fed to reformer=0.01336*2.1=0.2806Kmol/s

Flue gas= (17.7-(0.9*0.4332*44)) + (0.2806*32) + (1.9056) =11.428Kg/s

4.8. HEAT LOAD IN CONDENSER AFTER LTS

Q=m*C_{p1}*dT+ λ +m*C_{p2}*dT

2.704* C_{p1} *(190-100) +0.699*λ + 2.704* C_{p2}*(100-80)

C_{p1} = $C_{p\ at}$ 145^0C=32.01 KJ/Kmol

C_{p2} = C_p at 90^0C=31.83KJ/Kmol

λ=2256.2 KJ/Kg^{0}K ; Q=11,277KJ/s

In the pressure swing adsorption, feed enters at 80^0C and the temperature drop will depend on height of column so heat changes can be calculated only after design. Temperature drop is very less. Feed is admitted at ambient temperature. In hydrogenation section the sulfur levels are in ppm. Energy changes will be less. Temperature drop will be less. A temperature drop of 10^0C over hydrogenator and ZnS absorber.

4.9. HEAT AVAILABLE FROM FLUE GAS

Q=m* C_p *dT+ X*λ

X=moles of steam in flue gas

Flue gas composition:

H_2 =0.0157(3.5%)

N_2 =0.013(2.91%)

O_2 =0.01336(2.99%)

H_2O =0.026724(59.9%)

CO_2 =0.1336((29.9%)

CO =0.0039(0.67%)

m=0.44586 Kmol/s

$C_p = C_p$ at 525^{0}C

Q=0.44589* C_p * (1000-50) + (0.026724*2526.2)

=0.4459*37.89*950*603.58=16,714KJ/s

For preheating natural gas, steam mixture heat required is 14,733KJ/s

Heat available from flue gas is 16,714 KJ/s

Excess heat with the flue gas =16,714-14,755=1,959 KJ/s

This heat (excess) can be used for heating water to certain temperature.

So that it can be processed for steam production.

4.10. EMPIRICAL RELATIONS TO FIND OUT SPECIFIC HEAT OF GASES:

CO_2 C_p=10.34+0.00274T-195500T^{-2} cal/gmol ^{0}C

CO C_p =6.6+0.0012T cal/gmol ^{0}C

H_2O C_p =8.22+.00015T-0.00000134T^2 cal/gmol ^{0}C

H_2 C_p =6.62+0.0081T cal/gmol ^{0}C

N_2 C_p =6.5+0.001T cal/gmol ^{0}C

CH_4 C_p =5.34+0.0115T cal/gmol ^{0}C

1 cal/gmol ^{0}C = 4.187 KJ/Kgmol^{0}C

5. PROCESS DESCRIPTION

5.1. DESULPHURIZATION:

Natural gas at a temperature of 30^{0}C is preheated in heat exchanger by the flue gas to a temperature of 390^{0}C. The amount of natural gas is 0.3965 Kmol/s (6.712Kg/s). The recycle gas from stripper outlet (0.0401 Kmol/s, 0.4255 Kg/s) is added and the mixture is passed to the desulphurization section. The natural gas feedstock may contain a maximum of 50ppm by volume of sulfur. So, it must be desulphurized because the reformer catalyst as well as the low temperature shift conversion catalyst is sensitive to sulfur. The desulphurization takes place in two steps

1. Hydrogenation
2. H_2S absorption

5.1.1. HYDROGENATION:

During hydrogenation, the organic sulfur in the feedstock is converted to H_2S over the hydrogenation catalyst in the hydrodesulphurization reactor. The organic sulfur content is hereby reduced to less than 0.05ppm by volume. Temperature in the hydrogenator is 390^{0}C with Co-Mo based catalyst. The catalyst makes the following reactions possible.

$$RSH + H_2 \rightleftharpoons RH + H_2S$$

$$R_1SSR_2 + 3\,H_2 \rightleftharpoons R_1H + R_2H + 2H_2S$$

$$R_1SR_2 + 2\,H_2 \rightleftharpoons R_1H + R_2H + H_2S$$

$$COS + H_2 \rightleftharpoons H_2S + CO$$

$$C_4H_4S + 4\,H_2 \rightleftharpoons H_2S + C_4H_{10}$$

Besides the above reaction, the catalyst also hydrogenates olefins to saturated hydrocarbons. If the feed contains CO or CO_2, then methanation reaction takes place. If the temperature goes beyond 400^{0}C, polymerization products can be formed on the surface of the catalyst and at lower temperature hydrogenation will not be complete. The catalyst is pyrophoric above 70^{0}C i.e. it burns without ignition when exposed to air. So it is cooled down to ambient and then removed.

5.1.2. H_2S ABSORPTION:

The second step is the absorption of formed H_2S, which takes place in series, connected ZnO absorbers. The catalyst used is ZnO and the operating temperature is 390 ^{0}C. ZnO reacts with H_2S and COS according to the following reactions.

$H_2S+ZnO \rightleftharpoons ZnS + H_2O$

$COS+ ZnO \rightleftharpoons ZnS + CO_2$

To some extent ZnO will also remove organic sulfur. ZnO is not pyrophoric.

The desulphurized natural gas is mixed with process steam before the preheating. Steam (1.48Kmol/s, 26.63 Kg/s) at 385^0C, $40Kg/cm^2$ is mixed with the desulphurized feed and then preheated in a heat exchanger using flue gas to a temperature of 520^0C. Then it is sent to the reformer.

5.2) REFORMING:

The desulphurized natural gas (1.9166 Kmol/s, 33.77kg/s) is converted into raw ammonia synthesis gas by catalytic reforming of hydrocarbon mixture with steam. The reformer operates at 800^0C, 35 Kg/cm^2. The following reactions take place in the reformer.

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H=206\ KJ/mol$$

$$CH_4 + 2H_2O \rightleftharpoons CO2 + 4H_2 \qquad \Delta H=165\ KJ/mol$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H=-41\ KJ/mol$$

All the reforming reactions are endothermic. The heat required for the reactions is produced by the combustion of natural gas (0.1191Kmol/s, 1.9056Kg/s) and recycle gas (0.0433 Kmol/s, 0.545 Kg/s) with oxygen. The flue gas leaves the reformer at 1000^0C. The catalyst used in the reformer is the sulfide nickel catalyst on gamma alumina support. Since steam methane ratio is 4, the conversion is 96%. The exit gas leaves at 800^0C.

5.3) CO CONVERSION:

The process gas leaving the reformer enters the CO conversion section. Here CO is converted to CO_2 and H_2. The heat evolved is primarily used for steam production and boiler feed water preheat. The shift reaction is carried out in two stages.

5.3.1) HIGH TEMPERATURE SHIFT:

The gas from the reformer which is at 800^0C is first cooled to 363^0C by using the heat removed for steam production. Then it comes to the high temperature shift reactor which operates at 32 Kg/cm^2. The outlet temperature is 430^0C. The catalyst used in the high temperature shift conversion reactor is chromium oxide promoted iron oxide. The catalyst is pyrophoric. The exit gas (2.704 Kmol/s, 33.77kg/s) leaves at 430^0C.

5.3.2) LOW TEMPERATURE SHIFT:

The exit gas from high temperature shift conversion reactor is cooled to 167^0C in a heat exchanger using boiler feed water. Then it enters the low temperature shift reactor which operates at 31 Kg/cm^2. The catalyst used for the low temperature shift conversion is Cu,Zn,Al based in the range of 170-250 ^{0}C.The optimum inlet temperature of both the CO converters depends on catalyst activity. So temperature of the reactor increases with catalyst age. The temperature rise depends on steam to dry gas ratio and conversion. The exit gas (2.704 Kmol/s,33.77Kg/s)leaves the reactor at 190^0C.

The gas is the cooled to 800^0C in a condenser to condense the steam present in it. It is then sent to a stripper to strip off all the water (0.699 Kmol/s, 12.582 Kg/s). Then 2% by volume of the gas is recycled to the hydrogenator. Then it is sent to the PSA unit for hydrogen separation.

5.4) CO_2 REMOVAL BY PRESSURE SWING ADSORPTION:

This process replaces the conventional CO_2 removal by carbamate process and methanation. From this process pure hydrogen is obtained. Pressure swing adsorption process uses molecular sieves as adsorbents in series of vessels operated in a staggered cyclic mode changing between an adsorption phase and various stages of regeneration. The regeneration of loaded adsorbent is achieved by stepwise depressurization and by using the gas from this operation to flush other adsorbers at a different pressure level. High purity hydrogen is obtained depending on the number of adsorbers used.

a) Adsorption:

The feed gas is introduced at high adsorption pressure (8 Kg/cm^2). Except H_2 all the other impurities are adsorbed and hydrogen is withdrawn as a product. When the adsorber reaches its capacity feed is switched to fresh adsorber.

b) Co current depressurization:

To recover the hydrogen trapped in voids, the adsorber is depressurized from product side. This H_2 is used to repressurize the adsorbers.

c) Counter current depressurization:

The saturated adsorbers are then regenerated in series of steps. The bed has impurities at the top. So it is partly regenerated towards feed end and impurities are rejected to PSA off gas.

d) Purge at low pressure:

The adsorbent is then purged with H_2 purge to regenerate the bed.

e) Repressurization:

The adsorber is then repressurized with H_2 prior to being returned to the feed step. The H_2 for repressurization is provided from the co current repressurization and with slip stream from product gas. Then the cycle is repeated.

The hydrogen (1.538 Kmol/s, 3.0636 Kg/s) separated from this PSA unit is mixed with nitrogen (0.5126Kmol/s, 14.3546 Kg/s) from the oxygen PSA unit. The impurities (0.4332 Kmol/s, 17.7 Kg/s) containing CO_2 is sent to other PSA unit for removal of CO_2. The same procedure is followed in this PSA unit. Here CO_2 (0.3899Kmol/s, 17.15 Kg/s) is separated. The PSA off gas (0.0433Kmol/s, 0.545 Kg/s) is then sent as a fuel to the primary reformer.

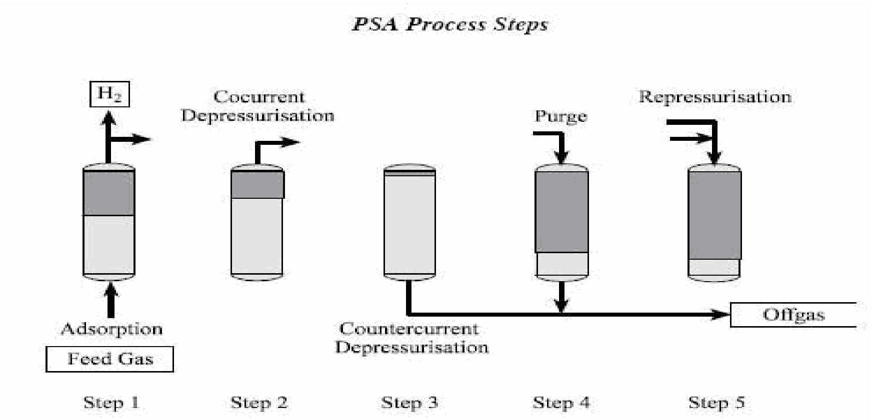


Fig 5.1 PSA process steps

5.5) OXYGEN SEPARATION BY PSA:

Oxygen separation by PSA is comprised of a two-stage concentration process using CMS for the first stage and zeolite for the second. In the first stage, Argon a non adsorbing component passes onto the CMS bed together with N_2 and a few O_2, and a mixture gas of O_2 and N_2 that is adsorbed onto CMS is taken out from CMS bed. This mixed gas is sent to the zeolite bed of the second stage adsorption column. N_2 is removed by selective adsorption, and high purity O_2 remains. It is also possible to use zeolite in the first stage and CMS in the second. The function of each adsorbent in this arrangement remains the same as the former arrangement. In this case, the O_2 recovery ratio is affected by the first stage O_2 recovery ratio, because O_2/N_2 selectivity of the zeolite is not good. Therefore this arrangement is not preferable.

Zeolites are aluminosilicate minerals with complex crystal structures made up of interlocking rings of silicon, aluminium and oxygen ions. The chemical composition of the zeolite used for oxygen separation is $Na_{12}[(AlO_2)_{12}((SiO_2)_{12}].27H_2O$. It is the zeolite's shape which provides most of the ability to selectively adsorb nitrogen. The zeolite used for oxygen production is shaped like a die with holes drilled on each face to form an internal cage. The corners of the die (providing the framework) are SiO_2 and AlO_2 units. Cations (either Na or Ca) are exposed throughout the crystal lattice. The relative advantages of PSA over the cryogenic oxygen production are

Table 5.1: **Comparison of Oxygen PSA and Cryogenic production**

Parameters	PSA	Cryogenic production
Temperature	ambient	low
Pressure	maximum is 150 kPa	Maximum is 13,000 kPa
Purity	95%	near 100%

6. DESIGN OF PSA SYSTEM FOR AIR SEPARATION

6.1 NOMENCLATURE:

b	Langmuir constant (atm^{-1})
C	concentration in gas phase (mole per m^3 of fluid)
D	intracrystalline diffusivity (cm^2 s^{-1})
d_p	diameter of particle (cm)
G	purge/feed volume ratio
K	Henry's Law constant
k	overall mass transfer coefficient (s^{-1})
L	total height of the column (m)
N	total number of components
P	pressure (atm)
Q	molar flow rate
q	adsorbed phase concentration (mole per m^3 of solids)
$q*$	equilibrium concentration of adsorbed phase (mole per m^3 of solids)
q_s	Langmuir constant (mol cm^{-3})
R	universal gas constant
T	temperature (K)
t	time (s)
v	superficial velocity (m s^{-1})
W	power (kW)
x	adsorbed phase composition
y	gas phase composition
z	height of the bed (=0 at feed end, =L at product end) (m)

Greek symbols

α	separation factor (dimension less)
ε	bed Porosity
γ	ratio of specific heats in gas phase
η	mechanical efficiency
ρ	density (kg m^{-3})
μ	gas viscosity (Cp)
t	residence time (s)

Subscripts

0	initial
1, 2	components
act	actual
ads	adsorption
blow	blowdown step
f	feed
g	gas phase
H	high pressure step
I	component
L	low pressure step
Min	minimum value
pres	pressurization step
prod	product
purg	purge step
s	solid phase

6.2. MODELING THE PSA PROCESS

Fig.6.1 shows a typical PSA process. The process consists of two fixed-bed adsorbers undergoing a cyclic operation of four steps such as adsorption, blowdown, purge, and pressurization. By employing a sufficiently large number of beds and using more complicated procedures in changing bed pressure, PSA may be carried out as a continuous process. Additional steps such as co-current depressurization and pressure equalization have been added to improve the purity and recovery of products as well as to make the process more energy-efficient. A common feature of all PSA processes is that they are dynamic, i.e. they have no steady state. After a sufficiently large number of cycles, each bed in the process reaches a cyclic steady state (CSS), in which the conditions in the bed at the end of a cycle are approximately the same as those at the beginning of the next cycle.

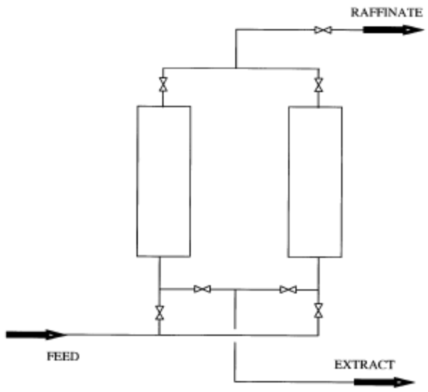


Fig. 6.1. Basic two-bed PSA process.

6.2.1.Assumptions:

1. The system is isothermal with negligible pressure drop through the adsorbent beds
2. The pressure change in the steps of pressurization and blowdown is so rapid that no significant exchange between adsorbed phase and gas phase occurs. This is also called the frozen solid assumption
3. Langmuir isotherm is valid for the system
4. The mass transfer rate is represented by a linear driving force expression
5. The ideal gas law is applicable
6. Plug flow is assumed, i.e. there is no axial or radial dispersion.

The component balance for species *i* in the bed is:

$$\frac{\partial C_i}{\partial t} + \frac{\partial vC_i}{\partial z} + \frac{(1-\varepsilon)}{\varepsilon}\frac{\partial q_i}{\partial t} = 0, \qquad i = 1 \text{ and } 2 \tag{1}$$

The last term in Eq. (1) is the mass transfer term between solid and gas, where q_i is the concentration of component *i* in the solid. For pressure changing steps (pressurization and depressurization) this term is zero due to assumption (2). Summation of Eq. (1) for all the components leads to the total mass balance equation. For constant pressure steps (adsorption and purge) the total concentration of the fluid remains constant in the bed, thus the total mass balance will be

$$C\frac{\partial v}{\partial z} + \frac{(1-\varepsilon)}{\varepsilon}\sum_{i=1}^{N}\frac{\partial q_i}{\partial t} = 0 \tag{2}$$

while for pressure changing steps the total mass balance is

$$\frac{\partial v}{\partial z} + \frac{1}{P}\frac{\partial P}{\partial t} = 0 \tag{3}$$

where it is assumed that the pressure drop in the bed is negligible. (1), (2) and (3) are applied for the flow from $z=0$ to L. If the flow is reverse, the term $\partial/\partial z$ will be negative. The mass transfer kinetics is modeled using the LDF approximation, based on the simplification of Fick's second law of diffusion

$$\frac{\partial q_i}{\partial t} = k_i(q_i* - q_i) \tag{4}$$

Where q_i* denotes the equilibrium concentration of component i. It is calculated using either extended Langmuir isotherm,

$$\frac{q_i*}{q_{si}} = \frac{b_i p_i}{1 + \sum_{j=1}^{j=n} b_j p_j} \tag{5a}$$

or using Henry's law,

$$q_i* = K_i C_i \tag{5b}$$

The following boundary conditions are considered for (1), (2) and (3). For the adsorption and pressurization steps, the concentration of fluid at the inlet is assumed to be equal to the feed condition, since axial and radial dispersion is neglected, namely

$$C_i\,|_{z=0} = C_{fi} \tag{6}$$

for the purge step it is

$$C_i|_{z=L} = \frac{P_L}{P_H}(C_i|_{z=L})_{ads} \tag{7}$$

and for the depressurization step

$$\frac{\partial C_i}{\partial z}\,|_{z=0} = 0 \tag{8}$$

The velocity boundary condition for the pressurization and adsorption step is

$$v|_{z=0} = v_\mathrm{f} \tag{9}$$

Where v_f is the superficial velocity of feed at $z=0$. (Velocity need not be constant with time during pressurization step unless specifically controlled. Normally, controllers are not used in PSA. Above could be seen as a simplifying assumption.) For the purge step the velocity boundary condition is

$$v|_{z=L} = G v_\mathrm{f} \tag{10}$$

where G is the purge-to-feed velocity ratio. For the blowdown step the velocity boundary condition is

$v|_{z=L}=0$ (11)

In the cyclic operation, the initial condition in the bed is the condition at the end of the previous step. For startup, either a clean bed or a saturated bed can be used. For a clean bed (12) the initial conditions are $C_i(z,0)=0$; $q_i(z,0)=0$

and for a saturated bed they are

$C_i(z,0)=C_0$; $q_i(z,0)=q_i^*$ (13)

6.3 DESIGN PROCEDURE:

When an adsorption for separating a gas mixture is determined, a logical sequence of decision steps in design of a PSA process is as follows:

1. Selection of a proper adsorbent based on its equilibrium and kinetic characteristics.
2. Selection of particle size distribution and particle shape.
3. Selection of operating pressure levels for a PSA system.
4. PSA cycle configuration and duration of each individual steps.
5. PSA bed dimensions.
6. Inclusion/exclusion of pressure equalization step.
7. Vacuum swing adsorption (VSA) as an alternative.

6.3.1. Selection of adsorbent

Adsorption is achieved due to the interaction forces between the adsorbing molecules and the adsorption surface. Different substances are adsorbed with different affinities. It is this 'selectivity' that provides the basis for adsorption separation processes. The task of adsorbent is to provide the surface area required for selective adsorption of the preferentially adsorbed species. A high selectivity is of user's interest. The separation factor (α) can be used as a measure of selectivity. The separation factor of an absorbent is defined as

$$\alpha_{12}=\frac{x_1/x_2}{y_1/y_2} \qquad (14)$$

where x_1 and y_1 are, respectively, the mole fraction of component 1 in adsorbed phase and fluid phase. The separation factor depends on the adsorption property, either adsorption kinetics or adsorption equilibrium, or both. In an equilibrium controlled adsorption process, it is simply the ratio of the equilibrium constants. For an extended Langmuir isotherm and a linear isotherm, this separation factor is the ratio of Henry's constants

$$\alpha_{12} = \frac{K_1}{K_2} \tag{15}$$

In a kinetically controlled adsorption, the selectivity depends on the difference of kinetic parameters. The time-dependent concentration within the adsorbent particle depends on the diffusivity of adsorbing molecules. For short time intervals this dependency can be approximated by

$$q_t \propto \sqrt{D} \tag{16}$$

Thus the separation factor for kinetically controlled process is calculated by

$$\alpha_{12} = \sqrt{\frac{D_1}{D_2}} \tag{17}$$

It is always useful that the separation factor is calculated by considering both equilibrium and kinetic effect. Thus the separation factor can be defined as

$$\alpha_{12} = \frac{K_1}{K_2}\sqrt{\frac{D_1}{D_2}}$$

a high separation factor is a key for a quick screening of various adsorbents.

6.3.2. Size distribution and shape of particles

In adsorption processes, the particle size distribution and particle shape decide the bed porosity. Porosity affects bed performance in two ways. If other parameters remain constant, a lower porosity leads to a higher bed pressure drop. On the other hand, a lower porosity means a higher adsorbent content of the bed and hence a higher adsorption capacity. Moreover, a lower porosity means less loss of the adsorbable component during the blowdown step and less requirement of product gas for an effective extraction during the purge step. Both of these properties increase the product recovery.

Bed porosity can be varied using different shapes and sizes of adsorbent particles and to some extent packing techniques. Simulation studies are made using various values of bed porosity. The effect of bed porosity on product purity is significant for both bulk separation and purification processes. The effect on product recovery is significant only in bulk separation cases. As porosity increases, both the product purity and recovery will decrease. It can be seen that as the porosity increases, product recovery remains almost constant for purification processes (where the highly adsorbing species is in very low concentration, e.g. air containing moisture).The effect of bed porosity on product purity and recovery is given in fig6.2.

On the other hand, the porosity of a bed also affects the bed pressure drop. In a packed bed the pressure drop can be calculated from Blake–Kozeny equation

$$-\frac{\partial P}{\partial z} = \frac{180\mu v}{d_p^2}\,\frac{(1-\varepsilon)^2}{\varepsilon^3}, \quad \forall z \in [0,\, L] \tag{18}$$

From Eq. (21), as the porosity increases the bed pressure drop will decrease. Fig. 4 shows the pressure drop versus the bed porosity. For a given system, Eq. (21) can be rewritten as

$$-\frac{\partial P}{\partial z} = \phi\,\frac{(1-\varepsilon)^2}{\varepsilon^3} \tag{19}$$

where φ is given as

$$\phi = \frac{180\mu v}{d_p^2} \tag{20}$$

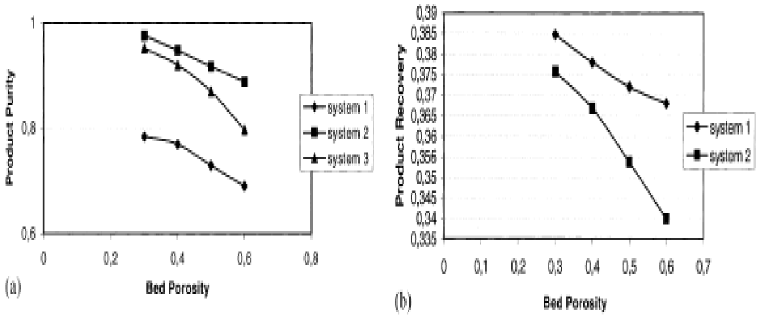


Fig.6.2. Effect of porosity on product purity and recovery

There are two opposite effects of porosity: high product purity requires low porosity and a low pressure drop is achieved with high porosity. From Fig. 4, it can be seen that for bed porosity lower than 0.3, the pressure drop increases rapidly. Thus this should be the lower limit of porosity (which can be achieved for most practical particle shapes and sizes). For bed porosity higher than 0.5, the change in pressure drop becomes moderate, thus this can be considered as the upper limit. Similarly, the effect of the porosity on the product purity, as shown in Fig. 6.3, indicates that when bed porosity is higher than 0.5, the purity will decrease significantly, thus confirming the use of 0.5 as the upper limit of the bed porosity.

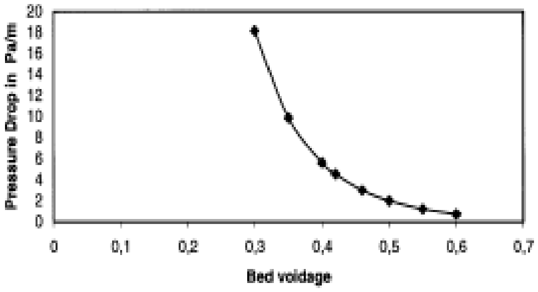


Fig6.3 porosity vs. pressure drop

6.3.3. Selection of adsorption pressure

Selection of the adsorption pressure is based on the equilibrium relationship of the system. An isotherm describes the equilibrium loading of a species, which is dependent on the partial pressure of the species in an adsorption process. As the adsorption pressure increases, the amount of fluid adsorbed on the adsorbent will increase. To determine the pressure level for adsorption, one should keep in mind that the larger the difference between the capacities of the competing adsorbates, the purer the raffinate will be. The selectivity of an extended Langmuir isotherm and a linear isotherm is constant. These isotherms are, therefore, called 'constant selectivity isotherm'. For constant selectivity systems, if the pressure is increased, which causes more adsorption of the highly adsorbed species, the product purity will be increased. The less favorable species is also adsorbed more, but in comparison to the more favorable species it is always less, as long as the more adsorbing species is present in significant quantities in the bulk phase. Therefore, for such systems a higher pressure always leads to a purer product.

Besides this advantage of high pressure for constant selectivity systems, there is one disadvantage too, that is energy loss. A higher pressure level leads to higher compression costs and a higher loss of energy in the blowdown step. If an adiabatic compression is assumed, the power requirement can be approximated as:

$$W = \frac{\gamma}{\gamma - 1} \frac{QRT}{\eta} \left(\left(\frac{P_H}{P_L} \right)^{(\gamma - 1)/\gamma} - 1 \right) \qquad (21)$$

where P_H and P_L are high and low pressure levels, respectively, Q is the volumetric flow rate, and T is the operating temperature. Simulation results of extended Langmuir and linear isotherms are given in Fig. 6.4 for various adsorption pressure levels. It can be seen that as the pressure increases, the product purity will be increased. At the same time the power required for compression also rises. If a high purity product is desired, the adsorption pressure should be as high as possible. The power requirement increases with the increase of the adsorption and the desorption pressure ratio. Considering the trade-off between product quality and power requirement, the adsorption pressure should be taken as the value at which the change of the adsorbed phase concentration with pressure becomes moderate

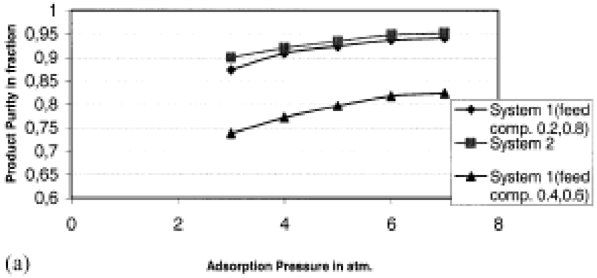


Fig 6.4. Adsorption pressure Vs product purity

If the selectivity varies with the operating pressure, the adsorption pressure should be that at which the selectivity is maximum. The effect of pressure for varying selectivity systems

6.3.4. Selection of adsorption time

In a PSA process, the duration of the adsorption step is determined by studying the breakthrough curve. The term breakthrough curve refers to the response of the initially clean bed to an influent with a constant composition. It can be seen by monitoring the concentration of the effluent. Breakthrough occurs when the effluent concentration reaches a specific value. The adsorbate concentration in the flow at any given point in a bed is a function of time, resulting from the movement of concentration front in the bed. The breakthrough curve for a gas containing a single adsorbate can be obtained by the solution of the mass balance equations for both the bed and adsorbent particles, along with the equilibrium isotherm. The duration of the adsorption step is the time period needed for breakthrough to occur. After this time the product purity will decline, and before this time the full bed capacity will not be employed. Thus the adsorption time should be near the breakthrough time. This time depends upon isotherm, diffusivity and residence time of the feed in the bed.

From simulation studies, it can be observed that beyond a certain value of the adsorption time, the change in product purity becomes insignificant. The product purity decreases as the adsorption of less adsorbable species increases. Fig. 6.5 shows how the change in the adsorption time affects the product purity. It can be seen that the time of the adsorption step should be where the product purity is maximum. This is the time when breakthrough occurs.

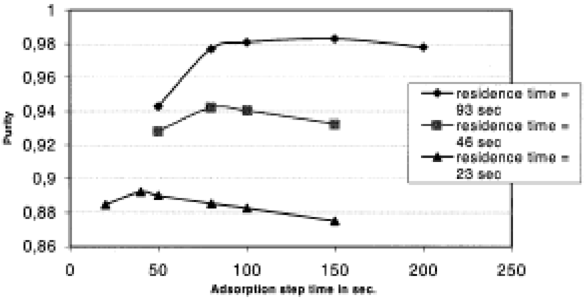


Fig 6.5 adsorption step time vs. product purity

6.3.5. Effect of distribution of adsorption time

In a two-bed, four-step PSA system, adsorption takes place in both the pressurization and adsorption steps. The apportion of the total adsorption time to these two steps affects the performance of PSA. Fig.6.6a and 6.6b show the simulation results corresponding to different time allocations to these two steps. it can be seen that as the ratio of the pressurization time and the adsorption time increases, the product recovery will decrease, but its purity will increase. With a higher time ratio, fewer products will be obtained. At the same time, higher time ratio improves product quality. Moreover, it can be seen from the simulation results that the rate of the decrease of product recovery is much greater than the rate of the increase of product purity. Thus, the change in recovery is a dominating factor to determine the adsorption time apportion. Having these two opposite effects and taking the fact that the recovery effect is more dominant, the ratio of the pressurization time to the adsorption time should be low. The upper limit should be 0.2, according to the simulation results.

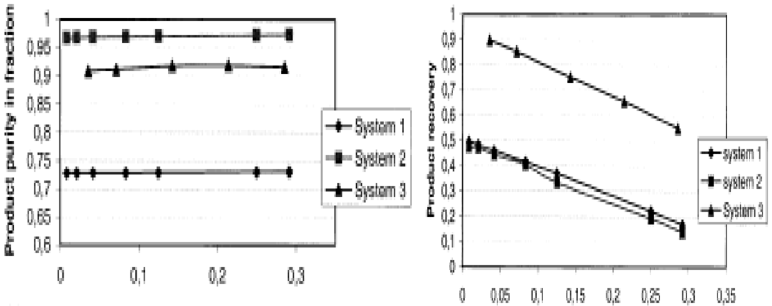


Fig 6.6.variation of product purity and recovery with t_{pres}/t_{ads}

6.3.6. Effect of purge-to-feed ratio

The purge step in PSA is a desorption step that regenerates adsorbents by desorbing the adsorbed species. In a PSA process, saturated adsorbents are regenerated by lower pressure, thus a low pressure purge step is required. Generally, from the product vessel with the raffinate at a high pressure, a fraction of the product stream is withdrawn to purge the bed and expended to a low pressure. The volume required in the purge step affects the product quality as well as its recovery. As the purge volume increases, purging becomes more effective, providing a regenerated bed with adsorbents of less loading and leading to increased product purity. In principal, the bed should be fully regenerated with adsorbents completely unsaturated, thus more purging is necessary. At the same time, since purging is done by utilizing the product, increase in the purge volume decreases the product recovery. Generally, the purge volume specification for PSA is given by the purge-to-feed volume ratio.

. The effect of this ratio on product purity and recovery is shown for two cases in Fig.6.7. It can be seen that as this ratio increases, the product purity increases as well, but the recovery decreases. The rate of the increase in purity is much slower than the rate of the decrease in recovery. From these results, one may infer that the purge-to-feed ratio should be neither too low nor too high. A guideline regarding this ratio from the simulation results is that it should be between 1.0 and 2.0, if purging is done by product. These are volumetric ratios. It should be noted that, although the volume of purge used is more than the volume of feed, the mass of purge is less than the mass of feed or product, since the pressure of purging is much lower than the feed pressure.

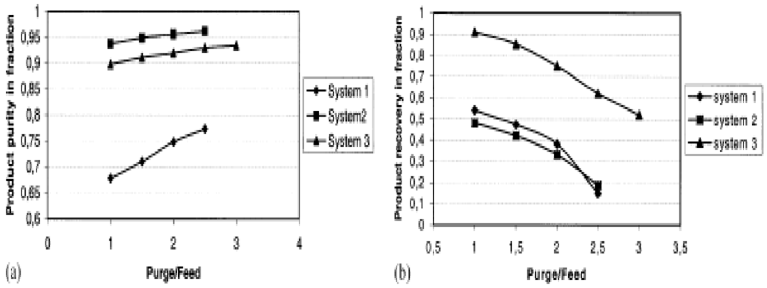


Fig 6.7. Effect of Purge/feed on product purity and recovery

6.3.7. Residence time determination

The residence time of species in a bed is the ratio of the bed holdup to the volumetric feed rate. Sufficient residence time should be provided, so that the desired product purity can be achieved. For species with lower diffusivities, greater residence time is required. The choice of residence time is critical in adsorption, since if the residence time is too short, there will be no significant adsorption. Increase in residence time can be made by reducing the feed rate or by increasing the bed volume. Since the feed rate is decided by the desired capacity of the unit, required residence can be achieved by changing the bed volume. However, in an existing unit, residence time can be altered only by adjusting feed rate or feed pressure or both.

Simulations were made to study the effect of residence time on bed performances. Fig. 6.8 shows the effect of residence time and feed composition on the product purity for system 2 (refer Appendix A). Similar profiles can be obtained for other systems too. For different systems, the shape of profiles remains the same. The main features of these plots are that, at low residence time, no high product purity can be obtained, and the relationship between feed composition and product composition is linear. When keeping the feed composition constant, product purity can be increased by increasing residence time. If the feed composition of the desired species is high, product purity will increase linearly with residence time

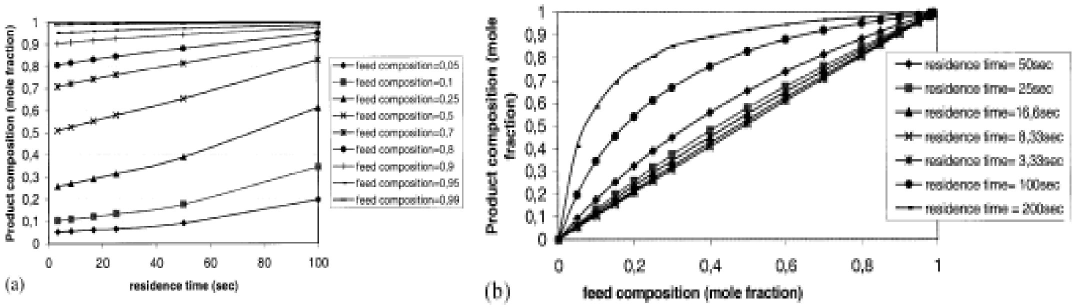


Fig 6.8. Variation of residence time with feed and product composition.

6.3.7.1. The minimum residence time

A PSA process reaches its cyclic steady state after a certain number of cycles of operation. A steady state PSA model can be developed using the same assumptions as stated before. The governing equations may be obtained as follows. First, by combining (1) and (4) and letting the time-differential terms be zero, the following equation can be gained

$$-\frac{\varepsilon}{(1-\varepsilon)}\frac{dC_i}{k_i(q_i*-q_i)}=\frac{dz}{v} \qquad (22)$$

If the maximum driving force is applied, i.e. by taking $q_i=0$ in the above equation, one has

$$-\frac{\varepsilon}{(1-\varepsilon)}\frac{dC_i}{k_i q_i^*}=\frac{dz}{v} \qquad (23)$$

The boundary condition for this equation is the same as given in Eq. (6). It is easy to solve this equation, and the solution for the highly adsorbed component will give the residence time for a system under the conditions of a constant velocity and the maximum driving force. Therefore, the solution of Eq. (23) gives the minimum residence time for a given feed and desired product composition. Initially, one may expect the existence of certain relationship between the ratio of the actual and the minimum residence time, with the kinetic parameters and separation factor. Fig. 6.9 gives the relationship between the separation factor and the time ratio. As the separation factor increases, the required ratio of actual-to-minimum residence time also increases. But this relation is less clear. As an explanation, one may argue that the ratio of actual-to-minimum residence time depends on the total amount of gas adsorption, rather than the kinetic selectivity (the ratio of diffusivities). Basis for this argument is that in the calculation of the minimum residence time, the maximum driving force is considered (taking q_i=0), but this is not the case of the actual residence time. The difference arises due to the difference in driving force, which is the adsorbed phase concentration in a practical cycle. The concentration in the adsorbed phase depends on the mass transfer of each component, which relies on the individual mass transfer coefficient. In this way, the total effect on the adsorbed phase concentration depends on the sum of the mass transfer coefficient, rather than the kinetic selectivity.

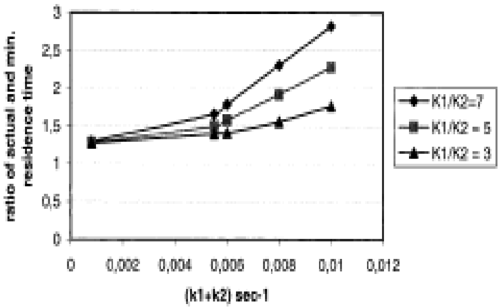


Fig 6.8 Residence time ratio vs. mass transfer coefficients

In calculation of the minimum residence time, the assumption of a constant velocity is taken, which is invalid if the concentration of the highly adsorbing species is high in the feed. If the concentration of the highly adsorbing species in the feed increases, the product flow rate will be low as compared with the feed flow rate, and the minimum residence time will be much less than the actual residence time. Thus the ratio of actual-to-minimum residence time will also depend on feed composition.

$$\frac{\tau_{act}}{\tau_{min}} = 1 + 100(k_1 + k_2)\left(\frac{K_1}{K_2}\right)y_{f1} \tag{24}$$

Most of the systems have $(k_1 + k_2)(K_1/K_2)\, y_{f1} < 0.015$, where the value of the time ratio is in between 1 and 2. From this result, a quick estimation of the bed size can be made.

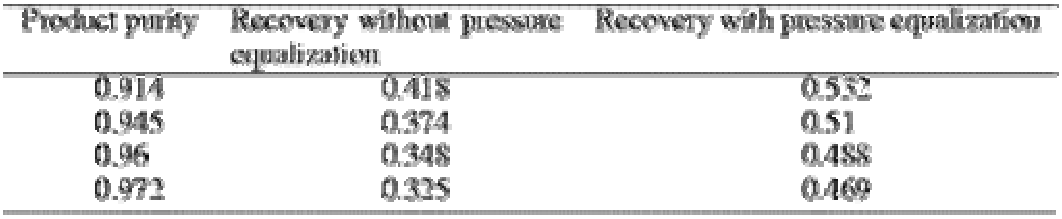
The bed volume is determined based on the required residence time. To specify the bed size, i.e. the bed diameter and bed height, some criteria should be kept in mind. The choice of the bed diameter depends on the fluidizing velocity, which is the minimum velocity required to fluidize a bed. The maximum velocity in the bed should not exceed 70% of the minimum fluidizing velocity. For velocities greater than this value, entrainment of adsorbents in effluent stream may occur and also the pressure drop in the bed would be very high. After determining the fluidizing velocity, the bed diameter can be calculated. Another important criterion for bed specifications is the crushing strength of the solids. The height should be such that no crushing occurs in the bed.

6.3.8. Pressure equalization

The first improvement over Skarstrom's cycle is the introduction of a pressure equalization step, as shown in Fig. 19. After the first bed has been purged and the second bed has completed its high-pressure adsorption step, instead of blowing down the second bed directly, the two beds may be connected to each other through their product ends in order to equalize their pressures. The first bed is thus partially pressurized with gas from the outlet region of the second bed. After the pressure equalization, the two beds are disconnected and the first bed is pressurized with feed gas while the second bed is vented to complete the blowdown. The pressure equalization step conserves energy, because the compressed gas from the high-pressure bed is used to partially pressurize the low-pressure bed. Since this gas is partially depleted of the strongly adsorbed species, the degree of separation is conserved and the blowdown losses are reduced. Based on these considerations, a pressure equalization step is often incorporated in the PSA process.

Table 6.1 indicates the PSA performance with and without a pressure equalization step. It can be seen that a pressure equalization step favors product recovery. But if the pressure swing is sufficiently low, the inclusion of a pressure equalization step may be impractical. Otherwise, the pressure equalization step should always be incorporated in the PSA process.

Table 6.1. Comparison of PSA process with and without pressure equalization step for air separation on CMS



Product purity	Recovery without pressure equalization	Recovery with pressure equalization
0.914	0.418	0.532
0.945	0.374	0.51
0.96	0.348	0.488
0.972	0.325	0.469

6.3.9. Vacuum swing adsorption

Vacuum swing adsorption (VSA) is also a Skarstrom cycle in which the low-pressure purge step is replaced by a vacuum desorption. The product end of the bed is kept closed and the vacuum is applied through the feed end, as shown in Fig.6.10.. In a VSA process, using the same high operation pressure as a Skarstrom cycle and for the same product purity, the loss of the less favorably adsorbed species in the evacuation step is normally less than the corresponding loss in the purge. The gain in raffinate recovery is achieved at the expense of the additional mechanical energy required for the evacuation step. A significant amount of energy can be saved, if the adsorption takes place slightly above the atmospheric pressure and the desorption is done at a very low pressure. A VSA cycle will, therefore, be advantageous over a normal Skarstrom cycle, if a low-pressure product is acceptable. In kinetically controlled separation, a major disadvantage using a normal Skarstrom cycle is that the slowly diffusing raffinate product would be continuously adsorbed during the purge step. This problem can be avoided by using VSA. In kinetically controlled processes there is a little difference in isotherms of feed components (e.g. nitrogen separation from air using zeolite 4A) but a large difference in diffusivity. In such a system, purging with the product to remove the highly diffusing species from the bed is undesirable. This is so because apart from wasting product (a certain fraction of nitrogen), the raffinate gas will be adsorbed during this step, thereby reducing the capacity for oxygen during the next adsorption step. For such type of systems a VSA process is worth considering. For the nitrogen separation from air using carbon molecular sieve (CMS). The results are shown in Table 6.2, which illustrate that the recovery of nitrogen is greater in a VSA process than in an ordinary Skarstrom cycle. From the results and the above explanation, it can be concluded that for kinetically controlled processes, VSA is a better choice over a normal Skarstrom cycle.

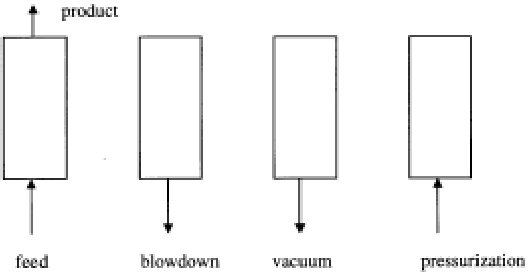


Fig 6.10 vacuum swing adsorption

Table 6.2. **Performance comparison of VSA cycle with ordinary Skarstrom** cycle

Product purity for nitrogen in %	% Recovery of nitrogen in Skarstrom cycle	% Recovery of nitrogen in VSA cycle
89.5	56.4	88.3
92.5	53.7	83.3
94.2	49.7	77.6
95.1	42.1	72.5
98.2	21.6	60.1

The blowdown pressure used is 1 atm and the vacuum pressure used is 0.25 atm.

Conclusion:

In PSA design and operation, heuristics developed in this study may be summarized as follows:

Rule 1**:** Adsorbent, which gives the largest separation factor, should be used.

Rule 2**:** Bed porosity should be in the range 0.3–0.5. Particle size distribution and shape should be such that bed porosity is within these limits.

Rule 3 **(*a*):** For systems whose isotherms are given either by the Henry's Law or by the extended Langmuir isotherm expression, the adsorption pressure should be as high as possible, subjected to the power requirement constraint.

Rule 3 **(*b*):** For systems with pressure dependent selectivity, adsorption pressure should be the pressure, which gives maximum selectivity.

Rule 4 **(*a*):** The adsorption time should be near the adsorption breakthrough time.

Rule 4 **(*b*):** For a two bed PSA process, the adsorption and desorption time should be equal.

Rule 5**:** The maximum limit for the ratio of the pressurization time to the adsorption time should be 0.2.

Rule 6**:** The ratio of purge-to-feed volume should be in the range 1.0–2.

Rule 7 **(*a*):** The bed diameter should be such that the velocity within the bed does not exceed 70% of the minimum fluidizing velocity.

Rule 7 **(*b*):** Bed height should not cross the crushing strength of adsorbent particles.

***Rule 7* (*c*):** The Ratio of actual-to-minimum residence time should be in the range 1–2. Eq. (24) may be used to calculate the ratio.

***Rule 8* (*a*):** For processes with high swing in pressure, a pressure equalization step should be included.

***Rule 8* (*b*):** The ratio of intermediate pressure to the low pressure should be in the range 0.5–0.8 of the ratio of the high pressure to the low pressure.

***Rule 9*:** For a kinetically controlled process, VSA should be considered.

6.4. DETAILED DESIGN

In our design, nitrogen is required for synthesis gas and oxygen is required for combustion of natural gas in shell side of the tubular reactor.

Amount of nitrogen required=510.62 mols/s

Amount of oxygen required =280.6 mol/s

Total air required =1336.19 mol/s. From this 510.62 mol/s of nitrogen should be separated first and then 280.6 mol/s of oxygen is separated. Rest of the nitrogen can be used for some other purpose. So our prime aim is the separation of nitrogen

1. Adsorbents available for air separation are zeolite 5 A and CMS 3 A. the separation factor for nitrogen in CMS is 41, where as in first case it is 0.16. Since nitrogen is desired product CMS has to be used.
2. Porosity: 0.3

   Adsorbent: CMS 3A

   Particle density: 0.9 g/cc

   Bulk density: 0.633 g/cc

   Particle size=0.158 cm

   Particle shape=spherical
3. Assuming that the adsorption isotherms for the adsorption of nitrogen on CMS are constant selectivity isotherms, the adsorption pressure has to be taken as high as possible.P_H=6 atm.
4. Purity of the product increases with increase in residence time. For higher residence time adsorption break through time is around 70 seconds. So adsorption time is taken as 60 seconds.
5. Purity is almost constant for increase in ratio pressurization time to adsorption time. But recovery increases with the ratio. Taking the ratio as 0.05.t_{pres} =3 seconds

6. Our main product is nitrogen. Use of purge will affect the purity and recovery of nitrogen. So no purge is required and VSA should be employed.
7. a) Minimum fluidization velocity can be evaluated from the following formula

$$\boxed{(150\,\mu V\,(1-\epsilon_m)/\varphi_s^2 D_p^2 \epsilon_m^3) + (1.75\rho V^2/\varphi_s D_p \epsilon_m^3) = g\,(\rho_p-\rho) \qquad (25)}$$

   For air the porosity at minimum fluidization velocity is around 0.5 and sphericity is 1. Minimum fluidization velocity is 0.3415m/s. So the maximum operating velocity is 0.2391 m/s.

   b) To find out the minimum residence time, the concentration of nitrogen in adsorbed phase and gas phase are calculated from table 5.2. τ_{min} = 89 sec

   c) τ_{min}/τ_{act}=1.07 so τ_{act}=98 sec
8. Since there is a large swing in pressure, pressure equalization step has to be employed. When the third bed finishes the vacuum desorption step the first bed is finished with the adsorption step. The product ends of these two may be connected $P_I/0.25=0.7*6/0.25$. P_I=2.52 atm.
9. As mentioned, VSA is used. Blowdown pressure is 1 atm. Vacuum pressure is 0.25 atm.

6.4.1. Determination of bed diameter and height:

Maximum velocity in the bed will be for the feed. So

$5.445/ (\pi/4\ D^2) < 0.2391$

$D > 5.385$ m

Actual residence time = (volume/ flow rate)

$D^2Z=679.41$.

Normally polybed PSA processes are employed. For this feed flow rate the number of beds should not exceed 6.

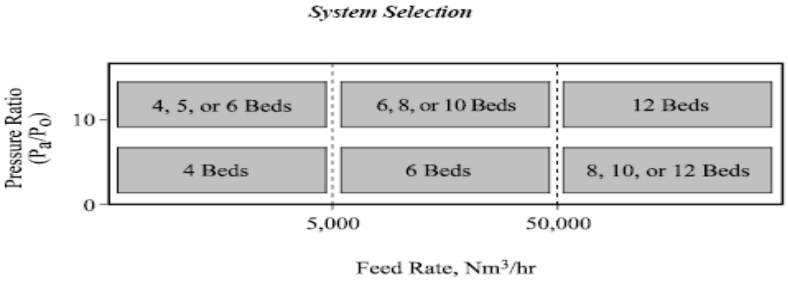


Fig 6.11. System selection

Table: 6.3: comparison of L/D ratio

Trial no.	No of beds	D m	D^2Z m^2	L m For D=6 m	L/D for D=6m
1	1	>5.385	679.41	18.87	3.145
2	2	>3.807	339.705	9.436	1.572
3	3	>3.1	226.47	6.29	1.044
4	4	>2.7	169.85	4.71	0.785

In industrial adsorbers the diameter usually ranges between 5-8 m. Assuming a diameter of 6 m, the length of the adsorber is 18.87,9.436,6.29,4.71 m for the above four trials. The L/D ratio ratio should be 1-3. So the second trial is satisfactory.

Length of the bed= 9.436m

Diameter of the bed=6m

7. DESIGN OF TUBULAR REACTOR

7.1. NOMENCLATURE:

λ_g	Thermal conductivity of gas ,W/m^0C
λ_s	Thermal conductivity of catalyst particle, W/m^0C
λ_E	Effective thermal conductivity of bed ,W/m^0C
λ_R	Radiative thermal conductivity of gas, W/m^0C
λ_o	Isotropic thermal conductivity of the bed ,W/m^0C
λ_t, λ_t'	Convective thermal conductivity of gas, W/m^0C
α_c	Tube side heat transfer coefficient , $W/m^2\ ^0C$
α_w	Wall heat transfer coefficient, $W/m^2\ ^0C$
U	Overall heat transfer coefficient, $W/m^2\ ^0C$
N_t	Number of tubes
d_t	Inside diameter of tubes, m
t	Thickness of tubes, m
$d_{t\,o}$	Outside diameter of tubes, m
d_p	Diameter of catalyst particle, m
u	Velocity of fluid ,m/s
V	Volume of tubes, m^3
Re	Reynolds number in packed bed
Pr	Prandtl number
ε	Bed porosity
ε_m	Emisivity of the catalyst particle
ρ_p	Density of the catalyst particle, Kg/m^3
ρ	Density of the gas, Kg/m^3
μ	Viscosity of the gas, Kg/m s
C_p	Specific heat of gas ,J/Kg^0K
T	operating temperature ,^0K
Φ_s	Sphericity of the catalyst =1
P	Design pressure, Kg/cm^2

J	joint efficiency
f	Allowable stress at operating temperature, Kg/cm^2
D_s	Inside diameter of shell , m
D_{so}	Outside diameter of shell ,m
t_s	Thickness of shell ,m

7.2. DESIGN FUNDAMENTALS:

In a catalytic tubular reactor, the temperature may not be same over the length and cross section of the reactor. In case of exothermic reaction, temperature will be more along the axis of the tube than near the wall (when coolant flows outside the tube) and vice versa when endothermic reaction takes place.

Heat transfer is a result of

i. Flow independent mechanisms
    1. Thermal conduction through solid particle
    2. Thermal conduction through contact point of two particles
    3. Radiant heat transfer between surfaces of two adjacent pellets

ii. Flow dependent mechanisms
    1. Thermal conduction through fluid film near contact surface of two pellets
    2. Convective heat transfer(solid-fluid-solid)
    3. Heat conduction within fluid
    4. Heat transfer by lateral mixing

As fluid is passing through a bed of particles, its repeated lateral displacement combined with mixing of volume elements gives rise to a certain degree of mixing perpendicular to the main flow. The degree of mixing can be characterized by means of an apparent transverse diffusion coefficient D_t.

Heat can be transported perpendicularly to the main flow by the same mechanism if a transverse temperature gradient exists, resulting in a convective heat conductivity λ_t.

Heat can be transferred by conduction through the fluid from particle to particle and with gases it is associated with thermal radiation between the particles. If there is no flow an apparent (isotropic) thermal conductivity of the bed λ_0 also exists.

$$\lambda_t = \lambda_0 + \lambda_t^{'} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 7.1$$

$$\lambda_t^{'} = \frac{(\rho C_p)_G d_p u}{8(2-(1-2\frac{d_p}{d_t})^2)} \forall 30 < \mathrm{Re}.\mathrm{Pr} < 600 \cdots\cdots\cdots\cdots\cdots 7.2$$

$$\frac{\lambda_0}{\lambda_g} = 0.67\varepsilon + A\sqrt{(1-\varepsilon)} \cdots \forall 0.26 < \varepsilon < 0.93 \cdots\cdots\cdots\cdots\cdots 7.3$$

$$A = \frac{2}{1-\frac{\lambda_g B}{\lambda_s}}(\frac{(1-{}^{\lambda_g}\!/_{\lambda_s})B}{(1-{}^{\lambda_g B}\!/_{\lambda_s})}\ln\frac{\lambda_s}{B\lambda_g} - \frac{(B+1)}{2} - \frac{(B-1)}{1-\frac{\lambda_g B}{\lambda_s}} \cdots\cdots\cdots\cdots 7.4$$

$$B = C(\frac{1-\varepsilon}{\varepsilon})^{1.11} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 7.5$$

C=1.25 for spheres and 1.4 for crushed particles and 2.5 for cylinders and rasching rings..

$$\lambda_R = \frac{0.23}{{}^{2}\!/_{\varepsilon_m} - 1}(\frac{T}{100})^3 d_p \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 7.6$$

$$\frac{\lambda_o}{\lambda_G} = (1-\sqrt{1-\varepsilon})(1+{}^{\lambda_R}\!/_{\lambda_G}) + A\sqrt{1-\varepsilon} + \frac{\sqrt{1-\varepsilon}}{{}^{\lambda_G}\!/_{\lambda_R} + {}^{\lambda_G}\!/_{\lambda_S}} \cdots\cdots\cdots\cdots 7.7$$

An additional heat transfer resistance should be taken for the transport of heat between fluid stream and the wall containing bed. Although the point velocity in the bed can be greater near the wall than its value averaged over the whole cross section, the intensity of transverse mixing decreases as wall is approached. A boundary layer exists at the wall itself, it has an average thickness determined by the velocity of the flow and by the produced by the particles adjacent to the wall. These effects can be conveniently combined into a wall heat transfer coefficient α_W given by

$$\frac{\alpha_W d_p}{\lambda_t} = 0.203\,\mathrm{Re}^{0.33}\,\mathrm{Pr}^{0.33} + 0.22\,\mathrm{Re}^{0.8}\,\mathrm{Pr}^{0.4} \cdots\cdots\cdots\cdots\cdots 7.8$$

The tube side heat transfer coefficient is given by

$$\frac{\lambda_E}{\lambda_G} = 5 + 0.1\,\mathrm{Re}\,\mathrm{Pr} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 7.9$$

$$\alpha_C = \frac{8\lambda_e}{d_t} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 7.10$$

The overall heat transfer coefficient can be given by

$$\frac{1}{U}=\frac{1}{\alpha_C}+\frac{1}{\alpha_W}+\frac{d_t}{6.13\lambda_t} \cdots\cdots 7.11$$

Reynolds number in a packed bed can be found out by

$$\mathrm{Re}=\frac{2\varepsilon d_p u\rho}{3(1-\varepsilon)\mu} \cdots\cdots 7.12$$

Prandtl number is given by

$$\mathrm{Pr}=\frac{C_p\mu}{k} \cdots\cdots 7.13$$

Ergun's equation is given by

$$\frac{\Delta P}{L}=\frac{150V_0\mu(1-\varepsilon)^2}{g_c\Phi_s{}^2 d_p{}^2\varepsilon^3} \cdots\cdots 7.14$$

7.3. DESIGN PROCEDURE:

1. The amount of catalyst required is known since the residence time is known with respect to the amount of catalyst.
2. The porosity of the bed depends on the d_t/d_p ratio. The d_t/d_p ratio should not exceed 10 and L/d_p should be more than 50.
3. Assume d_t/d_p. Find out porosity. From this get volume of the bed, since volume of catalyst required is known.
4. Evaluate constants A, B, C, λ_R, λ_0, u, Re, Pr, λ_t, Re.Pr, α_w, α_c and then get the overall heat transfer coefficient in terms of number of tubes and length of the tube.
5. From the volume one more equation is obtained relating the number of tubes and length of the reactor.
6. From the heat load one more equation relating heat transfer coefficient, length and number of tubes.
7. Get the length and number of tubes in the reactor and then check it for the pressure drop using Erguns equation.

Emissivity of the catalyst particle (ε_m) =0.19

Diameter of the particle (d_p)= 0.00175 m

Thermal conductivity of the particle (λ_S) = 33.32 W/m^{0}K

Bulk density of the catalyst = 3737.04 Kg/m^3

Mass of the catalyst = 1328.3 Kg

Volume of the catalyst = 0.3554 m^3

Thermal conductivity of gas (λ_G) = 0.09388 W/m^{0}K

Density of the gas =13.13 Kg/m^3

Specific heat of gas (C_p) = 2925 J/Kg^{0}C.

Viscosity of gas = 2.8*10^{-5} Kg/ms

The various trial are tabulated in table6.1.It has been found out that the result of the third trial is satisfactory. The length of the tubes is 0.616m and the number of tubes is 2546. If we have one reactor only then L/D_s is not satisfactory. If we have N identical reactors the L/D_s ratio will become satisfactory only if we have more than 3 reactors. So if we have 3 reactors L/D_s becomes greater than 1 which is satisfactory.

7.4. DESIGN OF TUBES AND SHELL:

7.3.1. Material of construction:

For the tubes the material of construction is authentic steel. For shell side the material of construction is INCONEL 600(80%Ni, 16%Cr, 7%Fe) for high temperature operation around 1100^{0}C.

7.3.2. Determination of tube thickness:

The equation for finding out the thickness of the tubes is

$$t = \frac{Pd_t}{2fJ} + C \cdots\cdots 7.15$$

P =35+0.1(35) =38.5kg/cm^2

d_t=21.4375mm

J = 0.85

f = 276*10^6 Pa

t= 3.2mm; $d_{t\,o}$= 27.635 mm

The standard tube size is $d_{t\,o}$= 31.75 mm ; d_t=22.606 mm with 16 BWG

TABLE: 7.1. Determination of length and number of tubes:

	Trial 1	Trial 2	Trial 3
d_t/d_p	10	15	12.25
ε	0.38	0.3675	0.3725
C	1.25	1.25	1.25
B	2.1523	2.29	2.23
A	17.318	17.0084	16.69
$\lambda_R(W/m^0K)$	0.0360	0.0360	0.0360
$\lambda_o(W/m^0K)$	1.5347	1.5009	1.466
u m/s	$5621.2388/N_t$	$2589.22/N_t$	$3821.35/N_t$
Re	$1.5144*10_6/N_t$	$0.6587*10_6/N_t$	$0.995*10_6/N_t$
Pr	0.9419	0.9419	0.9419
$\lambda_t'(W/m^0K)$	$3.4718*10^7/N_t$	$1.74*10^7/N_t$	$2.59*10^7/N_t$
$(d_t/6.13\lambda_t)^{-1}$ $m^2\ {}^0K/W$	$537.58+1.216*10^{10}/N_t$	$350.4958+.4063*10^{10}/N_t$	$422.897+.792*10^{10}/N_t$
$1/\alpha_w$ $m^2\ {}^0K/W$	$(22.85/N_t^{0.33}+1.9*10^4/N_t^{0.8})*$ $(876.9715+1.984*10^{10}/N_t$	$(17.3/N_t^{0.33}+0.97*10^4/N_t^{0.8})*$ $(857.65+9.943*10^{10}/N_t$	$(19.7/N_t^{0.33}+1.33*10^4/N_t^{0.8})*$ $(837.71+1.41*10^{10}/N_t$
$1/\alpha_c$ $m^2\ {}^0K/W$	$247.3143+7.01*10^6/N_t$	$164.9+2.046*10^6/N_t$	$203.708+3.7*10^6/N_t$
$L*N_t$ (from volume)	2383.196	1036.79	1569.2
1/U(load) $m^2\ {}^0K/W$	$6.999*10^{-4}$	$4.89*10^{-4}$	$6.039*10^{-4}$
N_t	5996	1064	2546
L m	.3972	0.97	0.616
ΔP (Kg/cm^2)	0.9559 (<4)	13.98(>4)	3.845(<4)

7.3.3. Determination of shell diameter:

Taking triangular pitch, the minimum pitch should be 1.25 times the tube outer diameter. The area occupied by one tube in a triangular pitch arrangement is $(\sqrt{3}/4)*(1.25* d_{to})^2$. So for our case (3 reactors) the total area required is $(2546/3)*(\sqrt{3}/4)*(1.25* d_{to})^2$. This is the total cross sectional area of the shell. So inside diameter of shell (D_s) =881.5mm. The standard shell diameter is 889 mm.

TABLE 7.2. Determination of average specific volume

GAS	mass flow rate kg/sec	specific volume	weight%
Methane	4.0101	2.592	0.125
Ethane	0.11	1.9896	0.0033
Propane	0.0047	1.012	0.0001
Nitrogen	0.0422	1.239	0.01012
Oxygen	8.9792	1.126	0.274
Carbon dioxide	17.154	1.88	0.5227
Hydrogen	2.426	1.234	0.0739
	Total= 32.8171		

Volumetric flow rate =mass flow rate *specific volume =32.82*1.706=55.99 m^3/s

Assuming ideal behavior,

P= (0.5523*0.0821*790.5)/ (55.99) = 0.6398 atm = 0.6481 Kg/cm^2

$t_s = Pd/2fj$

P = design pressure = 10% more than operating pressure

f=11.2056 MPa

t = (0.713*0.889)/ (2*110.61*0.8) = 3.58mm

Minimum shell thickness if diameter is less than 1m is 10mm

So the outside diameter=889+20mm=909 mm

7.3.4. Design of head:

The pressure in the reactor inlet is 36 kg/cm^2.For this pressure an ellipsoidal head is recommended. Any dished head consists of 3 integral parts namely central dishing, corner torus and end straight flange. All the three parts are having different meridional radius of curvature. as a result there are two junctions of discontinuity existing in a formed head. First one is between knuckle (torus) and crown (dish) and second one between knuckle and straight flange. Due to differential dilations at the junctions under pressure loading, bending moments and shear stresses

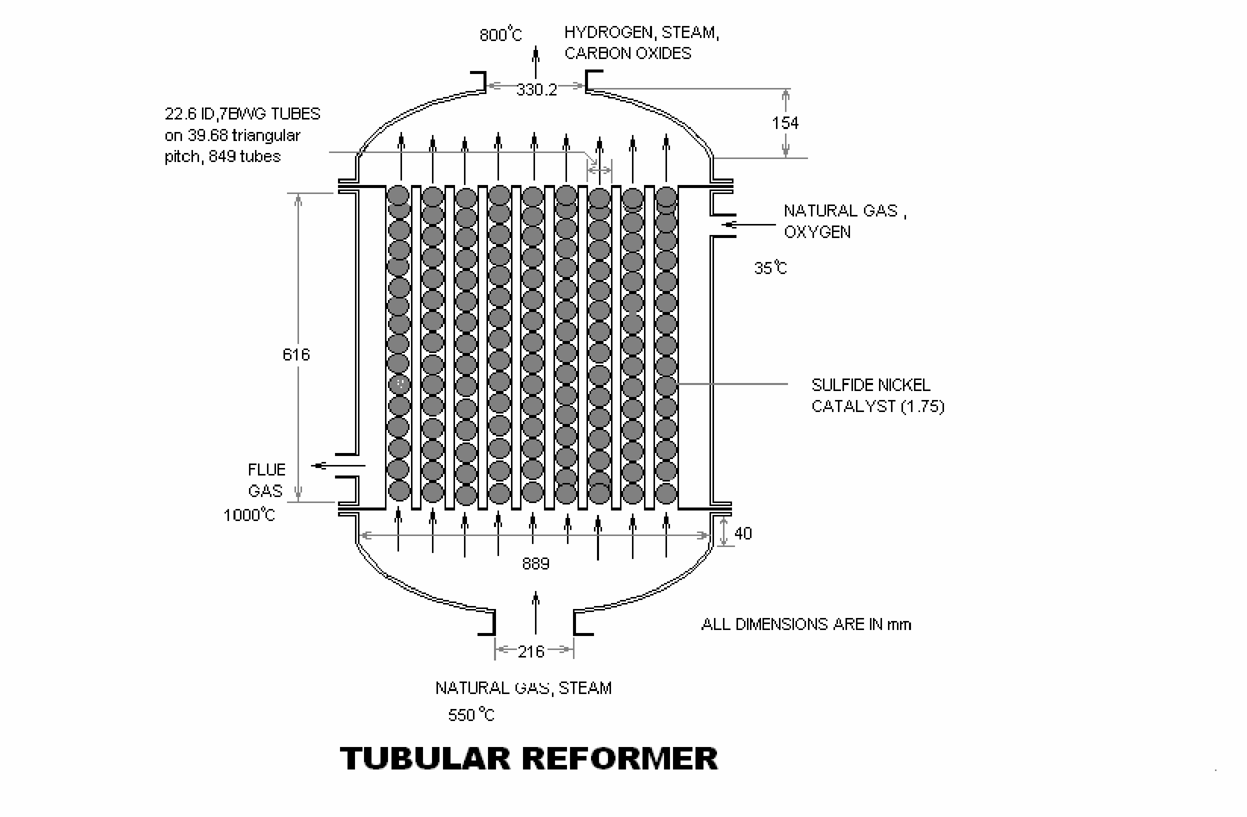


Fig.7.1. Tubular reactor

are induced, besides normal membrane stresses to maintain continuity between adjacent parts. As the torus section is small, these stress concentration factors cannot be neglected in the design equation. The maximum bending stress is the meridional bending stress in the knuckle due to discontinuity at the crown-knuckle junction. Introducing a shape or stress concentration factor C, the head thickness can be given by

$$t = \frac{PD_oC}{2fJ}$$

The factor C depends on h_E/D_0 and t/D_0 for the head without any opening or openings completely reinforced. In case of the heads unreinforced containing opening, C will depend on h_E/D_0 and $\frac{d}{\sqrt{tD_o}}$ Where h_E =the effective external height of the head.

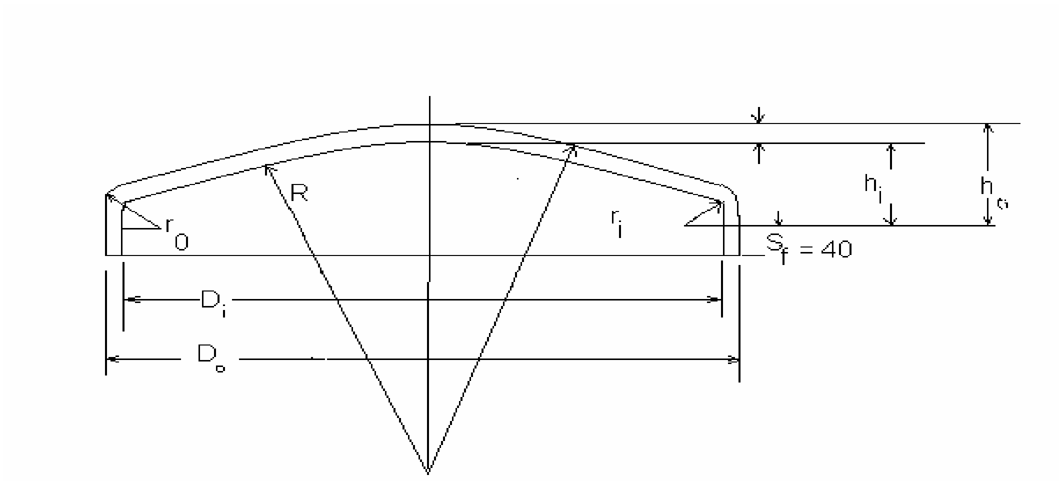


Fig 7.2 .Ellipsoidal head

h_E is the minimum of $h_o = R_o - ((R_o - \frac{D_o}{2}) * (R_o + \frac{D_o}{2} - 2r_o))^{0.5}, \frac{D_o^{\,2}}{4}, \sqrt{\frac{D_o r_o}{2}}$

Assuming R_i = Ro =Do = 909 m

$r_o = 0.06\ D_o$

So h_0=0.1546

$D_0^2/4R_0$ =0.17

$(Do*ro/2)^{1/2}$ =0.1574

From the above three solution 0.1546 is the minimum

So h_E /Do=0.1546/0.909=0.170

As the diameter of the shell (0.909 mm) is not very large the head can be fabricated from a single plate. So J=1. From Eq.4.2.20 (B.C. Bhattacharyya)

t/Do=(PC/2fJ) = $(1.1*36*9.8*10^4C/2*276*1)=7.03*10^{-3}$.

Several of t/DoC are to be tried to match the above relationship. It is found that for t/Do=0.013125 and corresponding value of C is found 1.86 gives t/DoC=$6.25*10^{-6}$ which is a very good approximation. From the above findings the corroded head thickness is obtained as follows

t/Do=0.013125 ; t=13.83mm

Blank diameter of the plate for head can be evaluated from the Equation given below.

Blank diameter =$D_0+D_0/42+2/3ri+2S_f$

Assuming S_f=40mm

Blank diameter=1076 mm

8. PIPING DESIGN AND INSTRUMENTATION DIAGRAMS

9.1. PIPING DESIGN:

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 9.1: Operating velocity for fluids

Fluid	Operating pressure Kg /cm^2	Optimum operating velocity m/s
Gases	<1.05 1.05 -2 >2	3-20 5-25 20-60
Steam	10- 40 >40	20- 40 30-60
Compressed air	In network	15-25

Table: 9.2: Inside diameter of pipes

From	To	T ^{0}C	P Kg/cm^2	n kmoles/s	V m^3/s	u m/s	D$_i$ m
Natural gas feed	Mixing valve	390	2	0.4336	12.187	25	0.7877
Boiler	Mixing valve	390	41	1.48	2.029	40	0.254
Mixing valve	HE$_1$	390	36	1.9166	2.993	35	0.329
HE$_1$	Reformer inlet	550	36	1.9166	1.2384	35	0.2122
Reformer outlet	HE$_2$	800	33	2.7039	2.485	34	0.304
HE$_2$	HTS inlet	367	33	2.7039	4.446	34	0.4080
HTS outlet	HE$_3$	430	32	2.7039	5.037	34	0.4342
HE$_3$	LTS inlet	167	32	2.7039	3.152	32	0.3541
LTS outlet	HE$_4$	190	26	2.7039	4.083	31	0.4094
HE$_4$	Stripper inlet	45	25	2.7039	2.916	31	0.3460
Stripper outlet	condensate	45	8	0.6978	2.352	18	0.4078
Flue gas	HE$_2$	1000	1	0.44586	16.041	32	0.798
HE$_2$	HE$_1$	520	1	0.44586	29.797	32	1.0880
HE$_1$	Vent	28	1	0.44586	11.379	32	0.6613
Natural gas	shell	25	1	0.1191	3.009	14	0.523

The volumetric flow arte is calculated by assuming ideal behavior of gas. From the area of cross section diameter of tube is calculated. The thickness of the 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

$$Schedule_{number} = \frac{2000t}{D_m}$$

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

TABLE: 9.3: Outside diameter of pipes

From	To	S MPa	t (from equation) mm	NPS	Type	OD inch	ID(standard pipe) inch
Natural gas feed	Mixing valve	82	1.03	-	-	-	-
Boiler	Mixing valve	82	7.6	10	40S	10.75	10.02
Mixing valve	HE_1	82	7.96	14	XS	14	13
HE_1	Reformer inlet	90.3	8.07	10	60N	10.75	8.5
Reformer outlet	HE_2	11.2	57	12	40S	12.75	12
HE_2	HTS inlet	99.56	7.37	18	80N	18	16.124
HTS outlet	HE_3	104.63	7.28	18	30N	18	17.124
HE_3	LTS inlet	110.4	5.57	16	100N	16	13.44
LTS outlet	HE_4	110.4	5.18	18	80N	18	16.124
HE_4	Stripper inlet	110.4	4.25	14	10S	14	13.624
Stripper outlet	condensate	110.4	1.57	18	80N	18	16.124
Flue gas	HE_2	3.45	12.58	-	-	-	-
HE_2	HE_1	90.36	0.596	-	-	-	-
HE_1	Vent	110.4	0.317	30	30N	30	28.75
Natural gas	shell	110.4	0.251	24	100N	24	20.938

In the pressure swing adsorption systems, normally polybed units are employed. So the volumetric flow arte depends on number of adsorbers required. From that the pipe diameter can be calculated by following the similar procedure.

9.2. INSTRUMENTATION DIAGRAM:

The number of controllers required to control the process variables can be determined, only when the degree of freedom is known for the process. the degree of freedom of a process is given by

Degree of freedom (F) =Number of variables (V) - Number of equations (N)

If a system consists of ‘n’ components then total continuity equation and n-1 component continuity equations are enough to describe the state of the system.

9.2.1. Heat exchangers:

The control objective is outlet temperature of the process fluid. So feedback controllers are employed and the manipulated variable is the mass flow rate of the other fluid, which exchanges heat with the process fluid.

9.2.2. Orifice meters:

Flow rate is measured by orifice meters. Here the control objective is the flow rate of the fluid. A controller is incorporated to maintain the flow rate of the fluid.

9.2.3. Hydrogenator:

In the hydrogenator natural gas is desulfurized. Since sulfur is present in small quantity, the density of the gas is almost constant. The volumetric flow rate of inlet and outlet streams is equal. The control objective is maintaining the composition of sulfur at the outlet stream. Since it is a exothermic reaction variation in temperature will be there.

Variables = partial pressure of sulfur, partial pressure of hydrogen, temperature

Equations = component continuity equation for hydrogen, energy balance equation.

The degree of freedom is 1.

A controller is incorporated to maintain the sulfur concentration in the outlet by changing the recycle gas flow rate.

9.2.4. Reformer:

In the reformer the methane steam reforming reactions are taking place in the tube side and I the shell side natural gas and oxygen are used as fuel.

9.2.4.1. Tube side:

Total number of components

Inlet = methane, steam, hydrogen, carbon dioxide, carbon monoxide, nitrogen.

Outlet = steam, hydrogen, carbon dioxide, carbon monoxide, nitrogen.

Number of variables= temperature, partial pressure of the components (6).

Number of Equations= total continuity equation, 4 component continuity equations (except Nitrogen) and Energy balance equation.

9.2.4.2. Shell side:

Total number of components

Inlet = methane, hydrogen, carbon dioxide, carbon monoxide, oxygen, nitrogen.

Outlet = steam, hydrogen, carbon dioxide, carbon monoxide, oxygen, nitrogen.

Number of variables= temperature, partial pressure of the components (5).

Number of Equations= Total continuity equation, 4 component continuity equations (except Nitrogen and Energy balance equation.

Total number of equations= 12

Total number of variables = 14

Degree of freedom =2

So controllers are incorporated to maintain the inlet temperature of the fluid by a controlling the flow rate of other fluid in heat exchanger, maintain the outlet temperature of fluid by controlling the flow rate of fuel to the reformer.

9.2.5. Shift converters:

Total number of components = 6. They are Methane, steam, hydrogen, carbon dioxide, carbon monoxide, nitrogen. .

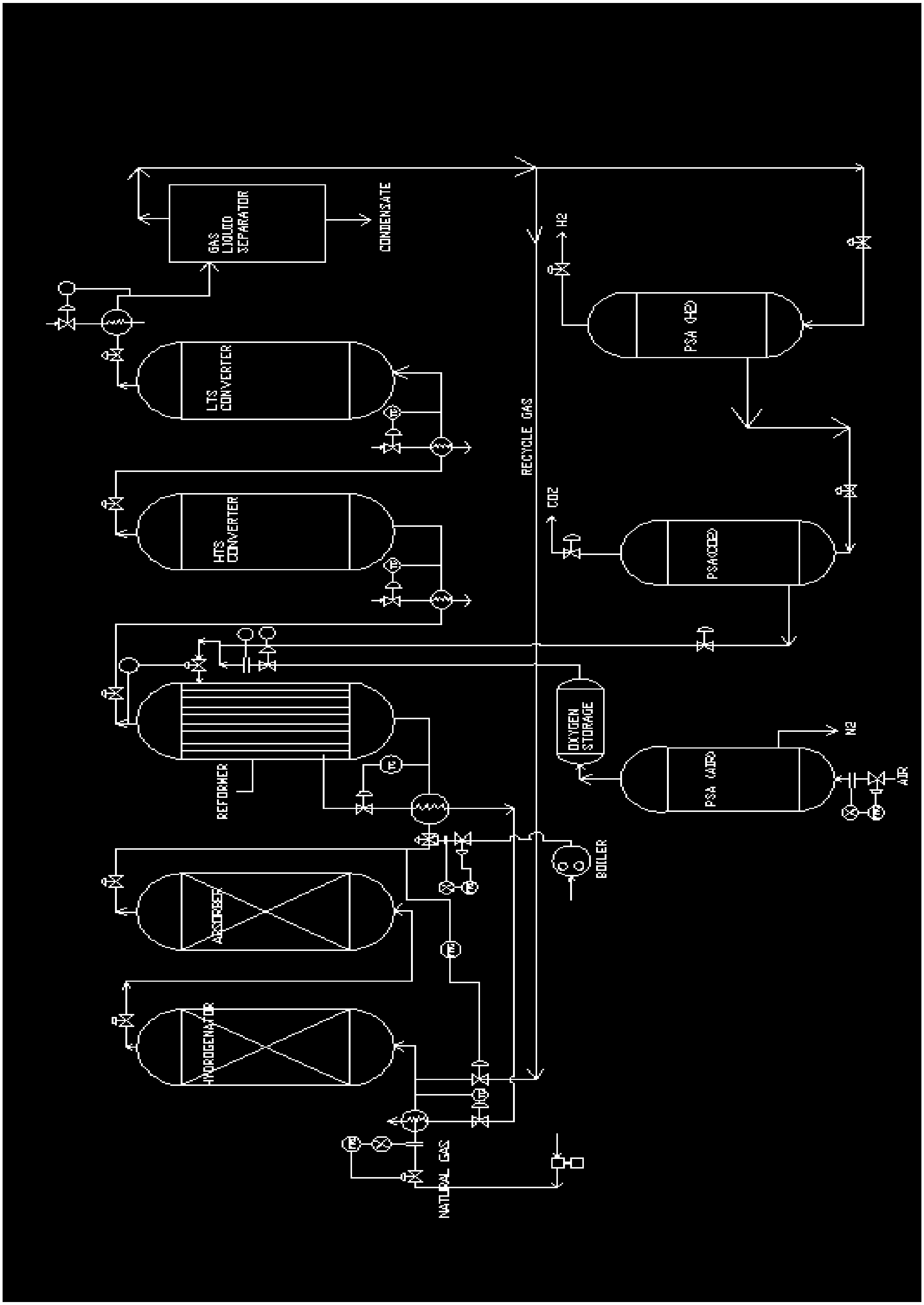
Number of variables= temperature, partial pressure of the components (6) = 7

Number of Equations= total continuity equation, 5 component continuity equations and Energy balance equation. =7

Degree of freedom = 0. So no controllers are required.

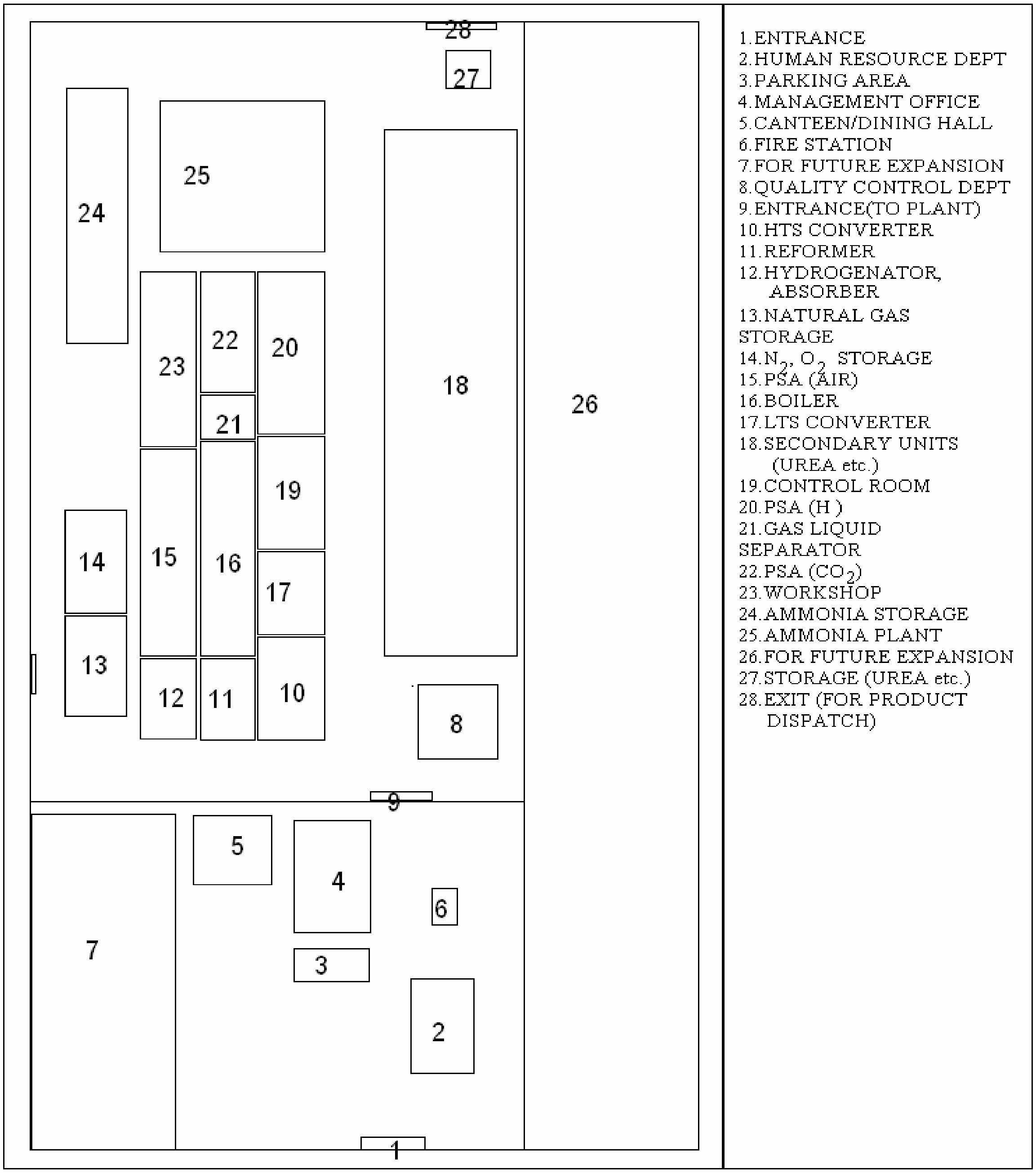
9.2.6. Other processes:

All the other processes such as PSA, gas liquid separator are separation processes. So no controllers are required


GAS LIQUID SEPARATOR
CONDENSATE
LTS CONVERTER
HTS CONVERTER
REFORMER
ABSORBER
HYDROGENATOR
NATURAL GAS
RECYCLE GAS
H2
PSA (H2)
CO2
PSA(CO2)
OXYGEN STORAGE
PSA (AIR)
N2
AIR
BOILER

10. PLANT LAYOUT

FERTILIZER PLANT LAYOUT



1. ENTRANCE
2. HUMAN RESOURCE DEPT
3. PARKING AREA
4. MANAGEMENT OFFICE
5. CANTEEN/DINING HALL
6. FIRE STATION
7. FOR FUTURE EXPANSION
8. QUALITY CONTROL DEPT
9. ENTRANCE(TO PLANT)
10. HTS CONVERTER
11. REFORMER
12. HYDROGENATOR, ABSORBER
13. NATURAL GAS STORAGE
14. N_2, O_2 STORAGE
15. PSA (AIR)
16. BOILER
17. LTS CONVERTER
18. SECONDARY UNITS (UREA etc.)
19. CONTROL ROOM
20. PSA (H)
21. GAS LIQUID SEPARATOR
22. PSA (CO_2)
23. WORKSHOP
24. AMMONIA STORAGE
25. AMMONIA PLANT
26. FOR FUTURE EXPANSION
27. STORAGE (UREA etc.)
28. EXIT (FOR PRODUCT DISPATCH)

Fig. 10.1 Plant Layout

11. CONCLUSION

From this present work it is found that single stage reforming is economical when compared to two stages of reforming and it is preferred at the expense of 21.94 % increase in heat load in the reformer. The percentage composition of hydrogen is more at the reformer outlet in case of single stage reforming. The design of tubular packed bed reactor is carried out and it was found that three reactors are required for the plant capacity of 1500 TPD of ammonia. From this it is found that for higher capacity plants fixed bed reformers are preferred over tubular reformers.

The number of stage of shift conversion is decided by the activity of catalyst over the temperature range. Here two stages of shift conversion are used, one at high temperature and the other one at lower temperature.

The conventional CO_2 removal process and methanation are replaced by the pressure swing adsorption process, since it is economical when compared with others. Design of a pressure swing adsorption system for air separation is carried out and it is found that polybed PSA systems are required for the separation.

11.1. Future scope of the project:

- Identification of more active methane steam reforming catalysts in future will lead to the increased conversion of methane in the reformer.
- In the PSA system, since the adsorbents are not much efficient, polybed units are required. The production of efficient, economical, commercial adsorbents in future will lead to reduction in number of PSA units, thereby reducing the total cost.
- Isothermal shift conversion is normally employed for higher capacity plants. Since it is very costly, it is not employed in all the plants. Improvement in design and operation of the isothermal shift conversion reactors will lead to the use of this in all plants and it will also be economical.

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