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# Optimization of natural gas sweetening process by Alkano-amines and membrane permeation in Aspen Hysys.

# Title page

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Title: Optimization of natural gas sweetening process by alkanoamines and membrane permeation in Aspen Hysys.

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Abstract:

This report is the written part of the 10th semester project work titled “**Optimization of offshore natural gas sweetening process in Aspen Hysys by Alkano-amines and Membrane Permeation.”**

The project work is carried out because of an interest in $CO_2$ capture from natural gas, the process is commonly known as natural gas sweetening combined with $H_2S$ capture. and an interest in necessity of carbon capture technologies.

As the natural gas is part of world energy supply chain, the introduction part starts with world energy usage at present, the predictions for future energy consumption, share of different forms of energy in global energy mix for future. The origin, history, present usage, and future of fossil fuels in general and natural gas in particular are discussed.

Which is followed by an overview of carbon capture technologies in general and their usage for natural gas process in particular. Most commonly used method for natural gas sweetening is the chemical absorption process also known as “Amine treatment.” Amine treatment process is discussed in detail, different kinds of amines, their chemistry with $CO_2$, reaction mechanism, solubility, mass transfer, mass transfer with chemical reaction, amine process and the equipment, operational difficulties etc are discussed.

Membrane permeation process is a comparatively new process for sour gas treatment. membrane process is modelled for sour gas treatment. and its efficiency and economy is compared with alkanoamine process. A combined membrane treatment and alkanoamine process is also modelled and their results are compared.

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# Introduction:

## World energy.

The energy is used mainly to serve four purposes i.e., power generation, transportation, industrial and domestic usage. Sun is the primary source of all energy, however different kinds of energy sources are used in the world depending upon the availability, purpose, technology, and cost. World population has increased manyfold during the past century and modern lifestyle has multiplied the per capita energy usage. Alongside that power has reached to the most underdeveloped regions of the world.

All these factors combined have resulted in an ever-increasing demand in energy and countries are always on the outlook to secure their energy supply and at the cheapest cost. Same is true for power generation companies, transport sector, industrial and domestic users.

Main sources of energy used in the world are fossil fuels, atomic energy and renewable energy that includes hydel energy, wind energy, solar energy, geothermal energy, biomass and biogas etc with more technologies on the way i.e. hydrogen gas.

Fossil fuels have remained the dominant source of fuel for all purposes during the 20th century. Fossil fuels are mainly of three types, Coal, Oil and Natural gas.

Coal has dominated the heating and power generation sector. oil has dominated the transport sector, share of natural gas increased in world energy mix post World War 2, mainly because of the technological advancements in natural gas pipeline technology. Natural gas has found its share in the power generation and transport sector along with applications in industrial sector i.e., urea production and domestic cooking and heating.

Natural gas is a comparatively clean burning fuel with lesser carbon emissions compared to coal and oil. Advancement in its storage and transport technologies i.e., reliable gas pipeline networks that can withstand harsh conditions and compressed natural gas “CNG” and liquified petroleum gas “LPG” technologies provide means of gas transportation over long distances, that has resulted in international trade of natural gas, which was first limited to the regional markets. Technologically gas turbines used for power generation are efficient and quick to start compared to coal and oil based power generation. For the past 2 decades renewables energies i.e., solar and wind are replacing fossil fuels in power generation sector, however due to their intermittent nature, a reliable power generation source is needed to maintain the base load and to make up for the supply shortages. Natural gas is an ideal candidate for this purpose and complements the renewable energy in power generation sector.

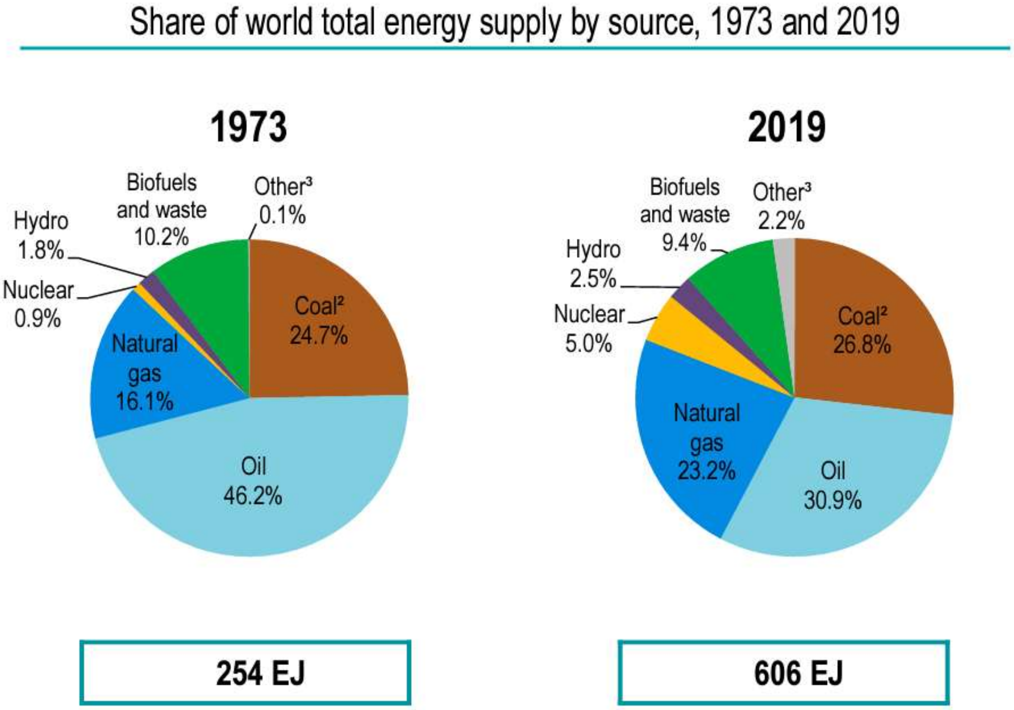

Figure 1: Share of world energy supply by source [1]

It can be seen from figure (1) that world total energy supply is more than doubled from 1973 to 2019, with natural gas share increasing from 16 percent to 23 percent which means 3 times increase in its supply.

Natural gas:

Natural gas is extracted from underground wells or from offshore wells, often along with liquid hydrocarbons, water and some solid impurities. Natural gas and oil are separated through flash separators. Gas is transported through pipelines for consumption. However, before transportation, the gas needs to be sweetened i.e. to remove toxic and low calorific value gases i.e., carbon dioxide and hydrogen sulfide. These gases are combined named as sour gases. The concentration of sour gases varies from well to well and it is seen that concentration often rises as gas well ages.

The concentration of hydrogen sulfide and carbon dioxide varies a lot at different well locations. At some places the concentration of one of the two gases remains inside the allowable limits, therefore the gas must be treated for only one sour gas, either hydrogen sulfide or carbon dioxide.

As the demand of natural gas is on a rise, it has resulted in the production of natural gas from wells having high percentage of $CO_2$ which were first considered not economic due to high cost of $CO_2$ removal.

The concentration of sour gases for pipeline is restricted legally and the restriction is slightly different at different places i.e. gulf of Mexico, north sea and arabian gulf.

The process for removing contaminants from natural gas i.e. $CO_2$, $H_SS$ etc is known as natural gas sweetening. Different methods are used for natural gas sweetening, many different processes are developed over time.

## Natural Gas Sweetening methods.

Different commercial processes are available for natural gas sweetening, most widely used are categorized as,

| **Chemical solvent processes** | | **Physical solvents** | **Membrane separation** | | |
|---|---|---|---|---|---|
| **Chemicals** | | | **Flow pattern** | **Configuration** | **Membrane material** |
| Primary amines | Monoethanolamine (MEA) | Selexol process | Co-current flow | Flat sheet | Cellulose acitate. |

| | | | | | |
|---|---|---|---|---|---|
| | Diglycolamine (DGA) | | | | Cellulose triacetate. |
| Secondary amines | Diethanolamine (DEA) | Flour solvent process | Counter-current flow | Hollowfiber | Hollow fibre carbon membranes. |
| | Diisopropanolamine (DIPA) | | | | Ceramic membranes. |
| Tertiary amines | Triethanolamine (TEA) | Purisol | Cross flow | Spiral wound | Cellulose acitate. |
| | | | | | Zeolite membranes. |
| | Methyldiethanolamine (MDEA) | | | | Mixed matrics. |
| | | | | | Carbon molecular sieve membranes. |

Table 1: comparison of different natural gas sweetening processes.

## Physical solvent process:

Physical absorption works on the principle of Henry's law i.e. solubility of a gas in liquid is directly proportional to the partial of the gas over the liquid. therefore, physical solvent processes are favorable at high pressure applications. The regeneration of physical solvents can be carried out at low pressure in regenerator column and unlike chemical absorption method, heat of regeneration is not necessary [5]. physical solvents have higher absorption capacity as compared to chemical solvents. Physical solvents are not as effective for low pressure applications , they also have difficulties to meet gas pipeline specifications [5].

## Membrane permeation process:

Membrane permeation process is based upon the fact that some membranes let different components in a gas mixture permeate at different rates through the membrane material. This property is also termed as membrane selectivity. In this way membranes let some materials pass through them while restrict others, causing a separation. In the same way a hydrocarbon gas mixture can be separated from sour gases. Membrane permeation process is generally recommended for bulk removal of sour gases from the natural gas stream.

## Chemical solvent process:

As chemical reactions take place between $CO_2$ and the absorbent therefore the process is called chemical absorption. The chemical reaction increases the $CO_2$ absorption rate because,

- The chemical reaction between $CO_2$ and solvent in the liquid phase reduces the equilibrium partial pressure, which results in a pressure gradient that increases the mass transfer driving force.
- The $CO_2$ is consumed at the liquid film interface and the concentration gradient of $CO_2$ between the liquid phase and gas phase is increased which results in higher mass transfer [5].

The main advantages of chemical solvent process are sour gas capture level up to a few ppm, high absorption and desorption mass transfer coefficients, the main disadvantages are high energy requirement for solvent regeneration, high heat of absorption, high corrosion, and operational difficulties etc. [5].

As a number of different gas sweetening processes are available along with several chemical and physical solvents that vary in chemical and physical properties. A preliminary process choice can be made with the consideration of,

- Feed gas composition.
- Sales gas limitations for $CO_2$ and $H_2S$.
- Maximum area available for gas sweetening process.
- Feed flowrate.
- Feed gas pressure.
- Feed gas temperature.

## Natural gas sweetening processes:

This work is mainly intended to study the membrane permeation process and chemical absorption process by alkanolamines, therefore the theoretical chapter is restricted to only these 2 processes and their combination i.e. hybrid process.

### Membrane permeation process:

Transport of solute to the permeate side of the membrane is described as follows,

### Membrane transport theory:

Membrane transport theory is mainly described by 2 models i.e.,

1) Pore flow model.
2) Solution diffusion model.

Pore flow model:

In pore flow model permeants are transported by pressure driven convective force through tiny pores [1]. Microporous membranes follow pore flow model for separation. Membrane transport by pore flow model is given by Darcy's law. And is mathematically represented as,

$$J_i = K'ci\frac{dp}{dx}$$

Where,

$J_i$ = flux

$\frac{dP}{dx}$ = Pressure gradient within a system.

$K'$ = Coefficient of proportionality for the nature of material.

$ci$ = concentration of component i.

Solution diffusion model:

In this model , solute dissolves in the membrane material and diffuses through the membrane down a concentration gradient, the feed components are separated because they have different solubilities in the membrane material and their rate of diffusion through the membrane are different[1]. Diffusion is the phenomenon through which molecules are transported from one place to another within a system. The individual molecules within a membrane are in a continuous random motion, it was first discovered by Fick that molecules in a system move from an area of high concentration to low concentration, this was later called  Fick's law. The equation of Fick's law is given as,

Fick's law of diffusion:

$$J_i = -Di\frac{dc_i}{dx}$$

Where,

$J_i$ = flux

$\frac{dc_i}{dx}$ = concentration gradient of component i,

$Di$ = Diffusion coefficient , "-" sign depicts that molecular movement is from high concentration to low concentration region.

The membranes having small pores follow solution diffusion model and membranes having relatively large and fixed pores follow Pore flow model. According to [1] membranes with nominal pore diameter of 1-10 angstrom follow solution diffusion model and dense polymer membranes normally used for gas separations fall within this range.

The diffusion in membranes can be described by the preposition that driving forces of pressure, temperature, concentration, and electrical potential are inter-related and the overall driving force producing movement of a permeant is the gradient in its chemical potential [1]. This approach is useful in a sense as normally a process can have more than 1 driving forces i.e., pressure, concentration. The relationship between chemical potential and flux of a component i  through a membrane is given by (1) and is described as follows,

$$J_i = -L\frac{d\mu_i}{dx} \tag{1}$$

Where,

$J_i$ = flux of component i.

$\frac{d\mu_i}{dx}$ = chemical potential gradient of component i.

$Li$ =  Coefficient of proportionality.

Restricting the chemical potential to concentration and pressure gradients, the chemical potential can be given as,

$$d\mu_i = RT\, d\, ln(\gamma ini) + v_i\, dp \tag{2}$$

where,

ni = mole fraction of component i.

$\gamma i$ = activity coefficient.

$P$ = Pressure.

$v_i$ = Molar volume of component i.

for compressible fluids, i.e., gases liquids, the molar volume changes with pressure, using ideal gas law.

## Membrane transport Modelling:

Assumptions.

- Materials on either side of the membrane are in equilibrium with the membrane material at the interface. Which means chemical potential gradient is continuous and the rate of absorption and desorption are faster than rates of diffusion in the membrane. [1]
- The applied pressure in the membrane is constant throughout the membrane area.
- The chemical potential is only expressed as concentration gradient.

The chemical potential gradient is a gradient in solvent activity $\gamma ini$, assuming $\gamma i$ is constant

$$J_i = -\frac{RTL_i}{n_i} \cdot \frac{dn_i}{dx} \tag{3}$$

In terms of concentration, equation (2) can be re-written as,

$$c_i = m_i \rho_{n_i} \tag{4}$$

Where,

Ci= concentration of component i.

Mi = molecular weight of component i.

$\rho$ = Density of component i.

Flux of component i can be written in terms of concentration as,

$$J_i = -\frac{RTL_i}{c_i} \cdot \frac{dc_i}{dx} \tag{4}$$

Replacing $\frac{RTL_i}{c_i}$ with D " diffusion coefficient, equation (5) becomes

$$J_i = -D \cdot \frac{dc_i}{dx} \tag{6}$$

Integration over thickness of membrane gives,

$$J_i = \frac{D_i\left(C_{i_0} - C_{i_l}\right)}{l} \tag{7}$$

$$u_{i_0} = u_{i_{0(m)}} \tag{8}$$

Equation (8) relates the chemical potential of solution and membrane at feed interface, membrane is a non-compressible fluid, however gas mixture is a compressible fluid, equation (8) can be re-written as,

$$+RT\ln\left(\gamma i_0^G \eta_{i_0}\right) + RT\ln\frac{P_0}{Pi_{sat}} = \mu_i^0 + RT\ln\left(\gamma_{io(m)} n_{i0(m)}\right) + v_i(\rho_0 - P_{isat}) \tag{9}$$

Where,

term $\mu_i^0 + RT\ln\left(\gamma i_0^G \eta_{i_0}\right) + RT\ln\frac{P_0}{Pi_{sat}}$ is the chemical potential of gas i “compressible fluid”

and $\mu_i^0 + RT\ln\left(\gamma_{io(m)} n_{i0(m)}\right) + v_i(\rho_0 - P_{isat})$ is the chemical potential of membrane “incompressible fluid.

$P_{isat}$ is taken as reference pressure, and is the saturation pressure of component i.

Equation (9) can be re-arranged as,

$$n_{io(m)} = \frac{\gamma_{i_0}^G}{\gamma_{i_0(m)}} \cdot \frac{P_o}{Pi_{sat}} \cdot n_{i_0}.\exp\left(\frac{-v_i(P_o - P_{isat})}{RT}\right) \tag{10}$$

As exponential term in equation (10) is close to 1, (10) can be re-written as,

$$n_{io(m)} = \frac{n_{i_0}\gamma_{i_0}^G}{\gamma_{i_0(m)}} \cdot \frac{P_o}{Pi_{sat}} \tag{11}$$

The term $P_o n_{i_0}$ is the partial pressure of component i in the feed gas $P_{i_0}$

$$n_{io(m)} = \frac{\gamma_{i_0}^G}{\gamma_{i_0(m)}} \cdot \frac{P_o}{Pi_{sat}} \tag{12}$$

Or

$$c_{io(m)} = m_i\rho_m \frac{\gamma_{i_0}^G}{\gamma_{i_0(m)}} \cdot \frac{Pi_o}{Pi_{sat}} \tag{13}$$

The sorption coefficient $Ki^G$ can be defined as,

$$Ki^G = m_i\rho_m \frac{\gamma_{i_0}^G}{\gamma_{i_0(m)}P_{isat}} \tag{14}$$

At feed interface equation (13) becomes,

$$c_{io(m)} = Ki^{G}.Pi_{o} \tag{15}$$

And at membrane permeate interface,

$$c_{il(m)} = Ki^{G}.Pi_{l} \tag{16}$$

Combining (15) and (16) in Fick’s law expression, flux of component i through a membrane can be given as,

$$J_{i} = \frac{Dik_{i}^{G}\left(p_{i_{0}} - p_{i_{l}}\right)}{l} \tag{17}$$

Where $Dik_{i}^{G}$= $P_{i}^{G}$ = permeability coefficient,

Equation (17) becomes,

$$J_{i} = \frac{P_{i}^{G}\left(p_{i_{0}} - p_{i_{l}}\right)}{l} \tag{18}$$

Equation (18) is used to accurately measure the properties of a gas permeation membrane.

Permeability coefficient can also be expressed in terms of,

$$Pi^{G} = \frac{\gamma_{I}^{G} D_{i} m_{i} \rho_{m}}{\gamma_{i_{m}} Pi_{sat}} \tag{19}$$

Mass flux can be converted to molar flux as,

$$\mathbf{j_{i}} = j_{i}\frac{v_{i}G}{m_{i}} \tag{20}$$

And mass permeability can be converted to molar permeability as,

$$Pi^{G} = \frac{p_{I}^{G} v_{I}^{G}}{m_{i}}$$

$$Pi^{G} = \frac{\gamma_{i}^{G} D_{i} v_{i}^{G} \rho_{m}}{\gamma_{i_{m}} Pi_{sat}} \tag{21}$$

Equation (21) shows that,

Permeability coefficient is directly proportional to diffusion coefficient and have High affinity for the membrane material.

## Important parameters in Process design:

Different parameters that influence the membrane separation process of a gas mixture are described as,

### *Permeability:*

is the ability of a component to diffuse through a membrane.

Units of permeability are given as,

Permeability =1 Barrer = $10^{-3}$cm$^{3}$(STP)/ cm$^{2}$.s.cmHg.

1 Barrer = 0.33*$10^{-15}$mol.m/m$^{2}$.s.Pa

Permeance = Diki/l = GPU= $10^{-6}$cm$^{3}$(STP)/ cm$^{2}$.s.cmHg

### *Selectivity*:

Selectivity is the ability of a material to pass through a membrane. It is the ratio of permeabilities of different components in a feed stream to pass through a membrane. As different components in a feed stream have different permeabilities. This difference in permeability can be exploited to separate the materials. The higher the ratio of permeability between two or more components, easier it becomes to separate the components. A higher selectivity is desired to separate the feed components. Expression for selectivity is given as follows,

$$a = \frac{p_i}{p_j}$$

### *Pressure ratio:*

It is the ratio of feed pressure to permeate pressure, and is described by the expression as follows,

$$\varphi = \frac{P_0}{P_i}$$

The separation through a membrane can only take place if partial pressure of component i in feed is greater than partial pressure of component i in permeate. Therefore,

$$n_{i_o} p_{i_o} > n_{i_l} p_l$$

Maximum separation that can take place is termed as,

$$\frac{n_{i_l}}{n_{i_0}} \le \frac{p_0}{p_l}$$

It also means that maximum separation that can be achieved can never exceed pressure ratio, even if the membrane selectivity is higher,

$$\frac{n_{i_l}}{n_{i_0}} \le \varphi$$

The relationship between pressure ratio and membrane selectivity is incorporated in Fick's law for components i and j and are given as,

$$j_i = \frac{p_i(p_{i0} - p_{il})}{l}$$

$$j_j = \frac{p_j(p_{j0} - p_{jl})}{l}$$

Total pressure on feed side is given as,

$$p_o = p_{i0} + p_{jo}$$

And permeate side is given as,

$$p_l = p_{il} + p_{jl}$$

The volume fractions of i and j in feed, in terms of partial pressure are given as,

$$n_{i_0} = \frac{p_{i_0}}{p_0}\ , \qquad n_{j_0} = \frac{p_{j_0}}{p_0}$$

And the volume fractions of i and j in permeate, in terms of partial pressure are given as,

$$n_{i_l} = \frac{p_{i_l}}{p_l}, n_{j_l} = \frac{p_{j_l}}{p_l}$$

The mass balance is given as,

$$\frac{j_i}{j_j} = \frac{n_{i_l}}{n_{j_l}} = \frac{n_{i_l}}{1 - n_{i_l}} = \frac{1 - n_{j_l}}{n_{j_l}}$$

$$n_{i_l} = \frac{\varphi}{2}(n_{i_0} + \frac{1}{\varphi} + \frac{1}{a - 1} - \sqrt{\left(n_{i_0} + \frac{1}{\varphi} + \frac{1}{\alpha - 1}\right)2 - \frac{4an_{i_0}}{(\alpha - 1)\varphi})} \qquad (22)$$

Equation (22) can be written differently for 2 limiting cases,

Case 1): when selectivity is much higher than the pressure ratio,

$$a \gg \varphi$$

Then equation (22) becomes,

$$n_{i_l} = n_{i_0}\varphi \qquad (6)$$

Which means the separation is controlled by the pressure ratio and a large selectivity is of no practical value.

Case 2): when pressure ratio is much higher than the membrane selectivity,

$$\alpha \ll \varphi$$

In such a case separation is controlled by membrane selectivity and is given as,

$$n_{i_l} = \frac{\alpha n_{i_0}}{1 - n_{i_0}(1 - \alpha)} \qquad (7)$$

Therefore, it is realized that very large pressure gradient or a very high value of selectivity is of no practical value, a process design should be based upon a balance between the pressure ratio and membrane selectivity.

### *Stage cut:*

A stage cut is the ratio between permeate flow and feed flow rate. As stage cut is increased to get more permeate flow, the fraction of the components from the retentate stream also increases in permeate stream resulting in lower purity of the permeate stream, same is true for the retentate stream. Therefore, larger separation “more recovery” means lower purity levels. A stage cut is expressed as follows,

$$\theta = \frac{permeate\ flow}{Feed\ flow}$$

### *Temperature:*

High to low pressure change , decreases the gas temperature that may cause condensation of heavier hydrocarbons on membrane surface and may cause fouling. This can be countered by achieving a predetermined dewpoint before the membrane and heating the gas in case necessary, before entering the membrane.

## Design of gas permeation process:

Membrane material used for $CO_2/CH_4$ separation is typically dense polymer of rubbery or glassy type. And structural configuration normally employed are flat membranes, spiral wound membranes or hollow fibre membranes. In $CO_2/CH_4$ separations either spiral wound or hollow fibre membranes are used. Spiral wound membranes bear more mechanical strength and are applicable for high pressure applications.

## Flow types:

Different flow types are used for membrane permeation for various separation purposes, the most used flow model for $CO_2/CH_4$ separations is the cross flow model.

In the cross-flow model, there is less likelihood of retentate accumulation on the membrane surface as retentate flows perpendicular to the membrane surface and is not completely mixed.

Symbols used in the equations:

$p'_A$ = Permeability of A in membrane.

$p'_B$ = Permeability of B in membrane.

$A_m$ = Area of membrane.

$t$ = Membrane thickness.

$q_f$ = Flowrate of A in feed.

$q_O$ = Flowrate of A in retentate.

$q_p$ = Flowrate of A in permeate.

$x_f$ = Mole fraction of A in feed.

$y_p$ = Mole fraction of A in permeate.

$x_o$ = Mole fraction of A in retentate.

$p_h$ = Pressure on the feed side and retentate i.e., high pressure.

$p_l$ = Pressure on the permeate side i.e., low pressure.

Cross flow model is described by [2] and Local permeation over a differential area of $dAm$ is given by

$$-y\,dq = \frac{p'_A}{t}[p_h x - p_l y]dAm \tag{25}$$

$$-(1-y)\,dq = \frac{p'_B}{t}[p_h(1-x) - p_l(1-y)]dAm \tag{26}$$

$$\frac{y}{1-y} = \frac{\alpha[x-(p_l\,/\,p_h)y]}{(1-x)-(p_l\,/\,p_h)(1-y)} \tag{27}$$

Due to the limitations of complete mixing model, and wide applicability of cross flow model for membrane permeation, this study has moved forward by selecting cross flow model for membrane permeation simulations.

## Chemical absorption:

As this research work is focused on the optimization of chemical absorption process i.e., amine treatment, therefore it will be discussed in detail as,

## Amine treatment:

Amines are organic compounds with ammonia $NH_3$ as base compound. by replacing one or more hydrogen atoms with an organic hydrocarbon group, different types of amines are formed.

The amine process for sour gas absorption is briefly described as, Aqueous solutions of amines chemically absorb the sour gases in an absorber column at low temperature and high pressure. the sweet natural gas leaves the absorber at the top and amine solution rich with sour gases is fed to a regenerator column at low pressure and high temperature. Where the chemical reactions are reversed, and sour gases leaves the amine solution and are collected from the top of regenerator column, while clean amine solution called as lean amine is circulated back to absorber column at low temperature. The most commonly used amines are of five types, based upon their chemical structure.

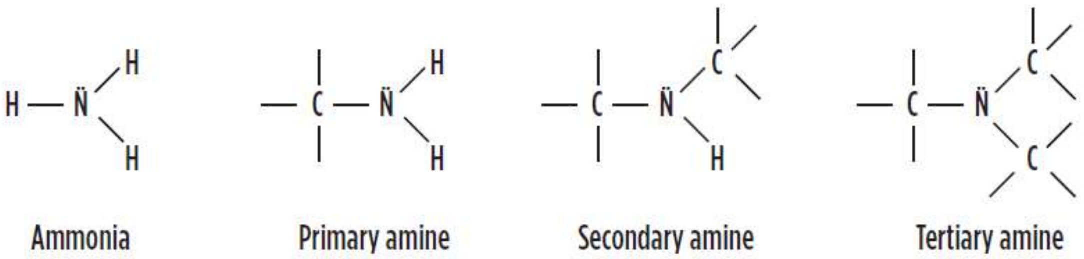

Figure 2 : chemical structure of different amines [6]

## Types of Amines:

1) Primary amines:

In this type of amine, one of the three hydrogen atoms in ammonia is substituted by an alkyl or aromatic [5]. The most commonly used primary amine is monoethanolamine or MEA. It is an organic compound with formula $HOCH_2CH_2NH_2$, it is a primary amine and also a primary alcohol. It is a colorless and viscous liquid and is produced by reacting ethylene oxide with aqueous ammonia. MEA is generally used as 10-20 wt% solution in water. MEA reacts with acidic compounds dissolved in natural gas and turn them into an ionic form, make them polar and more soluble in a cold amine solution.

Due to corrosion problem, the acid gas loading is limited to 0,3 to 0,35 moles acid gas per mole of amine. The heat of reaction of MEA with $CO_2$ is about $1,1919*10^6$ Joule/Kg. this high heat of reaction can cause very high reboiler duty or poor stripping if the concentration of $CO_2$ is very high in the feed gas [8]

2) Secondary amines:

Secondary amines have two organic substituents "alkyl, aryl or both" attached to the nitrogen with one hydrogen [5], example of a secondary amine is Diethanolamine or (DEA) which Is an organic compound with formula $HN(CH_2CH_2OH)_2$. It is a white solid at room temperature but has a tendency to absorb water, it produces a colorless, viscous liquid at room temperature. It has an advantage over MEA as it can absorb more acid gas as compared to MEA with same or less corrosion potential, therefore use less amine circulation and less energy consumption. It is normally used in 25 to 35 weight % range. The total acid gas loading for DEA is limited to 0,3 to 0,35 mole per mole of diethanolamine. The heat of reaction for DEA with $CO_2$ is $1,519*10^6$ joule/kg [8]

3) Tertiary Amines:

In tertiary amines the nitrogen has three organic substituents. Tertiary amines have different chemical reaction with sour gases as compared to primary or secondary amines. They donot react directly with sour gases. Therefore, water must be present for the reaction to proceed [5].

Most used tertiary amine for natural gas sweetening is Methyl-Diethanolamine or MDEAIs a tertiary amine. It Is a clear, colorless liquid. it is miscible with water and alcohol. It is commonly used in 20 to 50 wt % range aqueous solution. Acid gas loading is as high as 0,7 to 0,8 mole/mole MDEA. It has a lower vapor pressure and lower heat of reaction as compared to MEA and DEA. Its heat of reaction for $CO_2$ is $1,396*10^6$ Joule/kg $CO_2$. Due to this lower heat of reaction MDEA can be used for bulk $CO_2$ removal in pressure swing plants and no or very little heat is added for stripping [8].

MDEA amine has high acid gas loading as compared to MEA and DEA. It has high thermal stability, low vapor losses, low enthalpy of reaction. The absorption rate of $CO_2$ in tertiary amine is very slow as it doesnot directly reacts with $CO_2$ but promotes $CO_2$ hydrolysis to form carbonate. To increase the absorption rate, different kinds of activators are used that includes piperazine, as higher reaction rate of PZ and lower heat of reaction of MDEA with $CO_2$ may result in an overall faster reaction with lower heat requirement for regeneration [9].

| Amine | MEA | DGA | DEA | MDEA |
|---|---|---|---|---|
| Heat of reaction for $CO_2$ KJ/kg | 1922 | 1729 | 1520 | 1396 |
| Weight% aqueous solution | 10-20 | 50-60 | 25-35 | 40-50 |
| Acid gas loading mole/mole | 0,3-0,35 | 0,3-0,35 | 0,3-0,35 | 0,4-0,5 |
| Cost | Low cost | High cost | Low cost | High cost |
| Vapor pressure | High | High | low | low |
| Solvent loss | Highest loss | Low loss | Low loss | Low loss |
| reactivity | High | High | Low | lowest |
| Corrosion | highest | High | low | lowest |

Table 2: comparison of different amines, References [6,8,9]

Parameters for solvent selection.

| | |
|---|---|
| 1 | Good selectivity. |
| 2 | High absorption capacity. |
| 3 | Good chemical stability. |
| 4 | Good thermal stability. |
| 5 | Low rate of corrosion. |
| 6 | Low volatility. |
| 7 | Low cost. |
| 8 | Low heat of reaction. |
| 9 | Low viscosity. |
| 10 | Low tendency to form foams or emulsions. |
| 11 | Low energy consumption in regeneration. |

Table 3: Parameters for solvent selection for chemical absorption. [2]

Amine process economics:

| | Operating cost | Capital cost |
|---|---|---|
| Amine cost | Amine make up | Initial filling |
| Amine circulation cost | Pump duty, amine loss | Pump cost, solvent cost |
| Column diameters | | Higher costs for low circulation rate, and lesser concentration of amines. |
| Reboiler. | Reboiler duty | Lower duty results in higher capital cost of regenerator. |
| Lean amine cooler. | Cooler duty | High lean amine circulation rate means high capital cost. |

Table 4: economy of amine process.

## Chemistry of $CO_2$ with amines.

The transfer of $CO_2$ from the bulk gas to bulk liquid is governed by diffusion, dissolution and dissociation of species in the liquid phase and finally absorption of $CO_2$ by dissolved species. [10]

For primary and secondary amines, carbamate formation reaction Predominates and is much faster than CO2 hydrolysis reaction . These carbamates are stable and require high heat of desorption corresponding to high heat of regeneration [10].

The stoichiometry of carbamate reaction limits the capacity of primary and secondary amines to 0,5 mole CO2 per mole of amine.

DEA can achieve more loading through partial hydrolysis of carbamate (RNHCOO-) to bicarbonate (HCO-), which regenerates some free amine[10].

The sterically hindered amines form less stable carbamates due to large group attached to the nitrogen atom, however their loading capacity is low i.e. 0,5 mole $CO_2$ per mole of amine[10].

Tertiary amines cannot form carbamates with $CO_2$, it facilitates the $CO_2$ hydrolysis reaction forming bicarbonates as the final product and the $CO_2$ loading capacity is 1 mol $CO_2$ per mol of amine. [10]

## Reaction mechanism.

The reaction mechanism of $CO_2$ absorption in aqueous amine solution is normally described in three ways.

- Zwitterion.
- Termolecular.
- Base catalyzed hydration.

The reaction with primary and secondary amines in this study is described by Zwitterion mechanism and reaction mechanism for $CO_2$ with tertiary amine is described by the base-catalyzed hydration of $CO_2$ [10].

## Zwitterion mechanism:

For primary and secondary amines, the chemistry with $CO_2$ is described by [10] as,

Formation of carbamate

$$CO_2 + R_1R_2NH \leftrightarrow R_1R_2NCOO^- + H^+ \qquad (27)$$

Formation of protonated alkanoamine

$$R_1R_2NH + H^+ \leftrightarrow R_1R_2NH_2^+ \qquad (28)$$

The Overall 2nd order reaction becomes,

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \qquad (29)$$

Zwitterion mechanism:

Formation of zwitterion from the reaction of $CO_2$ with amine,

$$CO_2 + R_1R_2NH \leftrightarrow R_1R_2NH^+CO \quad (30)$$

In 2nd step Base B removes the proton

$$R_1R_2NH^+COO^- + B \leftrightarrow R_1R_2NCOO^- + BH^+ \quad (31)$$

By assuming steady state, the chemical reaction of $CO_2$ with amine is given as,

$$rCO_2 = k_1[CO_2][R_1R_2NH]/(1 + (k_{-1}/\Sigma k_B[B])) \quad (32)$$

Where $K_1$ and $k_{-1}$ are the forward and backward rate costants and $K_B[B]$ is the contribution to the zwitterion by all bases present in the solution. The zwitterion deprotonation depends upon free amines, water and hydroxide ion concentrations [10].

When alkanoamine is the only deprotonation base,

$$R_1R_2NH^+COO^- + R_1R_2NH \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \quad (33)$$

The overall reaction rate becomes the sum of reactions in equation 4 and 7 and is given as,

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NCOO^- + R_1R_2NH^+ \quad (34)$$

For sterically hindered amines , zwitterion reacts with water to form bicarbonate as,

$$R_1R_2NH^+COO^- + H_2O \leftrightarrow HCO_3^- + R_1R_2NH_2^+ \quad (35)$$

In this case, the bicarbonate formation reaction is the sum of reactions from equation 4 and 9 and is given as,

$$CO_2 + R_1R_2NH + H_2O \leftrightarrow HCO_3^- + R_1R_2NH_2^+ \quad (36)$$

Stability of the carbamates formed are reduced by the steric effects, therefore sterically hindered amines may undergo hydrolysis and form bicarbonates and release free amine molecules [H] as,

$$R_1R_2NCOO^- + H_2O \leftrightarrow HCO_3^- + R_1R_2NH \quad (37)$$

From equation 11 one mole of $CO_2$ is absorbed per mole of amine, the free amines again react with $CO_2$ to form more bicarbonate ions and the following reactions take place [10]

$$R_1R_2NH + H_2O \leftrightarrow OH^- + R_1R_2NH^+ \quad (38)$$

$$H_2O \leftrightarrow H^+ + OH^- \quad (39)$$

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \quad (40)$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \quad (42)$$

$$r_{overall} = k_1[CO_2][R_1R_2NH]/(1 + (k_{-1}/\Sigma k_B[B])) + (k_{H2O}[H_2O] + k_{OH-}[OH^-])[CO_2] \quad (43)$$

$$r_{overall} = k_{obs}[CO_2] \quad (44)$$

## Base catalyzed hydration mechanism:

Tertiary amines do not react with $CO_2$ , they have base catalyzed effects on hydration of $CO_2$ [10], represented as,

$$CO_2 + R_3N + H_2O \leftrightarrow R_3N^+H + HCO_3^- \quad (45)$$

Amine is dissociated in aqueous solution as,

$$R_3N + H_2O \leftrightarrow R_3N^+H + OH^- \quad (46)$$

The total rate of all $CO_2$ reactions in an aqueous solution can be represented by sum of reaction rates of eqs 5, 14 and 23 and is given as,

$$r_{overall} = (k_{H2O}[H_2O] + k_{OH-}[OH^-] + k[R_3N][CO_2] \quad (47)$$

$$k_{obs} = Kh_2o[H_2O] + K_{OH-}[OH^-] + k'[R_3N] \quad (48)$$

$$k_{ap} = k'[R_3N] \quad (49)$$

## Mass Transfer:

Absorption of $CO_2$ in amine solutions is a mass transfer with chemical reaction. Chemical reaction between $CO_2$ and amine solution speeds up the mass transfer rate for absorption. Reaction takes place in liquid phase and reduces the partial pressure of $CO_2$ over the solution. A pressure gradient is created that provides the driving force for mass transfer. [10]

Physical solubility of $CO_2$ in amine solution is expressed by Henry's constant "H". Henry's law states that solubility of a gas in liquid is directly proportional to the partial pressure of the gas over the liquid. [10]

$PCO_2 = HCO_2 * CCO_2$

Where $PCO_2$ is the partial pressure of $CO_2$ over the amine solution, $CCO_2$ is the solubility of $CO_2$ in amine solution. $HCO_2$ is the henry's law constant for $CO_2$, its value depends upon concentration of solute, solvent and temperature, its units are $m^3$.kPa/kmol. [10].

## Two Film theory:

Mass transfer in a liquid-gas chemical absorption reaction is widely described by two film theory.

It is supposed that gas phase consists of two parts, gas bulk and gas film at the boundary of the bulk. Same is supposed for liquid phase, which consists of liquid bulk and a liquid boundary film. These films are supposed to be stagnant, have a uniform thickness "δ", diffusion through the stagnant layer is assumed to be in steady state. The mass transfer equation is determined from the mass balance of the solute at the steady state. [10]

$$Dco_2 \frac{d^2CCO_2}{\partial x^2} = 0 \quad (50)$$

Where boundary conditions are,

$X = 0, C_{CO2} = C_{CO2,i}$

$X = \delta, C_{CO2} = C_{CO2,b}$

Applying boundary conditions,

$$C_{CO2} = C_{CO2,I} + ( C_{CO2,b} - C_{CO2,I} )x/\delta \quad (51)$$

The mass transfer flux becomes,

$$N_{CO2} = (D_{CO2}/\delta)^* ( C_{CO2,i} - C_{CO2,b} ) = k_L( C_{CO2,i} - C_{CO2,b} ) \quad (52)$$

Where $k_L$ is the mass transfer coefficient for the liquid side,

$$K_L = D_{CO2}/\delta \quad (53)$$

## Mass transfer with chemical reaction:

Mass transfer flux of $CO_2$ can be given as,

$$N_{CO2} = (P_{CO2,b} - P'_{CO2})/((1/k_g) + (H_{CO2}/E_A k_L) \quad (54)$$

$$\emptyset = t_D/t_R \quad (55)$$

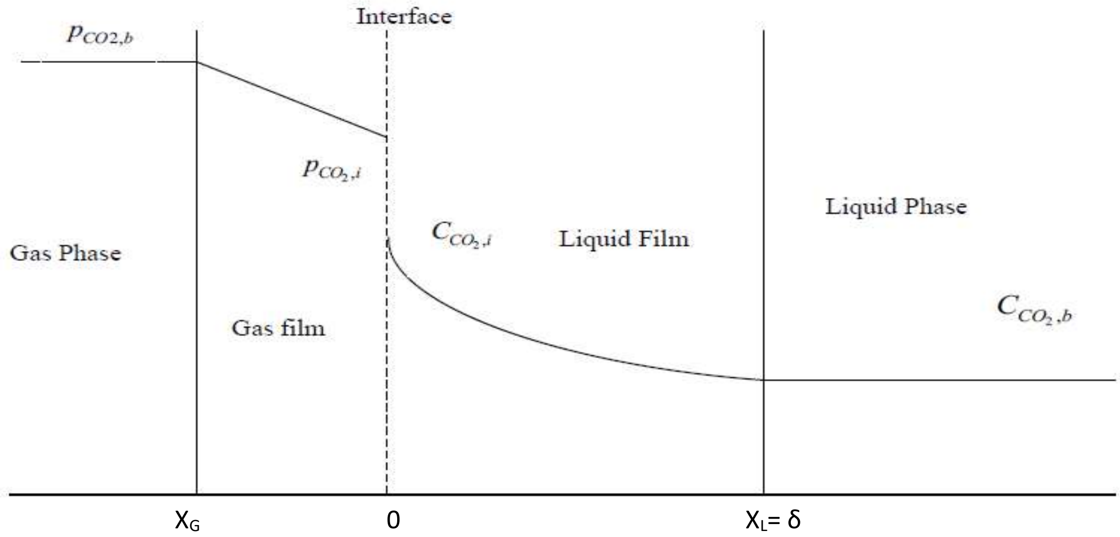

Figure 3: mass transfer mechanism by Two film theory [H]

## Thermal effects:

Heat is released by absorption and reaction of acid gases in the amine solution. The lean amine enters the top of absorber column at a temperature slightly higher than the feed gas i.e. 5°C , it is done to avoid higher hydrocarbon condensation. Therefore, the heat is transferred from the liquid solution to the gas even in the absence of chemical absorption process. As the reaction takes place in liquid phase, heat of reaction is generated in the liquid phase, it raises the liquid temperature, which results in more heat transfer from the liquid to the gas phase. The absorption and heat transfer process takes place towards the bottom of the absorber column. Gas is first heated by the liquid and then cooled by the liquid solution on its upward movement near the top of the column [12].

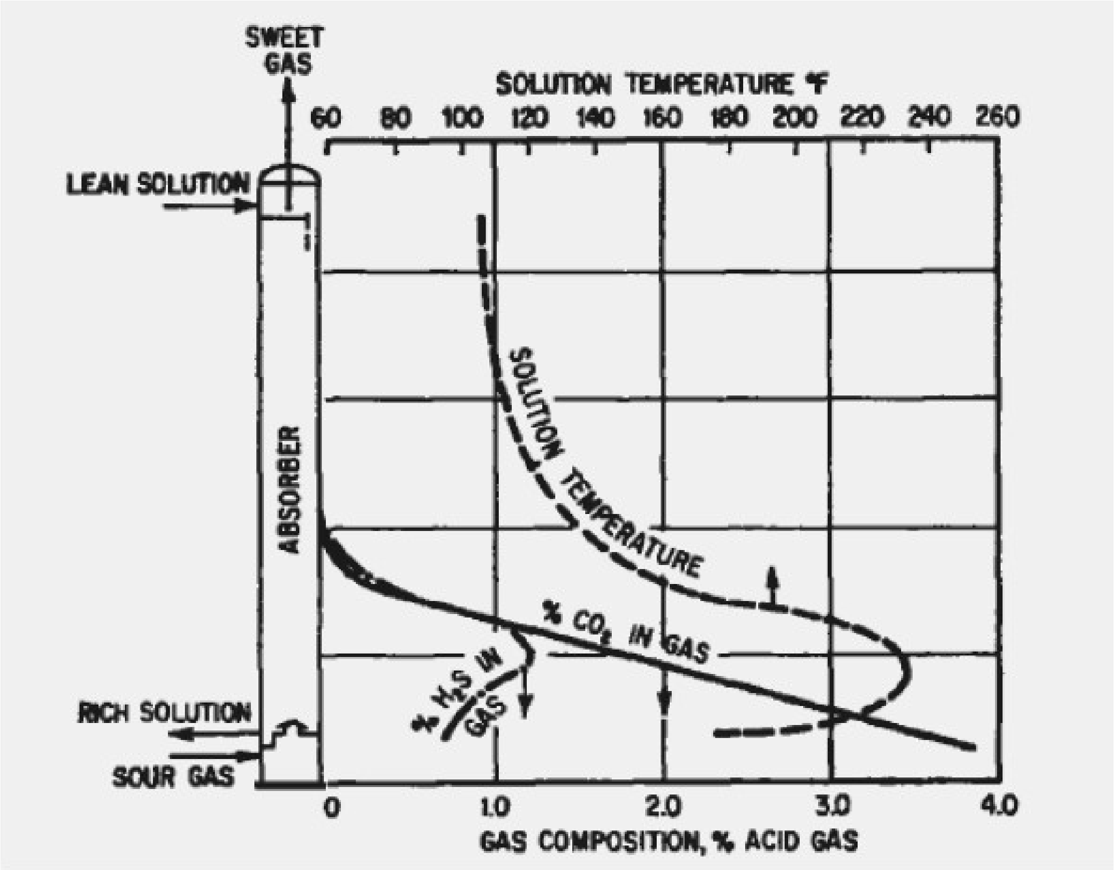

Figure 4: Temperature bulge in the absorption column [12]

The temperature bulge seen in figure 7 is a result of cool inlet gas absorbing heat from the amine solution near the bottom of the column and then losing this heat to the cooler solution as it move upward towards top of the column. The size, shape and location of the bulge depend upon the absorption location and the location where the chemical reactions take place.

For $CO_2$ absorption, the bulge is sharper and lower for primary amines, broader for secondary amines and very large for tertiary amines as their reactions are slow and heat of reaction is also low [12].

## Amine sweetening process and Equipment:

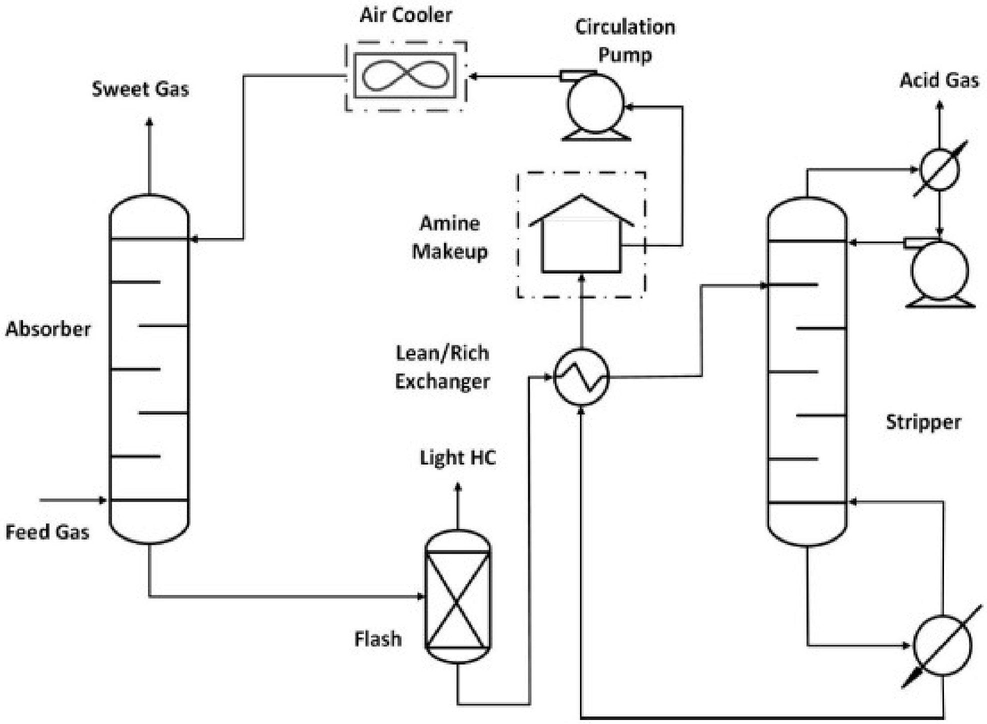

Figure 5: Typical amine sweetening process flowsheet [13]

The sweetening process for different kinds of amines and their blends is very much the same with a few exceptions.

The general process and process equipment is described below,

### Absorber column:

The feed gas enters the absorber column from the bottom and flows upward. The amine solution is introduced from the top and is called lean amine. The lean amine absorbs the sour gases when meets the upcoming feed gas [17]. The amine solution rich with sour gases leaves the absorber column from the bottom and is named as rich amine. The clean natural gas leaves at the top and is called sweet gas.

The most widely used absorber column for gas sweetening is tray type, although packed bed columns are also used. The rotating packed bed columns are also of interest for gas sweetening process as they provide more efficiency, and less diameter is needed for rotating packed bed columns as compared to packed bed columns [14].

The objective of the absorber column is to provide contact between lean amine solution with the feed gas, so that $CO_2$ and $H_2S$ can be transferred to the liquid phase effectively.

In a tray column a liquid level is maintained on each tray by a weir of about 2-to-3-inch height. The gas passes underneath the trays through opening in the trays. These openings are either perforations, bubble caps or valves [k]. The gas disperses into bubbles through the liquid and form a froth. The gas disengages from the froth and travel upwards. The amine solution falls back on the liquid. Almost all absorption takes place on the trays and not in the vapor between the trays [14].

The degree of separation achieved depends upon the number of trays or height of the packed bed column. 20 number of trays or equivalent height of the packed bed column is normally a standard design [14].

A mist eliminator pad is installed near the top of the absorption column to capture any traces of amine solution going up with the gas and also an outlet knock out drum is installed for the sweet gas to capture any entrained liquids [14].

The factors affecting the choice of design and type of absorber are final specification of the sweet gas to meet, volume of the gas to be processed, composition of natural gas, type and concentration of impurities present in the gas and the economy of the process.

### Three phase Flash tank:

A three-phase flash tank is installed after the absorber tank for rich amine solution. The rich amine solution may contain traces of hydrocarbon, both gas and liquid. the flash tank is at low pressure, the light hydrocarbons flash as the solution enters the tank. These are in gaseous phase and are separated from the top. The liquid hydrocarbons are of heavy density as compared to amine solution and they make a layer over the amine solution and are skimmed off at the top of the rich amine solution [14].

Flash tank is important as it separates the hydrocarbon contaminants from the amine solution. Their presence may result in foaming and alters the composition of lean amine in the absorber column over time. It may also result in equipment fouling.

### Lean-Rich Heat Exchanger:

The regenerator column that regenerates the lean amine operates at a higher temperature than absorber column. Therefore, the rich amine is preheated before it enters the regenerator.

The lean amine that enters the absorber column should be at low temperature.

It provides an opportunity to exchange the heat between rich and lean amine streams to save energy cost. Therefor a Rich-Lean heat exchanger is used for this purpose.

This heat exchanger is usually of shell and tube type with rich solvent passing through the tubes normally made of stainless steel [14].

### Regenerator column:

The regenerator column is also like an absorber column and is basically a distillation column. The normal number of trays used in regenerator column is 20 or the equivalent packing [14].

To minimize amine loss the regenerator column may be installed with trays for water wash at the top. The preheated rich amine enters towards the top of the column and flows downward countercurrent to a stream of sour gases and steam.

The steam is generated in the re-boiler, it lowers the partial pressure of sour gases and enhance the removal of sour gases from the rich amine solution. The overhead gas passes through a condenser to recover water and traces of vaporized amine.

The condenser, reboiler tubes and upper section of regenerator column are prone to corrosion; therefore it is recommended that these parts should be made of stainless steel. Thermal degradation of amines can be countered by using a low temperature heating medium for re-boiler [14].

In the amine regeneration system a concentration purity of lean amine greater than 99,1 % w/w can be obtained. If the rich amine solution absorbs higher hydrocarbons in absorber section, it can produce foaming in regeneration section [14].

### *Reboiler:*

Reboiler is at the bottom section of regenerator column, the purpose of reboiler is to produce steam therefore it needs a heating medium.

The heat duty of reboiler includes,

- Sensible heat needed to increase the temperature of rich amine, and the reflux.
- The heat of vaporization of water to produce a stripping vapor of steam.
- To heat up the makeup water to the temperature of reboiler as some steam is lost in the process.
- The heat of reaction to break the chemical bonds between sour gases and amine solution.

The reflux ratio between the moles of steam to moles of acid gas upstream of the condenser normally ranges from 5:1 to 4:1 [14] . If reboiler duty, condenser duty and reflux ratio are high, then lesser number of trays are required. Normally 20 number of trays are used. The temperature range of reboiler is normally from 240 to 260 F and the pressure ranges from 7-12 psig [6].

The reboiler duty increases with increase in lean amine circulation as more rich amine is fed to the stripper column.

### Filteration:

A filtration scheme is very important to have a good solution control. Mechanical filters remove particulate materials while carbon filters remove chemical contaminants. Mechanical filters are located before the carbon filters as they capture the particulate material which can otherwise damage the carbon filters [14].

Filters are located both in rich amine lines and lean amine lines and sometimes in both.

Filters in the rich amine line upstream of the heat exchanger protect both heat exchanger and the regenerator column from plugging, reduces the corrosion and reduces or eliminates foaming. However as rich amine solution is loaded with sour gases, the filters may result in pressure drop and block the flow [14].

In terms of workers safety to dismantle, change and clean filters, it is hazardous to locate filters in the rich amine line. For this safety reason many a times filters are in lean amine line. However, in any case the mechanical filters should be upstream of the carbon filters [14].

### Hybrid membrane permeation-amine process:

## Problem statement:

Different methods for natural gas purification are in service. All processes have their own advantages and disadvantages. Different methods are suitable for different operating conditions i.e. temperature , pressure, flowrate, sour gas content, location of the treatment plant and sales gas specifications. And there are continuous improvements in all technologies.

The area of interest for this project is to provide an economic solution for a high pressure i.e. 70 bar, high $CO_2$ content i.e. 20 percent, medium size gas feed stream i.e. 2000 kmol/hr, with low $H_2S$ content that fulfills the sales gas specifications i.e. 3 mole percent $CO_2$ content.

Chemical absorption by alkanolamines is by far the most used method for natural gas sweetening. However chemical absorption is considered not suitable for high pressure feed system because physical solvent systems are considered more suitable as the solubility of $CO_2$ increases in physical solvents with increase in pressure. however physical solvents have their own limitations. They are not considered suitable for feeds with high content of higher hydrocarbons and not suitable for $CO_2$ removal to pipeline specifications.

Membrane separation for gas sweetening is less energy intensive process as compared to chemical and physical solvents, membrane process has its own disadvantages i.e., loss of methane in $CO_2$ “permeate” stream, mechanical strength of the membrane skid for high pressure natural gas stream, limited permeation, and selectivity of commercial membrane material.

It is suggested in literature [5] to place a membrane permeation module upstream of amine treatment to use the advantage of membrane system for bulk removal of $CO_2$ and the advantage of amine process to reach the specifications of sales gas to increase the process economy.

This research work is carried out to economically optimize the natural gas sweetening process for an offshore separation platform, which means to minimize the overall cost, that include capital cost and operational cost of gas sweetening process with regards to pipeline specifications i.e., $CO_2$ and $H_2S$ specifications for sales gas.

Data from a typical North Sea offshore platform is used, Sour gases will be treated to meet the specifications of a North Sea separation platform.

Natural gas feed stream characteristics are given as under,

| | |
|---|---|
| Feed flow rate | 2000 kmol/hr |
| Temperature | 35 °C |
| Pressure | 70 bar |

Feed composition is given as,

| Component | Mole fraction |
|---|---|
| $CH_4$ | 0,74 |
| $C_2H_5$ | 0,03 |

| | |
|---|---|
| $C_3H_6$ | 0,02 |
| $CO_2$ | 0,20 |
| $H_2S$ | 0,005 |
| $H_2O$ | 0,01 |

Required specifications that need to be met for sour gases are given as under,

| **Components** | **Maximum allowable limit for sales gas** |
|---|---|
| $H_2S$ | 4 ppmv |
| $CO_2$ | 3 mole percent |

The target characteristics of the sweetening process are given as under,

- Required removal of sour gases is achieved.
- Most efficient gas sweetening process is identified.
- Overall cost of the sweetening process is optimized that include capital cost and operational cost for 10 years.
  That will include,
- Investigation of best amine solution in terms of efficiency and overall economy of the process from primary, secondary and tertiary amine solutions.
  Investigation of membrane process for required $CO_2$ removal and calculate its economy.
- This study will also investigate on hybrid "Membrane permeation-alkanoamine treatment process" for the stated feed conditions.
  The research work will be carried out in the form of computer simulations in Aspen HYSYS, which is a reliable and renowned computer simulator for sour gas treatment by alkanolamines. Computer simulations for this study, both amine simulations and membrane simulations will be validated from the literature available on the subject. Capital and operational costs will be calculated by Aspen process economizer, which is a built-in function in Aspen Hysys. The capital and operational costs that are not possible to calculate with Aspen Hysys i.e., amine cost, membrane skid cost etc. will be taken from available literature on the subject. Optimized solution will be the cheapest solution, provided it fulfills the gas sweetening requirements.

# Process modelling:

## Membrane process modelling:

### Membrane process design:

The design of membrane permeation process for product purity and recovery, besides other factors depend upon membrane configuration, various types of membrane configuration can be used, and are given as follows,

## Membrane configurations:

### *Single membrane*

A single membrane is the simplest form of membrane configuration, in this configuration, feed enters the membrane and retentate and permeate are separated by pressure drop and membrane selectivity towards retentate and permeate material. However, a higher purity is achieved at the cost of low recovery and a high recovery is achieved at the cost of low purity.

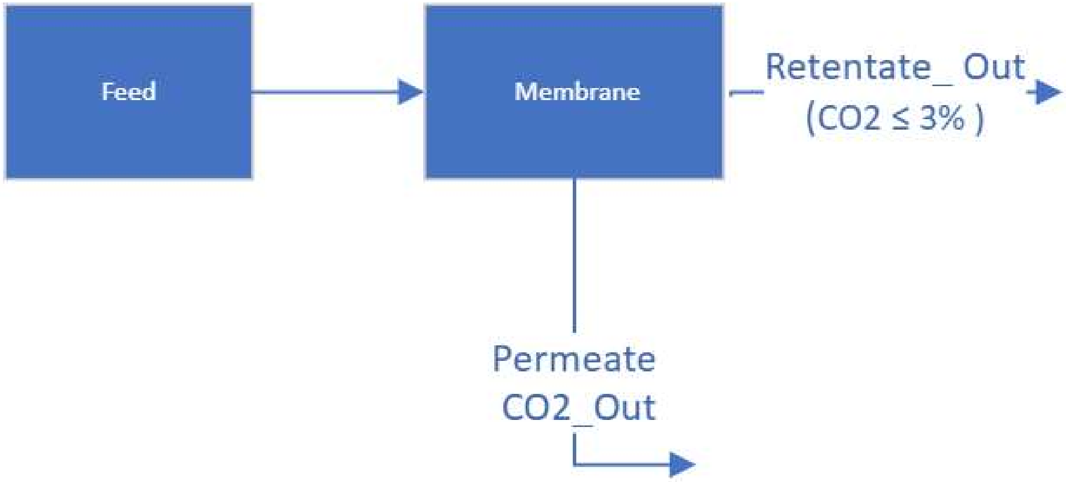

Figure 6: single stage membrane configuration

## Single membrane with recycle:

In order to compensate for the low purity of retentate and permeate streams, permeate stream is splitted and a part of permeate is compressed, cooled and sent back to the feed stream. This technique results in high purity of both retentate and permeate outputs.

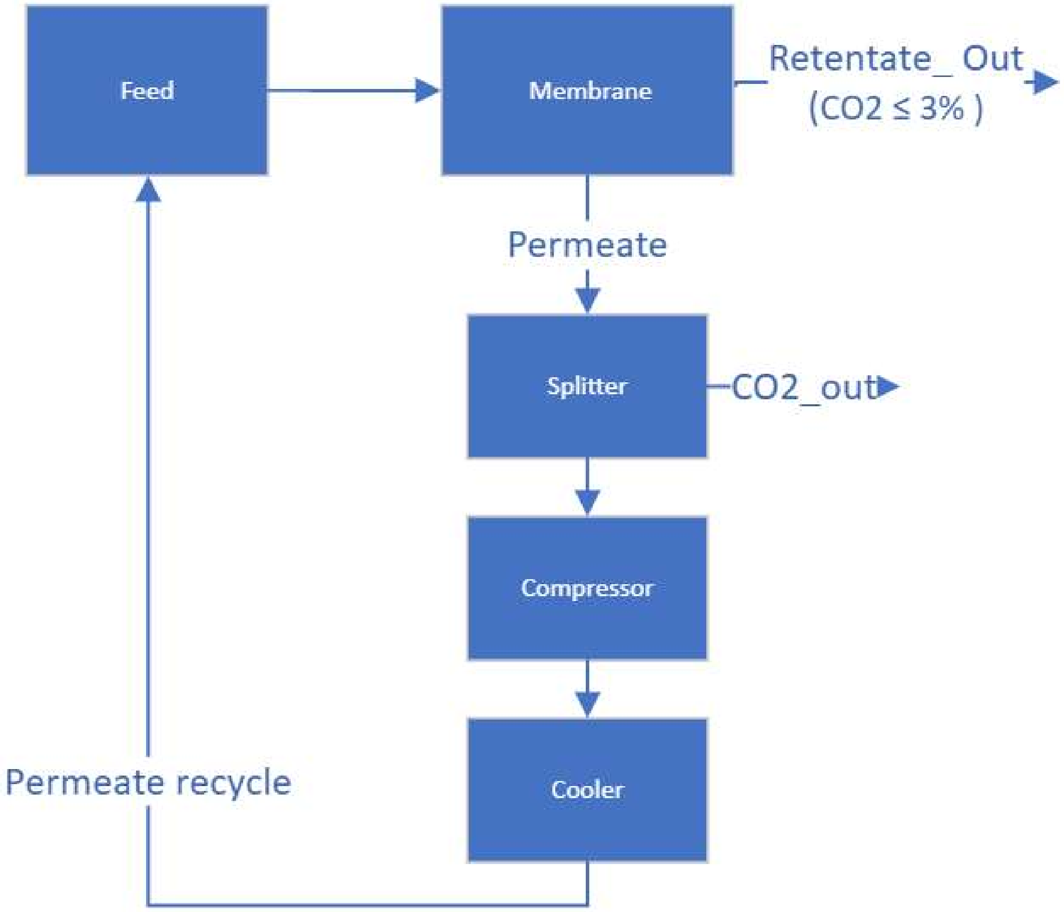

Figure 7: single stage membrane with recycle configuration

## 2 stage membrane:

In 2 stage membrane configurations, the product purity of retentate stream is achieved in first membrane, i.e. less than 3 mole percent $CO_2$ in $CH_4$ stream. The 1st low pressure, low purity permeate stream is sent to a compressor to attain desirable pressure and is cooled back to a suitable temperature and is feed to a smaller second membrane to capture more retentate material from the 1st permeate stream. 2 retentate streams make the product and 2nd permeate with relatively low retentate material is achieved.

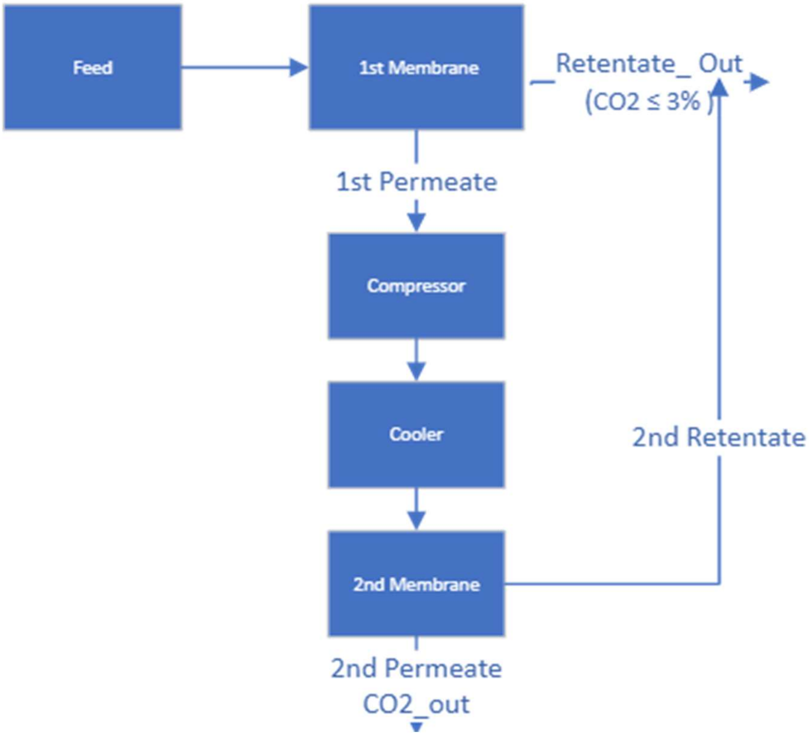

Figure8: 2-stage membrane configuration

### 2 stage membrane with recycle:

This scheme is similar to the 2 stage membrane, the only difference is, the 2nd retentate is sent back to the feed stream as it has the same pressure and temperature of the feed stream.

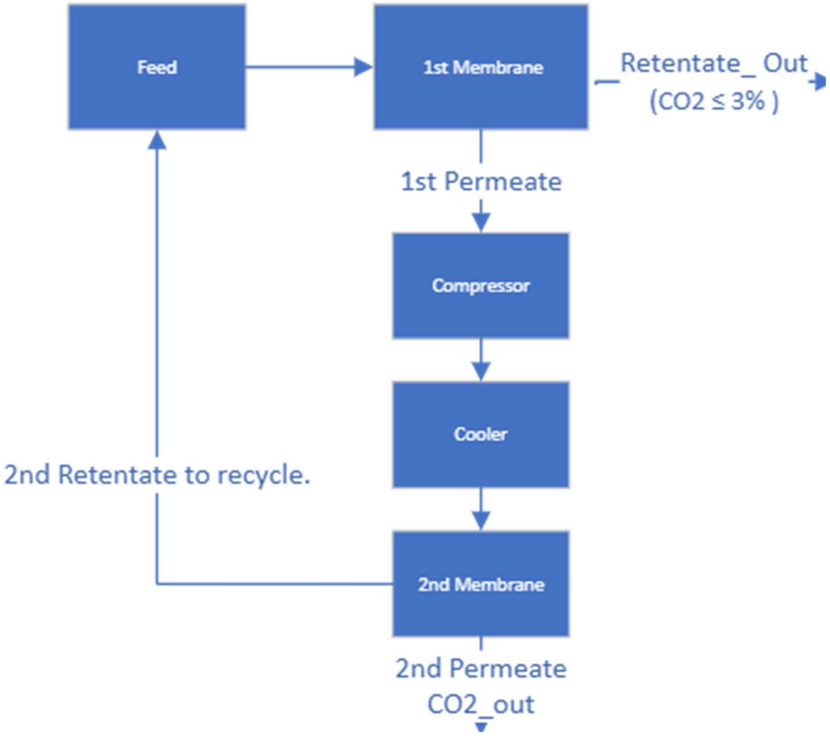

Figure 8: 2-stage membrane configuration

## Membrane properties:

The selection of membrane material, permeability and selectivity values should be carefully considered for membrane process design. There are many different membrane materials, and their permeability and selectivity values are available in literature.

Care is taken not to take the single gas permeability values as reported in literature, permeability values of a given component are different for a single component and for the same component in a mixture.

Selectivity values should also be taken for experiments conducted for a similar feed.

Material permeability values should be taken for same feed conditions, i.e. temperature, pressure as these values may hold for a specific temperature and pressure range.

The membrane permeability and selectivity values for this study are explored from literature and suitable values are taken from the most recent studies for the natural gas sweetening process by membranes at high temperatures i.e., 70 bar.

| Material | Permeability $CO_2$ | Permeability $CH_4$ | Units | Selectivity | Reference |
|---|---|---|---|---|---|
| Polymeric | 200 | 12,5 | GPU | 16 | (Ameen, Budd, & Gorgojo, 2020) |
| | 0,538 | 0,0336 | m3(STP)/m2.h.bar | | |

Cross flow model is available in aspen custom modeler, the key points used in the model and assumptions made are described below,

Assumptions:

- Cross flow unhindered permeate withdrawal.
- Permeate is removed from each cell and mixed to form total permeate.
- Retentate flow from one cell to the next.
- Isothermal conditions.
- Negligible pressure drop on feed and permeate sides. This is ensured by preferring cross flow model over complete mixing model as in complete mixing model retentate material may accumulate over membrane surface, causing hindrance for separation and choking the process, moreover a number of small membrane bundles constitute a membrane module, with a number of membrane cells, this practice ensure the negligible pressure drop on permeate and retentate sides.
- Permeabilities and selectivity of the components remains constant throughout the pressure range

## Membrane Model validation:

Cross flow model in aspen custom modeler is used in this study for simulation purposes. The results generated from the model are validated from an example case in [2]

**Cross flow model:**

Example 13.6-1 [2]

To Calculate $y_p$, $x_o$, $A_m$ , membrane permeabilites of both components, selectivity, feed composition, feed flow rate, retentate pressure, permeate pressure and stage cut are given. And permeate composition, retentate composition and area needed for membrane are to be calculated. The calculations are carried out in Aspen custom modeler and almost same results are obtained as by example case in the book.

Data:

Membrane thickness "t" = 2,54*10e-3 cm

Permeability of 'A' (P'A) = 500e-10 $cm^3$(STP).cm/(s.$cm^2$.cmHg)

Permeability of 'B' (P'B) = 50e-10 $cm^3$(STP).cm/(s.$cm^2$.cmHg)

Selectivity ' = 10

Feed rate '$q_f$' = 1*10e6 $cm^3$(STP)/s

Feed composition of 'A' = 0,209

Stage cut 'ø' = 0,20

$P_h$ = 190 cm Hg

$P_l$ = 19 cm Hg

Results by [2]

| | |
|---|---|
| "Yp" permeate composition of 'A' | 0,5690 |
| "$X_r$" Reject composition of 'A' | 0,1190 |
| Area needed for separation '$A_m$' | 2,893*10e8 $cm^2$ |

**Results by Aspen Custom Modeller :**

| | |
|---|---|
| "Yp" permeate composition of 'A' | 0,57 |
| "$X_r$" Reject composition of 'A' | Not applicable |
| Area needed for separation '$A_m$' | 2,9*10e8 $cm^2$ |

The results provided by the aspen custom modeler are almost the same, as produced by (2)

## Membrane Feed properties:

It has been cited in literature that permeability of ethane, higher hydrocarbons and water is less than methane and permeabilities of $CO_2$ and $H_SS$ are almost same, therefore for ease of calculations, methane and hydrocarbons are combined as $CH_4$. And feed mole fractions are rounded to decimals.

The actual feed dew point is calculated in Aspen Hysys and it is found that it is above the feed temperature, and therefore feed is not preheated to increase its temperature.

| | | |
|---|---|---|
| Feed composition. "Mol Fraction" | 0,2 $CO_2$ | 0,79 $CH_4$ |
| Feed flow rate. "kmol/hr" | 2000 | |
| Feed pressure. "bar" | 70 | |
| Feed temperature. "°C" | 35 | |

## Membrane properties:

| | | |
|---|---|---|
| Membrane material. | Polymeric "cellulose acetate" | |
| Membrane flow. | Cross flow. | |
| Membrane structure. | Spiral wound. | |
| Membrane thickness. " $\mu$m" | 0,5 | |
| Membrane permeance. | $CO_2$ | $CH_4$ |
| GPU | 200 | 12,5 |
| $m^3$(STP)/($m^2$.h.bar) | 0,54 | 0,0336 |
| Membrane selectivity. | 16 | |

Table 5: membrane properties

## Process Economy:

The model for process cost is derived from (Bhide, Voskericyan, & Stern, 1998) however the costs for different elements of the process are taken from recent studies, capital costs of compressor and cooler and the utility costs are taken from Aspen Hysys economic analyzer.

As natural gas is rapidly becoming a global commodity, therefore the Methane price is taken from Nymex monthly contract for June 2023 which is 3 USD/ MMBTU.

| | | |
|---|---|---|
| Total capital investment (TCI) | Membrane module cost "element + skid" | 100 $/m2 |
| | Membrane element cost | 20 $/m2 |
| | Installed Compressor cost | By Aspen Hysys |
| | Installed Cooler cost | By Aspen Hysys |
| | TCI = Membrane Module cost + installed Compressor cost + installed Cooler cost. | |
| Total Operating Costs (TOC) | Capital recovery cost (CRC) | 0,25*(TCI) |

| | | |
|---|---|---|
| | Methane price | 3 $/MMBTU |
| | Methane losses “ML” | $/MMBTU |
| | Membrane element replacement cost “MRC” | 10% replacement every year. “20 $ per $m^2$ |
| | Energy cost “compressor + cooler” | By Aspen Hysys. |
| | Labor cost “LC” | 25*2= 50 $/h |
| | Maintenance cost “MC” | 0,05* TCI |
| | Operating expenses “OE” | MRC + EC + LC + MC |
| | Total operating cost “TOC” | = CRC + ML + OE |

Permeability of $CO_2$ and $H_2S$ is considered the same for simulation purposes, it is found in literature that permeability of $H_2S$ is greater than $CO_2$

Selectivity $C_2H_6/CH_4$ = 0,423

Plant life : 10 years

Thermal efficiency of compressor: 75%

Total labor : 2*Direct labor

## Alkano-amine modelling :

## Amine process modelling

Amine process modelling is carried out in Aspen HYSYS version 9.

Component list: As the main purpose of this study is to focus on $CO_2$ removal from a high $CO_2$ content natural gas stream with low $H_2S$ content and low higher hydrocarbon content. Therefore, the component list is simplified to,

| Components | Mole fraction |
|---|---|
| $CH_4$ | 0,79 |
| $CO_2$ | 0,20 |
| $H_2O$ | 0,01 |

However, the dew point of the feed stream with actual component list is calculated and as the feed stream is above its dew point, therefore the temperature of feed stream is not raised.

**Fluid package:**

The Acid Gas- chemical solvents fluid package in Aspen HYSYS is selected as the property package. This property package provides thermodynamics based upon Electrolyte-non-random two liquid

"NRTL" model with all the necessary aqueous phase equilibrium and kinetic reactions required for rigorous calculations of the process and Peng-Robinson equation of state for vapor phase properties (Dyment & Watanasiri, 2015)

Two main approaches are present in the software for the process i.e., rate based model and equilibrium stage model. Rate based model utilize heat and mass transfer correlations based on transfer properties and tray/packing geometry, assuming that separation is caused by mass transfer between the contacting phases (Dyment & Watanasiri, 2015). Therefore rate based models are more accurate compared to the efficiency model. On the other hand equilibrium stage models require empirical adjustments for accurate simulation (Dyment & Watanasiri, 2015). Rate based models can be used for reliable modelling without having information about tray efficiencies and provide reliable simulation results.

In this project rate-based modelling is used for absorber simulation.

A total of 4 cases of single amines and mixed amines are studied:

Single amine cases:

MEA, DEA, MDEA, DGA

Mixed amine cases:

Mixed amine cases will be simulated if the required specification of $CO_2$ in the product gas stream is not reached.

MDEA+MEA, MDEA + DEA, MDEA +PZ.

**Amine solution strengths:**

| Amine | Weight percent aqueous solution |
|---|---|
| MEA | 18 |
| DEA | 28 |
| DGA | 50 |
| MDEA | 50 |

Table 6: Recommended amine solution strengths.

Different components of the process scheme are modelled as,

**Feed stream:**

Feed stream enters the absorber column at the bottom at the feed conditions i.e. 35°c, 70 bar and 2000 kmol/hr.

**Lean amine stream:**

Lean amine stream enters the absorber column from the top at 40°c, and 69 bar pressure.

**Absorber column:**

The feed conditions i.e., temperature, pressure and flow rate are kept the same.

There are several techniques used for specification of absorber stages.

In this project the initial guess is made by McCabe-Thiele graphical method. The VLE data for different amines is available in literature and is used for this purpose. However as the equilibrium is not reached for $CO_2$ treatment by alkanoamines in absorption column. Therefore, stage efficiency is used to compensate for it. The stage efficiency for this absorption process is between 10 to 20 percent [3]. It is suggested in literature to keep the same number of stages for different amine treatment scenarios in various studies. 20 absorber stages are suggested by [2,3,4]. However, it is also seen that absorber column in aspen Hysys fails to converge at times for 20 number of absorber stages.

The VLE data for the MCcabe thiele method is available in (Kohl & Nielsen, 1997). The operating line and equilibrium lines are constructed, both lines are not straight for all the amine cases and provides a rough estimation of 2 to 3 stages. As the amine process efficiency is reported from 10 to 20 percent in literature. Therefore the first guess for absorber stages is made to have 15-20 absorber stages.

Therefore, a strategy is used to start with 20 number of stages and decrease the number of stages upto the stage where absorber column is converged, the number of stages are further decreased as long as the $CO_2$ content remains inside the product specification for outlet natural gas product stream.

**Flash separator:**

The rich amine stream leaving the absorber column from the bottom is sent to a flash separator to separate any hydrocarbons trapped in the rich amine stream. Flash separator operates at low pressures for different amines i.e. 6-3 bars to separator the condensed hydrocarbon from the rich amine solution.

**Lean-Rich Heat exchanger:**

The heat is exchanged from the hot lean amine stream leaving the regenerator column to the rich amine stream as rich amine stream must enter the regenerator column at a higher temperature i.e. 100°c because regeneration process is carried out at a higher temperature i.e. 100-120 °c

**Regenerator column:**

Regenerator column is designed as a distillation column block with a reboiler and condenser, the number of stages for regenerator column are calculated by McCabe-Thiele method. It is suggest in literature to use 20 number of trays for regenerator column [2,3,4]. Regenerator have almost same number of stages as absorber column, therefore the initial guess is made number of absorber stages and McCabe-Thiele method. The column is converged by specifying the reboiler duty and condenser temperature. The reboiler duty is increased if the column is not converged which means increasing the steam flow rate for the reboiler. The regenerator column is run at near atmospheric pressure i.e. reboiler pressure 2,2 bar and condenser pressure 2 bar. The temperature of reboiler is around 120°c and condenser temperature is around 40°c.

**Lean amine cooler:**

lean amine leaves the regenerator from the bottom at a high temperature i.e. 120 °c. its temperature is lowered when it comes in contact with lean-rich heat exchanger. Lean amine leaves the heat exchanger around 60°c. but its temperature must be further lowered to 40°c . which is the temperature of lean amine entering the absorber column. Therefore, a lean amine cooler is needed to cool down the lean amine. An air cooler is used for this purpose in the simulation.

**Lean amine pump:**

As the lean amine is at near atmospheric pressure i.e. 2 bar and the pressure of absorber column is 70 bar. Therefore a pump is used to bring the lean amine back to absorber pressure.

**Amine makeup block:**

A makeup block is available in Aspen Hysys to account for the amine and water losses throughout the process. The make-up block has a spreadsheet built into it, which automatically calculates the necessary makeup flow rate. the user only needs to specify the inlet and outlet streams for the makeup block. The makeup block is used in this project for lean amine solution circulation.

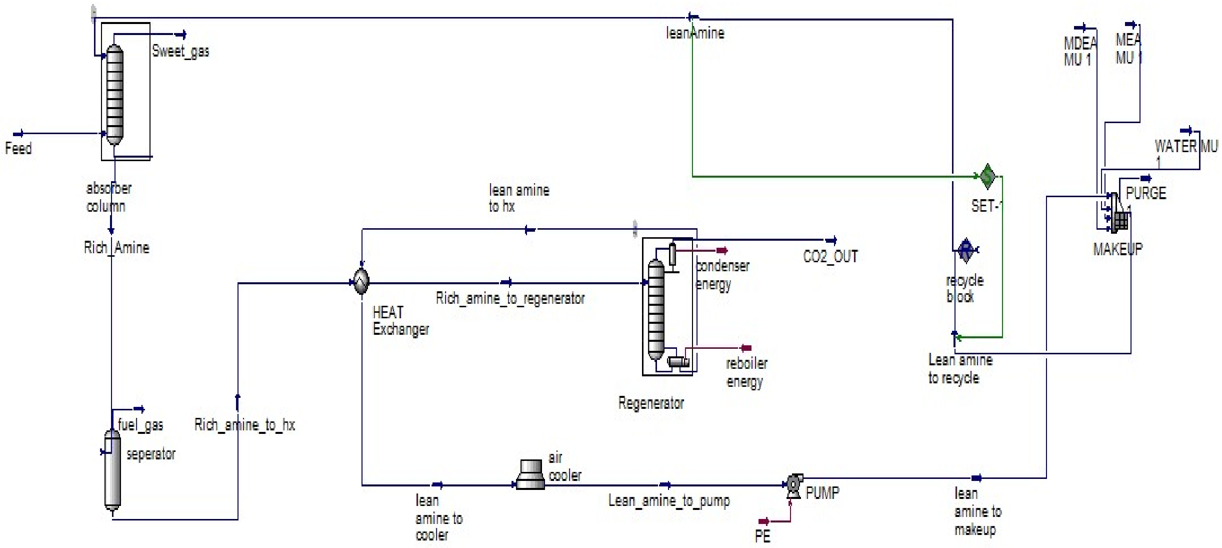

Figure 7: Amine process flowsheet built for the project

### Amine Process economy:

The process economy includes capital cost of the equipment and operational costs of the process.

**Capital costs:**

Include installed costs of feed separator, absorption column, rich amine pump, lean-Rich heat exchanger, regenerator column along with reboiler and condenser, rich amine pump and rich amine cooler. All these costs are calculated by Aspen process economizer.

**Operational costs:**

Include amine cost, rich amine pump duty, reboiler duty, lean amine cooler duty.

Amine cost is estimated from different sources and rich amine pump duty, reboiler duty and lean amine cooler duty is calculated by Aspen Hysys process economizer.

Operational costs also include capital recovery cost which is taken as 25 percent of the capital cost annually. Maintenance cost as 0,05 of the capital cost, and labore cost as 2 full time operators. With plant functioning for 360 days per annum.

Capital recovery cost, maintenance cost and labor cost are considered the same for both membrane permeation and amine process.

The overall cost is calculated as capital cost* operational cost of 10 years operation.

## Results and discussion:

Results and discussion for the both processes are described as follows,

## Membrane section results:

Single stage membrane has lesser area requirements but greater methane loss to reach the target value of 3 mole percent $CO_2$ in retentate. Single stage membrane with recycle can reach the target with higher membrane area but with lower methane loss. A 2-stage membrane system has comparatively lower area requirement , methane loss is less but at the expense of compressor and cooler capital cost and energy. 2 stage with recycle configuration has highest area requirement but lowest methane loss.

Membrane modules are built with a target of 3 percent $CO_2$ in retentate stream, following results are reached.

### *Total cost of investment:*

| Type | M Area | skid cost | compressor cost | cooler cost | TCI “USD” |
|---|---|---|---|---|---|
| Single stage | 2460 | 246000 | 0 | 0 | 246000 |
| SINGLE stage hybrid | 924 | 92400 | | | 92400 |
| Single stage with recycle. | 4700 | 470000 | 12086600 | 417700 | 12974300 |
| 2-Stage | 3250 | 325000 | 3680500 | 255300 | 4260800 |
| 2-Stage with recycle | 3650 | 365000 | 7000100 | 272600 | 7637700 |

Table 7: total cost of investment for amines.

Total cost of investment for all 4 configurations is compared with 1-stage scheme as the cheapest for feed gas purification as it does not require compressor and a cooler.

The single stage configuration for hybrid process has the minimum cost, as it is configured to remove only 70-75% $CO_2$ from retentate stream.

*Total operating cost (TOC):*

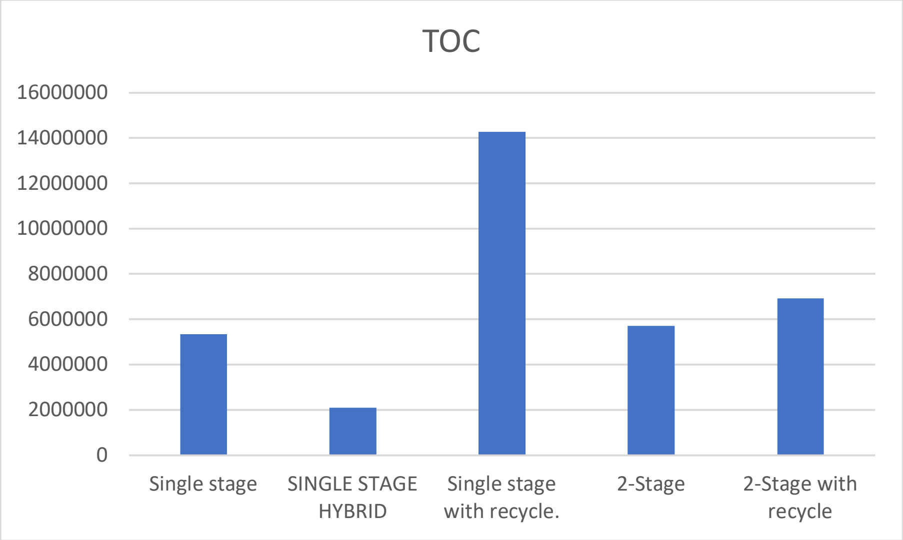

Table 8: Total operating cost for membrane configurations.

Total operating cost is highest for the single stage with recyle because of higher methane losses, a larger area requirement and because of compressor and cooler energy requirements. The total operating costs for 2stage configurations is almost the same.

*Total Cost:*

Total cost = Total capital investment + (Total operating cost*10)

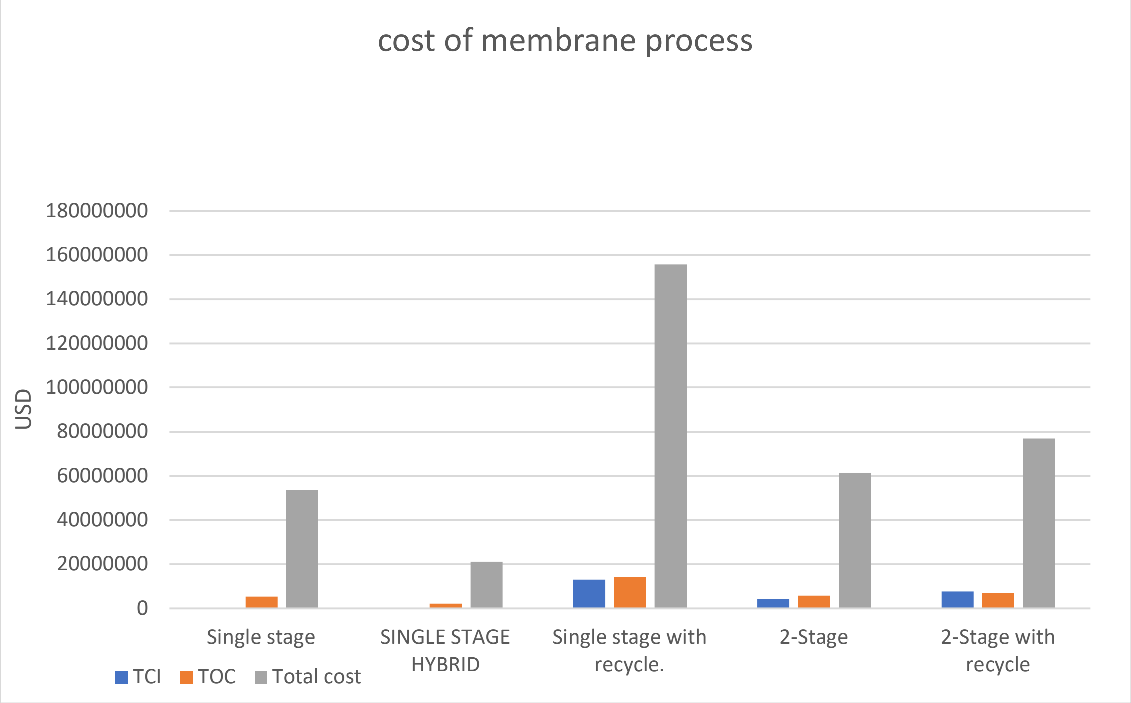

Table 9: Total cost for membrane process.

Total cost is a combination of capital investment and the operating costs for 10 years. It has been found that single stage with recycle is the most costly and 2-stage scheme is the cheapest. This is represented in chart below.

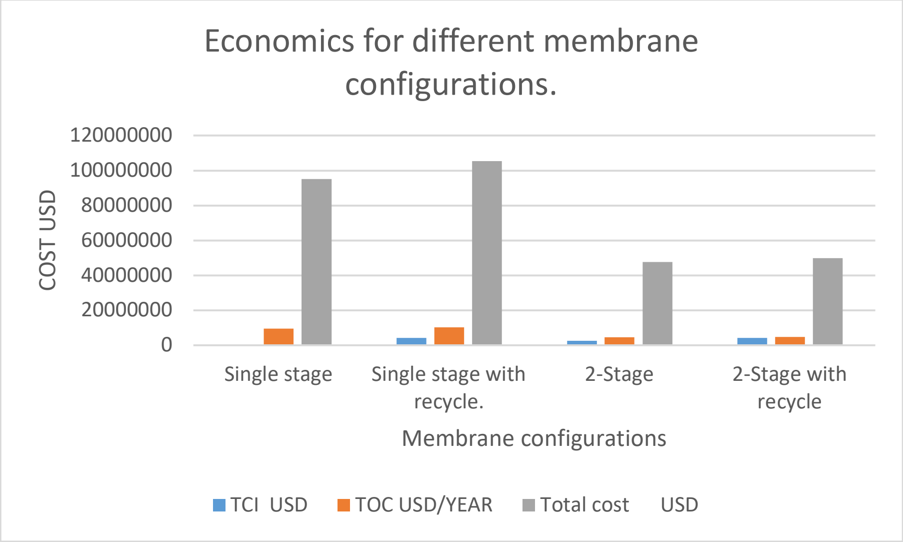

Table 10: Economy of membrane Processes.

## Amine section results:

The product specification for $CO_2$ for all 4 amine cases was achieved.

The results are described below,

| Amines | CO2 Loading | Wt percent solution | Mol Percent solution | Reboiler energy kj/hr | Lean amine loading | Absorber stages | Regenerator stages | Amine circulation. m3/hr | Solution Circulation m3/hr |
|---|---|---|---|---|---|---|---|---|---|
| MEA | 0,42 | 0,18 | 0,06 | 1,26*e8 | 1,74*e-002 | 13 | 20 | 60 | 339 |
| DEA | 0,45 | 0,28 | 0,063 | 4,36*e7 | 0 | 15 | 15 | 76,14 | 291 |
| DGA | 0,4 | 0,49 | 0,14 | 9*e7 | 2*e-002 | 13 | 21 | 90,84 | 191 |
| MDEA | 0,55 | 0,5 | 0,13 | 2,75*e | 2*e- | 16 | 20 | 76,73 | 156 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 7 | 002 | | | | |
| MDEA Hybrid | 0,43 | 0,46 | 0,13 | 1,36*E 7 | 2*e-002 | 16 | 20 | 36,8 | 75 |

## Solution circulation rate:

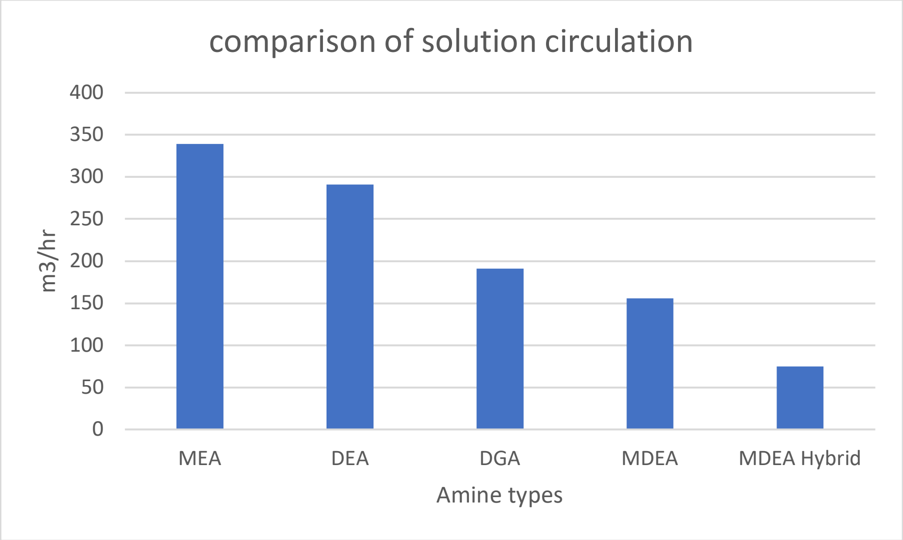

Table 11: amine solution circulation rate.

It can be seen from table that amine solution circulation rates are highest for MEA and lowest for MDEA. The solution circulation rate for MDEA hybrid configuration are much lower, however this configuration is used only to remove about 30% of $CO_2$ content present in the actual feed. The solution circulation rates are a direct consequence of higher water content in MEA solution and lowest in MDEA solution. The solution circulation rates have direct impact on process economy, as more circulation requires higher steam rate in reboiler, high lean amine pump load, and high cooler load to cool the lean amine before it can be used in absorber.

## Regeneration energy:

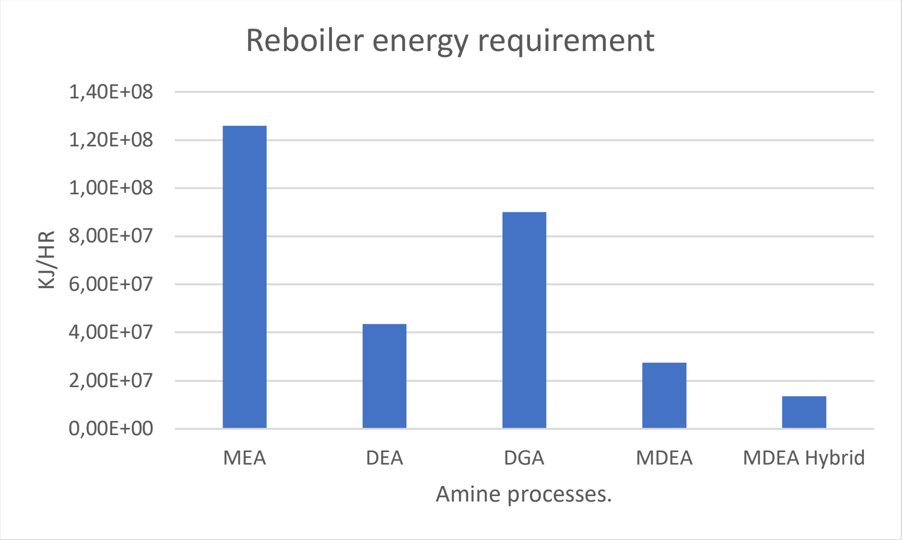

Table 11: Regeneration energy requirement.

The regeneration energy used in reboiler is highest for primary amines i.e. MEA and DGA, and lowest for MDEA. The steam used in the reboiler also has a major impact on overall plant economy. Reboiler energy requirement for MDEA hybrid process is considerably less.

## $CO_2$ Loading:

It is also seen that MDEA has the best performance in terms of Acid gas loading capacity, which is found to be 0,55 mol $CO_2$ per mole MDEA, which is found to be lowest for MEA as 0,42 mol $CO_2$ per mole MEA.

Therefore, MDEA has performed best in terms of amine solution circulation rate, reboiler duty and $CO_2$ loading. And is found to be most efficient Amine for this project.

## Hybrid section results:

A 20 percent sour gas feed is selected for hybrid process. With first 10 percent to be removed by membrane process and the final 7 percent to be removed by amine process to reach the specification of 97% pure methane. Single stage membrane configuration is used for this purpose along with the most efficient Amine i.e. MDEA.

## Amine Process Economy:

Capital cost:

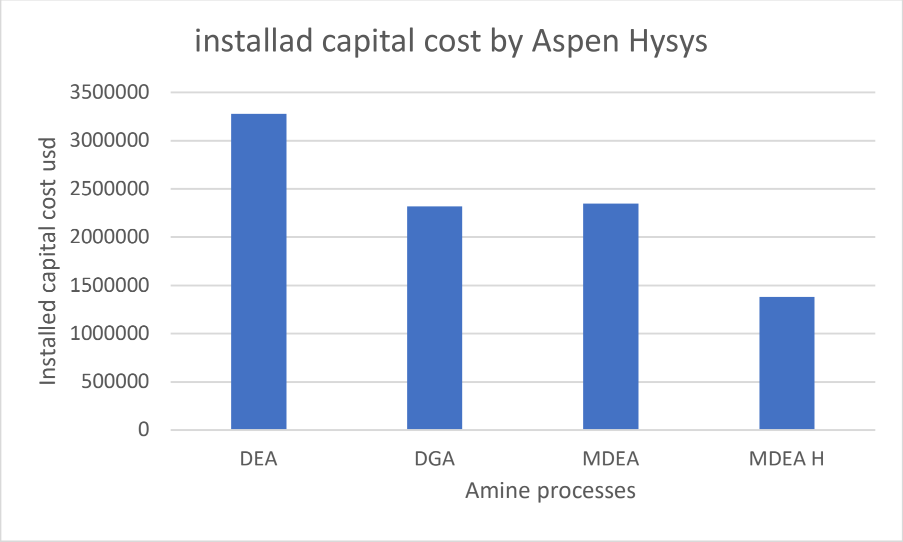

Table 13: amine process installation cost.

The capital costs for all the amine processes were calculated by Aspen Hysys process economizer, the capital cost for MEA is found to about 4 times the cost of 2nd highest cost i.e. DEA and is excluded from further analysis. The installed capital costs for DEA is comparatively large as compared to DGA and MDEA which are almost the same. The higher capital cost of DEA is due to larger heights and diameters of absorber column, regenerator, larger heat exchanger surface for lean-amine heat exchanger and cooler because of higher amine circulation rates.

## Operational cost :

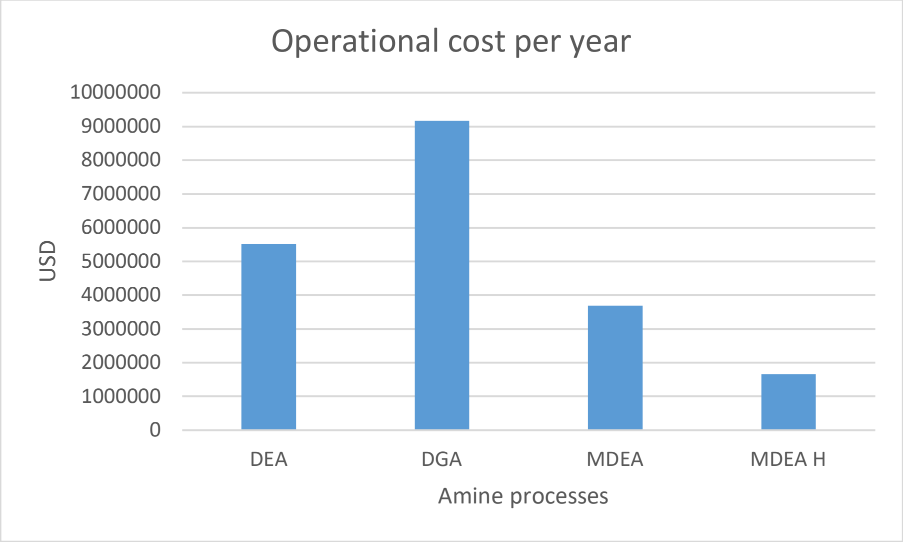

Table 14: Amine process operational cost.

The operational cost of DGA is much higher as compared to DEA and MDEA mainly because of much higher reboiler energy requirement. MDEA requires the lowest reboiler duty, therefore its cost is much lower as compared to other amines.

## Total cost:

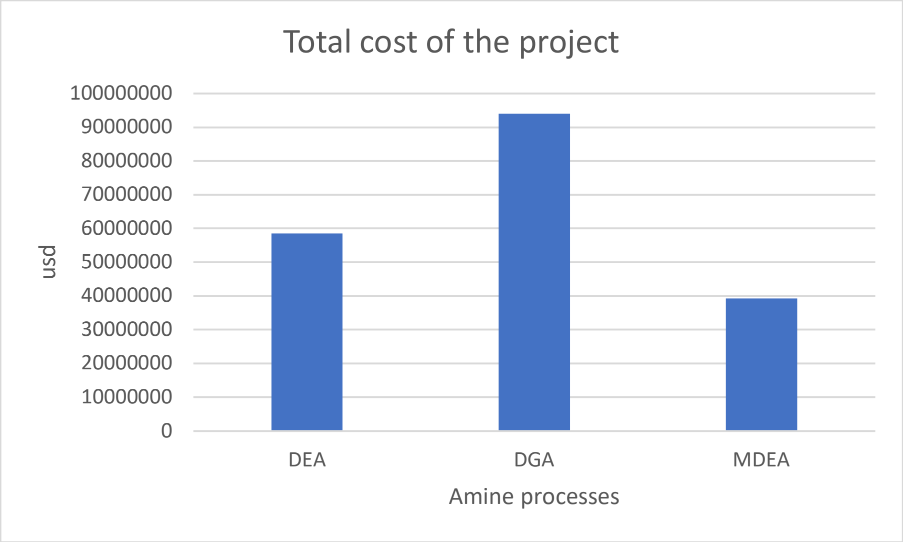

Table 15: Amine process total cost.

MDEA has proven to be the most efficient and most economic amine for $CO_2$ removal to product gas specifications. It has resulted because the case studied is at high pressure. and MDEA is more efficient at high pressure systems. MDEA system has reached the product specifications without addition of other amines into the mixture i.e. MEA, DEA, PZ and also without increasing its concentration or water flowrate.

For the regenerator column $CO_2$ was desorbed from MDEA without further addition of reboiler steam, reaching to lean amine loading of less than 1 percent.

## Total Cost comparison of all processes:

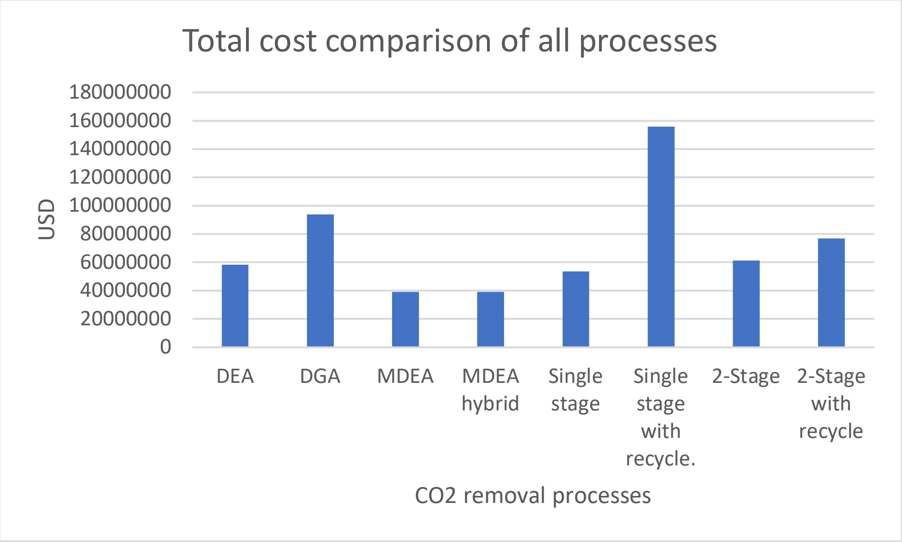

Table 16: Total cost comparison of all processes.

Finally total cost of all amine and membrane processes are compared, MEA system has the highest overall cost, however it is excluded from the report to make a visible comparison between the other systems. Among all other systems, single stage membrane with recycle has the highest cost, mainly because of compressor and cooler energy requirement to compensate for the methane loss.

The second highest cost is showed by the DGA system, its high cost is due to very high energy requirement for the reboiler section of regenerator column.

DGA is followed by 2 stage membrane with recycle, and then by 2-stage membrane. It can be seen that the compressor and energy required to recover the methane loss has costed more than the methane price itself. Perhaps the use of compressor and cooler is more suitable at much higher methane prices.

MDEA has performed very well and has cost slightly more than the hybrid single membrane-MDEA system. The hybrid single stage membrane and MDEA system has the lowest overall cost for the gas sweetening of the underlying process when about 70 percent $CO_2$ is removed by single stage membrane, as lesser permeate is taken out, the purity of permeate stream is increased, which has resulted in less than 5 % $CH_4$ loss compared to 14 percent of single stage membrane for the complete purification. The area required for the membrane has also reduced from 2400 $m^2$ to 950$m^2$. Like wise in the accompanying MDEA process the amine circulation rate is decreased along with the regenerator energy requirement.

All these factors combined have resulted in the lowest process cost for hybrid process.

However, the margin is small, a small decrease in methane price can further reduce the hybrid process cost. On the other hand, a small increase in methane price will result in an increase in hybrid process cost and reduce the cost of the 2stage membrane system.

## Conclusions:

It has been concluded that membrane process can efficiently remove the sour gas content from natural gas. Further advancements in membrane technology i.e. selectivity and permeability can reduce the present process cost. MDEA has proven to be a reliable chemical solvent for high pressure $CO_2$ removal applications. The hybrid membrane-amine process can further reduce the cost of the process and membranes can be applied for bulk removal of $CO_2$ and final polishing to pipeline specifications can be carried out by amine system.

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