Original Research Article

Optimization of CO_2 Removal Process for Liquefied Natural Gas Production

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Abstract: This paper present a comprehensive review of different processes available and suitable for removal of CO_2 from natural gas to meet LNG production specifications and explore the capability of Aspen HYSYS 8.6 process simulator to predict the CO_2 removal process operating conditions range at which hydrocarbon and chemical (amine solvent) loss can be minimized. Removal of CO_2 from natural gas is currently a global issue. Apart from meeting the customer's contract specifications and for successful liquefaction process in liquefied natural gas (LNG) plants, it is also a measure for reducing global CO_2 emission. The simulation program developed in this research work has been used to modify the physical, thermodynamics and transport properties of the gas streams and process units so as to improve process efficiency and environmental performance. It was observed that as the concentration of amine increases, the percentage mole concentration of CO_2 in the sweet gas decreases. This is attributed to the increase in amine solvent capacity with increase in concentration of amine in the solution. Also the mole percent of CO_2 in the sweet gas increased with contactor (absorber) operating temperature and decreased with increase in pressure, while the hydrocarbon (C_1) co-absorbed with the CO_2 in the solvent increased with pressure and decrease with increase in temperature. The simulated results showed that for a given partial pressure of CO_2 in the feed gas the amine loading increased with increasing amine wt% in the solution: with 25 wt%, 30 wt% and 35 wt% DEA, the loading [mol_{CO2}/mol_{DEA}] ranged from 0.6067 – 0.6369, 0.5316 – 0.5529 and 0.4638 – 0.4832 respectively.
Keywords: Simulation, thermodynamics, concentration

INTRODUCTION

The increase in demand for energy worldwide has aid the search for alternative sources of primary energy even to the remote part of the globe. The major alternative source with less environmental impact discovered some decade ago is energy from natural gas. Natural gas at its geological conditions in some deposits contain some complex contaminants (acid gases), such as Carbon dioxide (CO_2), Hydrogen sulfide (H_2S), Carbon monoxide (CO) and mercaptans, which hinders natural gas production processes and constitute great environmental hazards when it gets to the atmosphere. These impurities must be removed in other to meet the pipe-line quality standard specifications as a consumer fuel, enhance the calorific value of the natural gas, avoid pipelines and equipment corrosion and further overcome related process bottle necks.

Natural gas is relatively low in energy content per unit volume and it is expensive to transport. The most popular way to move gas from the source to the consumer is through pipelines. However, as transportation distance increases, pipelines become uneconomical, Liquefied Natural Gas (LNG), Gas to liquid and chemicals are more viable options. Liquefaction process which is the transformation of natural gas to liquid form involve operation at a very low temperature ($-161^{o}C$) and as low as atmospheric pressure. At these conditions CO_2 can freeze out on exchanger surface, plugging lines and reduce plant efficiency. Therefore, there is need for removal of CO_2 before liquefaction process, so as to meet the LNG product specifications, prevent corrosion of process equipment and environmental performance.

Removal of CO_2 from natural gas is currently a global issue. Apart from meeting the customer's contract specifications and for successful liquefaction process in liquefied natural gas (LNG) plants, it is also a measure for reducing the global CO_2 emission. There are many acid gas treating processes available for removal of CO_2 from natural gas. These processes

include Chemical solvents, Physical solvents, Adsorption Processes, Hybrid solvents and Physical separation (Membrane) [1]. The chemical solvents and physical solvents or combination of these two have been used extensively in existing base load LNG facilities [2]. The ability of the LNG option to continue to compete with existing and emerging gas monetization options will depend on the industry's success in reducing cost throughout the LNG value chain and maintaining exceptional safety, reliable and less environmental impact operations.

Today, computer-aided process simulation is nearly universally recognized as an essential tool in the process industries. Indeed, simulation software play a key role in process development – to study process alternatives, assess feasibility and preliminary economics, and interpret pilot-plant data; process design to optimize hardware and flow-sheets, estimate equipment and operating cost and investigate feedstock flexibility; and plant operation to reduce energy use, increase yield and improve pollution control.

The optimization method used in this study is based on process simulation and analysis, using data from an existing liquefied natural gas plant. ASPEN HYSYS 8.6 process simulator will be used to establish the operating conditions at which the CO_2 removal process from natural gas can be operated to meet the LNG specifications and minimize emission to the environment at the lowest energy requirement possible, through modification of the physical, thermodynamics and transport properties of the acid gas/amine process.

This paper present a comprehensive review of different processes available and suitable for removal of CO_2 from natural gas to meet LNG production specifications and explore the capability of Aspen HYSYS 8.6 process simulator to predict the CO_2 removal process operating conditions range at which hydrocarbon and chemical (amine solvent) loss can be minimized.

Acid Gas Impurities
Natural gas extracted from some wells can contain significant amounts of sulfur containing compounds and carbon dioxide. The composition of acid gases in natural gas varies widely depending on the gas field. Acid gas impurities, i.e. CO_2 and H_2S are detrimental to natural gas properties. For instance, in cryogenic conversion of natural gas to LNG, CO_2 transforms to solid state, hence, hinders the transportation of liquid in the pipes or the corrosive H_2S reduces the service time of the transportation pipes. In addition H_2S is hazardous for human beings and CO_2 has no heating value. As a result the concentration of

acid gas impurities in natural gas must be reduced to a specified level before further processing [3].

Liquefied Natural Gas (LNG) Production
Liquefied Natural Gas (LNG) production is one of the fastest growing process nowadays, LNG trade is said to account for about 24.2% of international natural gas trade [4]. LNG production value chains include the following steps:
- Gas Production and Field Processing
- Onshore gas treatment
- Gas Conversion Via Liquefaction
- LNG Shipping
- Receiving Terminal
- End use as Fuel (Power Generation, Fertilizer Industry, gas Distribution, etc.)

Gas Production and Field Development
The exploration and production of natural gas is the starting point for all gas utilization options. The source of natural gas feed to the LNG plant could be either associated gas or non-associated gas. Natural gas is naturally occurring gaseous mixture or hydrocarbon components and consists mainly of methane. Other constituents include ethane, propane and butane which is referred to as liquefied petroleum gas (LPG) and condensate which are heavier hydrocarbons. The compositions of the gas differ from one gas reservoir to another. The gas production steps include some field processing depending on the nature of the gas source and the requirement for pipeline transport to liquefaction site. Typically, field processing is needed to prevent hydrocarbon drop-out, hydrate formation or corrosion in the pipeline to the liquefaction site.

Onshore Gas Treatment
The gas from the reservoir may also contain components such as nitrogen, carbon dioxide and sulfur compounds. The feed gas has to be treated for removal of impurities before it can be liquefied. Hence onshore gas treatment is required to meet the specification set by the LNG buyers as well as requirements for the LNG liquefaction process. The onshore gas treatment typically comprises of gas reception facilities, Acid gas removal and disposal section, gas dehydration, mercury removal and particle filtration; as shown below in Figure .1. The gas reception facilities section provided for the removal of liquid entrainment gather in the system due to condensation and pressure reduction of the fluid (Joule Thomson effect). At this section the pressure of the LNG feed is adjusted to meet the requirement of the liquefaction facilities. If the pressure is lower than that of the liquefaction facilities a compressor may be installed to beef up the pressure difference.
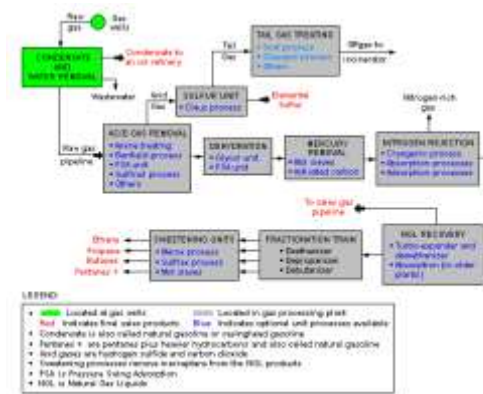
Fig-1: Schematic flow diagram of a typical natural gas processing plant

Acid gas removal and disposal section is provided to remove acid gases (CO_2, H_2S and other sulfur components) from the feed gas. The extent of removal is influenced by the LNG specification and the requirement of the liquefaction process. The dehydration section removes water from the fees gas. Water vapor must be removed to prevent corrosion, and freezing in the liquefaction process of the plant that operate at cryogenic condition. Trace of mercury in the feed gas, which attacks piping, and equipment made from aluminum and aluminum compounds is removed in the mercury removal section. Aluminum is universally used for the construction of cryogenic equipment. Filtration of the gas stream following the mercury removal unit is essential to prevent particle into the liquefaction section of the plant, thus prevent equipment plugging.

Liquefaction Process
The liquefaction section is the heart of LNG value chain. The process involves cooling the clean feed gas in succession (Pre-cooling, Liquefaction and Sub-cooling) to $-161^{o}C$ using mechanical refrigeration. The refrigerants for LNG process must have high evaporating temperature to reduce power needed for heat pumping. For effective cooling there should be a close match between the natural gas and refrigerants temperature curves and this could be achieved by the following:
- Using many stages of evaporating temperature (Cascade Process)
- Using refrigerant that evaporate at gliding temperature (Mixed refrigerants)

Figures 1 and 2 show typical Cascade process arrangement with three Different refrigerants combined together (Propane, Ethylene and Methane) and mixed refrigerant arrangement respectively.

LNG Shipping

After the liquefaction process and subsequent Storage, the LNG is pumped from the storage tank to a LNG ship via a loading jetty. LNG vapor return from the ship to the storage tank is always provided to avoid pressure build up in the ship. The LNG is then shipped commercially in a fully refrigerated liquid state. The ship cargo is kept cool by evaporating a fraction of the cargo which is referred to as "boil off". The carriers either consume boil off or re-liquefy the gas and use diesel as fuel.

Receiving and Re-gasification Terminal
The LNG from the ship is received in this section, stored and re-vaporize for sales on demand. The amount of reserve capacity depends on expected shipping delays, seasonal variation of supply and consumption

End use as Fuel
LNG can be applied in a wide range of energy needs as follow;
- As a feedstock for manufacturing of chemicals (Fertilizer, ammonia)
- An excellent fuel for powering boilers.
- For electrical power generation.
- As fuel for transportation (Train, Buses and LNG ships).

CO_2 REMOVAL PROCESSES
The removal of acid gases (CO_2, H_2S and other sulfur components) from natural gas is often referred to as gas sweetening process. Carbon dioxide present in the natural gas need to be removed in other to increase the heating value of the gas, prevent corrosion of pipeline and gas process equipment and crystallization of CO_2 during cryogenic process (liquefaction process). The removal of carbon dioxide can be accomplished in a numbers of ways. Varieties of processes and (improvement of each) have been developed over the years to treat certain types of gas with the aim of

optimizing capital cost and operating cost, meet Gas specifications and for environmental purpose [5]. The major processes available can be grouped as follows [7]:

- Absorption Processes (Chemical and Physical absorption)
- Physical Separation (Membrane, Cryogenic Separation)
- Hybrid Solution (Mixed Physical and Chemical Solvent)
- Adsorption Process (Solid Surface)

The decision of selecting a CO_2 removal process can be simplified by gas composition and operating conditions. High CO_2 partial pressure in the feed gas (345 KPa) enhances the possibilities of employing physical solvent, while the presence of significant amount of heavy hydrocarbon discourages the use of physical solvent. Low CO_2 partial pressures and low outlet pressure of the product stream may favour application of chemical solvents [5]. Process selection could prove difficult; a numbers of variables must be weighed prior to making final process selection. Figure 2 can be used as screening tools to make an initial selection of potential process choices.
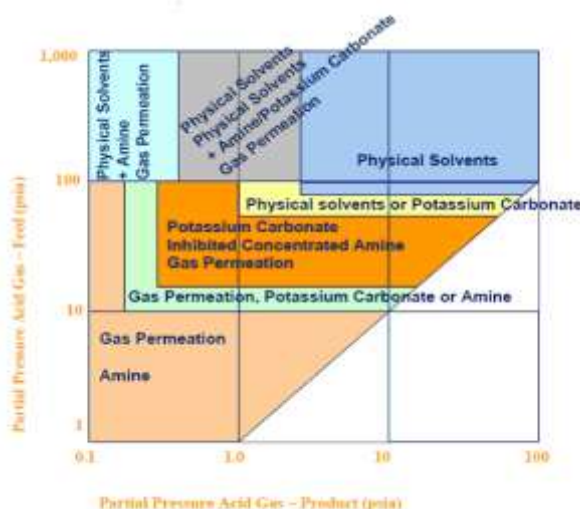

Fig-2: Process capabilities for gas treating process [6].

Each of the processes has advantages relatives to others for certain applications; therefore in selection of the appropriate process, the following factors should be put into consideration:

- Type and concentration of impurities in the feed gas
- The concentration of each contaminants and degree of removal required.
- Hydrocarbon composition of the gas
- Final specification
- Capital and operating cost
- Volume of gas to be processed
- Selectivity required for acid gas removal
- Conditions at which the feed gas is available for processing.

Physical absorption processes

Physical solvent processes use organic solvents to physically absorb acid gas components rather than react chemically. Removal of CO_2 by physical absorption processes are base on the solubility of CO_2 within the solvents. The solubility of CO_2 depends on the partial pressure and on the temperature

of the feed gas. Higher CO_2 partial pressure and lower temperature favors the solubility of CO_2 in the solvents (Absorbent), at these conditions complete removal of acid gas from natural gas is possible. Regeneration of the spent solvent can be achieved by flashing to lower pressure or by stripping with vapour or inert gas, while some is regenerated by flashing only and require no heat (Dimethyl ether of Polyethylene Glycol). Selection of physical processes for the removal of CO_2 from natural gas for LNG project is favored on the following conditions;

- The partial pressure of the CO_2 in the feed should be 50 psi or higher.
- The concentration of heavy hydrocarbon in the feed should be low. That is the gas feed is lean in C_3+.
- Only bulk removal of acid gas is required.
- Selective removal of CO_2 is required.

There are various physical processes for the removal of CO_2 from natural gas but not all the processes available are capable of removing CO_2 to meet LNG specification of 50-100 ppmv or 2.5% of

CO_2 in the product stream. The following physical processes will be discussed base on their suitability/modification to treat acid gas with high or low concentration of CO_2 in the feed gas.

- Selexol process
- Rectisol process
- Fluor process

MATERIALS AND METHODS
Selection of CO_2 Removal Process for LNG Production

Amine base solvent (DEA) was chosen in this paper to establish the operating conditions at which the CO_2 removal process from the natural gas can be operated to meet the LNG specifications and to minimized emission to the environment. The process justification was based on the following conditions:

- The CO_2 concentration of the feed gas to be treated is relatively low (5.23%) with high hydrocarbon contents, the amine process is considered more suitable [5].

- The solvent applied (DEA) is considered to be chemically stable; DEA can be heated to its normal boiling point of 269°C at 101325 Pa (Table 2) before decomposition. This reduces the solvent degradation during stripping and reduces solvent loss and accumulation in the units.

- The heat of reaction of DEA with CO_2 is low compared to other amines as shown in Table 3.1. The heat generated in the absorber is low. This increases the solvent loading capacity in the absorber, since solubility/loading of CO_2 increases at low temperature.

- The CO_2 recovery rates from amine base solvent can be as high as 98% and purity can be in excess of 99%. Amine base solvent process is more efficient for acid gas available at high or low partial pressure and with low or relatively high partial pressure acid gas product [6].

Table-1: Approximate Guideline for amine Processes (Kensell, 1979)

	MEA	DEA	DGA	MDEA
Acid gas pickup, mol/mol amine, Normal Range	0.33 – 0.4	0.35 – 0.65	0.25– 0.3	0.2 – 0.55
Solution Concentration, wt%, Normal Range	15 – 25	25 – 35	50 - 70	40 - 50
Approximate Reboiler heat Duty kJ/L	280 – 335	245 – 280	300 – 360	220 - 335
Reboiler Temperature, Normal Operation in °C	107 – 127	110 – 121	121 – 127	110 - 127
Approximate Heat Of Reaction, kJ/kg CO_2	1445 – 1630	1350 - 1515	2000	1325 - 1390

Table 2: Physical Properties of Amines (Source: GPSA)

	MEA	DEA	TEA	MDEA	DIPA	DGA
Overall Chemical formula	C_2H_7NO	$C_4H_{11}NO_2$	$C_6H_{15}NO_3$	$C_5H_{13}NO_2$	$C_6H_{15}NO_2$	$C_4H_{11}NO_2$
Molecular weight(kg/kmol)	61.08	105.14	149.19	119.17	133.19	105.14
Boiling Point at101325 pa , °C	170.6	269.2	360	247.4	248.9	221.3
Specific Gravity (20°C/20°C) (30°C/20°C) (45°C/20°C)	1.0179	1.0919	1.1258	1.0418	0.9890	1.0572
Absolute Viscosity at 20°C (pa.s) (30°C) (45°C) (15.6°C)	0.0241	0.380	0.1030	0.1010	0.198	0.0400
Melting point, °C	10.5	28.0	22.4	-23.0	42.0	-12.5
Specific Heat at15.6 (J/kg.K) (20°C) (30°C)	2546	2512	2931	2238	2889	2391
Flash Point °C	93.3	137.8	185.0	129.4	123.9	126.7

Process description

The general process flow diagram of an amine - CO_2 removal process is shown in Figure 1. The sour gas enters the plant through a separator to remove any free liquid or entrainment solids. The sour gas leaves the top of the separator and enters the bottom of the absorber in countercurrent contact with aqueous lean amine solution. Sweet gas leaves the top of the absorber and flow to a dehydration unit before being considered ready for liquefaction. Lean amine flow downward

counter currently to the sour gas and absorbed the CO_2 constituent and become rich amine solution. The rich solvent from the bottom of the absorber is flashed in a separator to recover some absorbed hydrocarbon in the rich solvent and then pass through amine-amine heat exchanger to the stripper where the acid gas absorbed is stripped off at a very high temperature and low pressure. The acid gas then leaves the top of the stripper column. The lean amine from the bottom of the reboiler attached to the stripper flow through amine-amine heat exchanger and through a water air cooler before being introduced back to the top of the absorber. The amine-amine (rich/lean) heat exchanger serves as a heat conservation device.
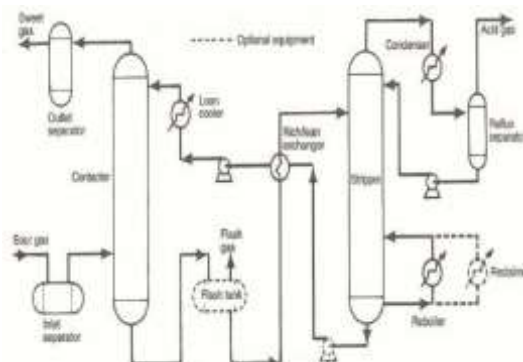

Fig-3: A typical amine base

CO_2 removal process diagram

A part of absorbed acid gas is flashed from the heated rich solution on the top tray of the stripper. The reminder of the rich solution flows downward through the stripper in countercurrent contact with vapour generated in the reboiler; which strips the acid gas from the rich solution. The stripper overhead products (acid gas and steam) pass through a condenser where the steam is condensed and cooled and returned to the top of the stripper as a reflux, while the acid gas is separated in a separator and sent to the flare or compressed for sequestration process.

RESULTS

The simulation objectives are to meet the LNG specifications of about 50 – 100 ppmv or 2- 3 % CO_2 concentration in the product stream, and then establish optimum conditions to reduce CO_2 emission and chemical loss. The result in figure 4 shows that for a given pressure of CO_2 in the feed gas, the amine loading increase with amine wt% in the solution. The specifications range was reached at 25 wt% DEA and above. With 25 wt% DEA, the loading [mol_{CO2}/mol_{DEA}] ranges from 0.6067 – 0.6369 as shown in Figure 4. For 30 wt% and 35 wt%, the increase loading capacity ranges from 0.5316 – 0.5498 (Figure 5) and 0.4638 – 0.4832 (Figure 6) respectively. The loading was observed to decrease with increase temperature at a given CO_2 partial pressure. Figure 8 shows the treatment of sour feed gas with different amine concentrations (at Contactor temperature of 35^oC) and the observed % mole concentration of CO_2 in the sweet gas. It was observed that as the concentration of amine increases, the % mole concentration of CO_2 in the sweet gas decreases. This is attributed to the increase in Amine solvent capacity with increase in concentration of amine in the solution. The % mole of CO_2 in the sweet gas increases with contactor (Absorber) operating temperature and decrease with pressure (Figure 7). While the hydrocarbon (C_1) co-absorbed with the CO_2 in the solvent increases with pressure and decrease with increase in temperature. This is due to decrease in amine loading capacity as its viscosity decrease with temperature. The effect of lean amine circulation rate on amine loading capacity was also investigated. It was observed that the loading capacity decreases with increase in circulation rate as illustrated below in Figure 9. Also, Figure 10 shows that the CO_2 emission/present in the sweet gas and amine loss with the acid gas increases with solvent circulation rate.
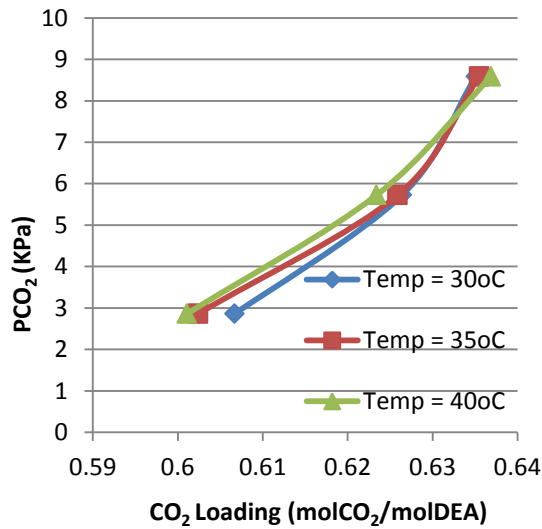
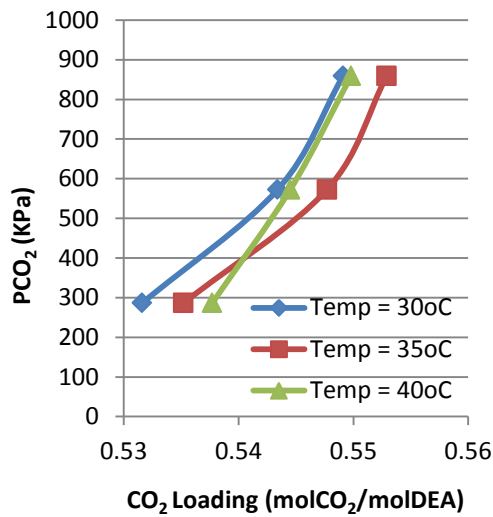**Fig-4: Partial pressure of CO_2 in solution as function of CO_2 loading of 25wt% DEA**

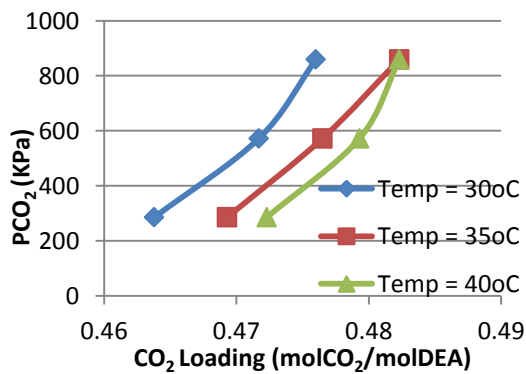**Fig-5: Partial pressure of CO_2 in solution as function of CO_2 loading of 30wt% DEA**

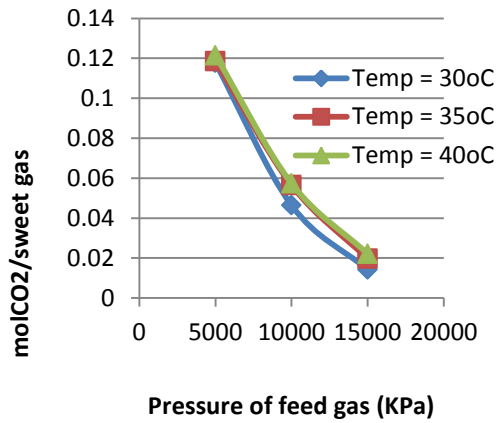**Fig-6: Partial pressure of CO_2 in Solution as function of CO_2 loading of 35wt% DEA**

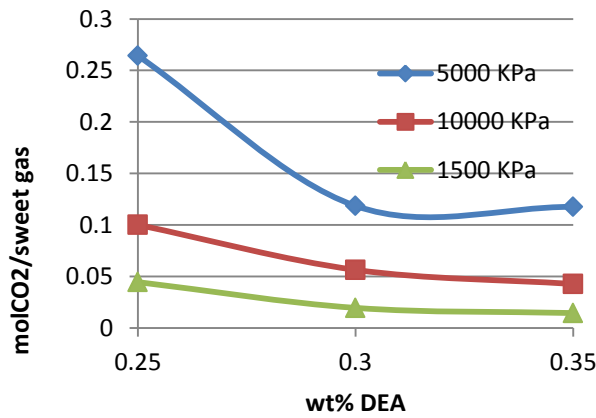**Fig-7: Effects of pressure and temperature on % C$_{O2}$ in the sweet gas with DEA concentration of 30 wt%**
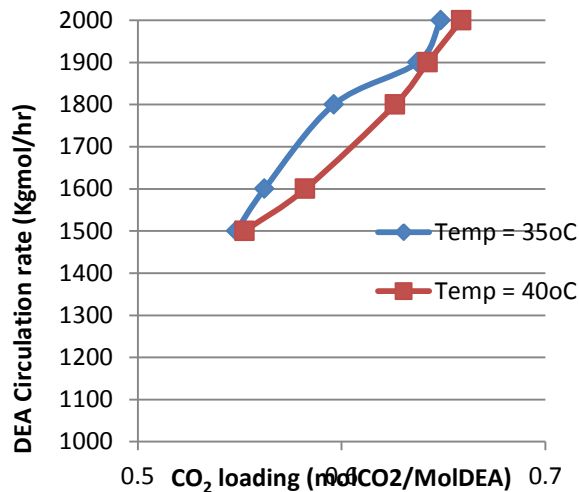

Fig-8: % of CO$_2$ in the absorber pressure

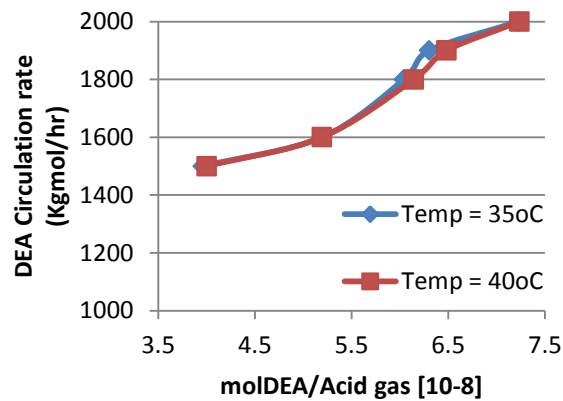**Fig-9: Lean DEA circulation rate vs. CO$_2$ loading in 35wt% DEA**

Fig-10: Lean DEA circulation rate vs. mol CO_2 in the acid gas with 35wt% DEA

Table-3: Data Generated from the Simulation Model

Pfeed gas (Kp)	PCO2 (kpa)	Temp °C	mol_{CO_2}/Mol_{DEA}	mol_{C_1}/Mol_{DEA}	molCO2/sweet gas
35 wt%DEA					
5000	286	30	0.4638	0.008168	0.1175
		35	0.4693	0.007951	0.1177
		40	0.4723	0.007802	0.2736
10000	573	30	0.4717	0.01584	0.0406
		35	0.4765	0.01548	0.0428
		40	0.4793	0.01523	0.0442
15000	859	30	0.4760	0.02286	0.0105
		35	0.4801	0.02240	0.0146
		40	0.4823	0.02209	0.0219
30 wt%DEA					
Pfeed gas (kpa)	**PCO2 (kpa)**	**Temp °C**	mol_{CO_2}/Mol_{DEA}	mol_{C_1}/Mol_{DEA}	**molCO2/sweet gas**
5000	286	30	0.5316	0.01034	0.1177
		35	0.5352	0.01006	0.1186
		40	0.5377	0.00986	0.1214
10000	573	30	0.5434	0.02320	0.0464
		35	0.5477	0.01941	0.0565
		40	0.5445	0.01987	0.0573
15000	859	30	0.5491	0.02858	0.0142
		35	0.5529	0.02798	0.0196
		40	0.5498	0.02767	0.0221
25 wt%DEA					
Pfeed gas (kpa)	**PCO2 (kpa)**	**Temp °C**	mol_{CO_2}/Mol_{DEA}	mol_{C_1}/Mol_{DEA}	**molCO2/sweet gas**
5000	286	30	0.6067	0.01351	0.2388
		35	0.6024	0.01316	0.2643
		40	0.6011	0.01298	0.2989
10000	573	30	0.6264	0.02575	0.0964
		35	0.6259	0.02513	0.1002
		40	0.6234	0.02481	0.1093
15000	859	30	0.6351	0.03689	0.0431
		35	0.6355	0.03609	0.0446
		40	0.6369	0.03568	0.0488

CONCLUSION

The acid gas removal unit in a liquefied natural gas plant has been successfully simulated in this paper for a more efficient CO_2 removal process from natural gas, using an amine based solvent (DEA). It was observed that as the concentration of amine increases, the % mole concentration of CO_2 in the sweet gas decreases. This is attributed to the increase in amine solvent capacity with increase in concentration of amine in the solution. The % mole of CO_2 in the sweet gas also increased with Contactor (Absorber) operating temperature and decreased with increase in pressure, while the hydrocarbon (C_1) co-absorbed with the CO_2 in the solvent increased with pressure and decrease with increase in temperature. This is due to decrease in amine loading capacity as its viscosity decrease with temperature. The simulation results showed that for a given partial pressure of CO_2 in the feed gas the amine loading increased with increasing amine wt% in the solution: with 25 wt%, 30 wt% and 35 wt% DEA, the loading [mol_{CO2}/mol_{DEA}] ranged from 0.6067 – 0.6369, 0.5316 – 0.5529 and 0.4638 – 0.4832 respectively.

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