A Hybrid Membrane-Absorption Process
for Carbon Dioxide Capture:
Effect of Different Alkanolamine on Energy Consumption

Nasir, Qazi*+

Department of Chemical and Petrochemical Engineering, College of Engineering and Architecture,
University of Nizwa, OMAN

Suleman, Humbul

Department of Chemical and Biochemical Engineering, AT-CERE, Technical University of Denmark,
DENMARK

Elumalai, Manivannan

International Maritime College, OMAN

ABSTRACT: *Amine and membrane-based processes are commonly used to treat acid gases such as carbon dioxide and hydrogen sulfide. Carbon dioxide adversely affects the environment, therefore, its utilization and storage are critical. In this work, a simplistic approach of single-stage membrane units combine with amine absorption processes with different commercial amines was investigated. An increase in CO_2 concentration in the feed gas results in a substantial increase in the thermal energy consumption of the stripper reboiler were using a hybrid amine-membrane setup can effectively reduce energy consumed in the reboiler. Both the amine absorption process and membrane process are simulated using Aspen HYSYS V10. Since the membrane is not available in Aspen HYSYS V10 unit operation package; it is programmed and added as custom user operation. Moreover, a new acid/ amine-based fluid package builds in a combination of the Peng-Robinson equation of state for vapor phase and electrolyte non-random two liquid-based activity model for the liquid phase were used in this study. Furthermore, energy consumption in CO_2 capture using different alkanolamine such as N-methyldiethanolamine (MDEA), monethanolamine (MEA), deithanolamine (DEA), piperazine (PZ), triethanolamine (TEA) are also studied. As membrane unit help in CO_2 reduction in feed to amine absorption process in hybrid amine-membrane setup. This significantly reduces the energy requirement as compared to the conventional standalone alkanolamine process. In comparison with various amines used in the amine absorption process, MEA offers the lowest total energy consumed, whereas, MDEA is considered to be the highest in terms of energy consumption.*

KEYWORDS: *Amine absorption process; Membrane process; Hybrid process; Aspen HYSYS; MEA; DEA.*

INTRODUCTION

Natural gas that is brought to the well head from underground is much different from the gas which is consumed as a fuel in various applications worldwide. Natural gas composition is not consistent and varies with different geographical location of the World. Methane is a primary component of natural gas accounting $75 - 90$ %, whereas, ethane, propane, butane accounts for $1 - 3$ % and the rest consists of higher hydrocarbons [1]. Natural gas deposits may also contain complex contaminants such as carbon dioxide (CO_2), hydrogen sulphide (H_2S), mercury, water and Benzene, Toluene and Xylene (BTX), which contributes to the environmental hazards. In recent years, the removal of CO_2 from natural gas has captured interest due to high demand of pipeline-grade gas specification. The presence of CO_2 in the well in combination with water tends to cause corrosion to pipelines and process equipment. Moreover, the existence of CO_2 in the NG not only reduces the heating value of gas but also cause crystallization during liquefaction process [2, 3].

Across the globe, considerable variation of CO_2 content in natural gas has been encountered, where CO_2 percentage in raw natural gas varies from 4 to 50 % and some cases even as high as 98% [4]. Efficient process scheme is required to remove CO_2 from NG. Presently, processes such as absorption (chemical and physical), adsorption (solid surface), hybrid (physical and chemical), membrane and cryogenic separation are used to remove CO_2 from natural gas [5]. To capture CO_2 from flue gas, alkanolamine-based absorption processes are considered as a well-commercialized technology due to their large handling capacity, and capability to operate at low CO_2 concentrations and low pressure of exhaust/flue gases. However, increase in CO_2 concentration, the process becomes energy intensive [6]. The post-combustion treatment of the flue gas in a fossil fuel power plant is commonly employed using a chemical solvent based approach where usually an alkanolamine solution is used for CO_2 absorption [7]. In this approach, the feed flue gas with CO_2 concentration of 12-15 mol% is in contact with 30 % aqueous monoethanolamine (MEA) solution in the absorption column. Then the CO_2-rich aqueous MEA solution is sent to the stripping column for the regeneration using steam temperature of 120 ℃ and CO_2 is subsequently recovered after condensation of the water vapors [8]. This solvent regeneration in the stripper is an energy intensive step in a conventional alkanolamine based absorption process. This happens due to the reboiler heat duty where extensive amount of heat is required for stripping the gas from the liquid solvent by using steam, the heat of reaction for CO_2 desorption and lastly, the sensible heat that is used to raise the temperature of the rich solvent [8]. A Gas Pessurized Stripping (GPS) is an adaptive alternative route which uses high pressure and non-condensable stripping gas to strip the CO_2 off the CO_2 laden solvent stream [9]. The advantage of GPS column of being less energy intensive which significantly reduced heat loss due to stripping heat. But the additional separation requirement for CO_2 and the stripping gas is a mere drawback.

Alternatively, membrane based CO_2 separation is a maturing and commercially proven technology for natural gas processing [1, 10-12]. In contrast to the traditional amine process, membrane processes are relatively simpler and have low energy cost due to no phase change during the separation [13]. Polymeric or inorganic membrane consisting of zeolite, sol-gel silica or carbon molecular sieve is used for CO_2 separation by difference in diffusion rates and adsorption strength of resulting component mixture in polymer matrix or in organic membrane pores. In membrane process, the gas permeation involves dissolution in high pressure side of the membrane, diffusion across the membrane wall and subsequently, evaporation from the low-pressure side. As a result, some gases are more soluble and permeate through polymeric membrane and other gases retentate [14-16]. However, the post-combustion treatment of flue gases (e.g. in coal fired power plants) using membrane separation processes are challenging due to the low CO_2 partial pressure of flue gas and requires a significant partial pressure drive for effective separation [10, 17]. Therefore, compression on the feed side (membrane upstream) and vacuum on permeate (downstream) side is subsequently required. However, considering the sheer volume of flue gas, compression and vacuum process results in a substantial increase in equipment and energy costs which ultimately, increase Cost of Equipment (COE) over amine absorption process [10, 18]. Furthermore, power plants require large surface area of membrane which could expand up to millions of square meters of membrane area. Such large surface area of high performance membrane is difficult to manufacture and handle and it is operationally enviable at such a scale.

Research Article

The membrane and GPS technology could be possibly an attractive option to treat gas mixture with high CO_2 content. Moreover, most of contaminates are already removed in pretreatment stage, which enhances the separation of acid gases in the amine unit and also enhance life of membrane. Therefore, to benefit from technologies, CO_2 capture in combination with membrane and amine, also known as hybrid CO_2 capture process could be used as an attractive option on a large scale separation processes.

In this work, a hybrid scheme of membrane technology, and amine absorption unit, is conjoined to achieve acid gas removal economically. Alkanolamine based absorption process is simulated in Aspen HYSYS environment and since membrane unit is not a predefined unit in Aspen HYSYS, complete mixing model for membrane is coded in the custom user operation module of Aspen HYSYS. The model is then used for the prediction of CO_2 separation using membrane process and connected with Aspen HYSYS, respectively [19].

THEORITICAL SECTION
Membrane process

Different arrangement/ configuration of permeator are commonly employed for the design of the membrane separation processes along with the specification of process unit such as size and its operating conditions. Therefore, the most common and simplest design arrangements are the single stage or double stage with either permeate or retentate with or without recycle stream. The recovery of the desired component can be enhanced using recycle or multistage with recycle configuration [20]. However, in this study to avoid calculation complexities which could arise later in hybrid process scheme, a simple single stage arrangement without recycle is used for the membrane unit. The complete mixing model on permeate and high-pressure side is assumed for the membrane permeation. Therefore, any point along the membrane is determined by relative rates of the feed composition. The model is based on the mass balance over a differential element of hollow fiber membrane. Since, the model is not available in a standard version of Aspen HYSYS, it was implemented/ coded in Aspen HYSYS program, using custom user unit operation with the help of visual basic language [19].

Table 1: Feed conditions for membrane process[21].

Membrane	Hollow fiber
Flow configuration	Cross-flow (complete mixing)
Components permeance $\dfrac{cm^3\ STP}{s.\ cm^2.\ cm\ of\ hg}$	$CH_4 = 8.50e^{-11}$
	$CO_2 = 3.50e^{-11}$
	$C_2H_5 = 5.80e^{-9}$
	$H_2S = 4.0e^{-9}$
Temperature (ºC)	37.8
Feed pressure / retentate (bar)	36.2
Permeate pressure (bar)	1.013

Membrane replacement is usually cost intensive, therefore pretreatment of feed gas is commonly required to extend the life of the membrane. In this study, the feed gas was considered pretreated, and assumed that the minor components such as SOx, NOx, CO, H_2O and ash are not present. Such components especially moisture content in the feed gas decrease the life of the membrane therefore, pretreatment are necessary. In the calculation, the gas used in this work was assumed free from moisture and considered to contain overall high composition of CH_4 and CO_2, which is most common in CO_2 rich natural gas reservoirs. The conditions such as flow rate, composition, temperature and pressure for the feed gas used in the Gas Permeation Unit (GPU) is presented in Table 1. The CH_4 content in the feed gas ranges from 30 to 70 %, whereas the concentration of CO_2 varies from 10 to 50%. The product target varies, and the goal is to reduce the CO_2 content in the feed gas by the membrane process, before being treated in the amine process.

Membrane model used

Complete-mixing model used in this study for gas separation by membrane is shown in Fig. 1. There is a minimal change in the composition if the separation element is operated at a low recovery which means the permeate flow rate is a small fraction of the entering feed rate. Complete mixing model provides a reasonable estimate of permeate purity. As shown in Fig. 1, q_f, q_0 and q_p is feed, retentate and permeate total flow rates, θ is fraction feed permeated. Detailed description of the derivation of the model equations is stated elsewhere [22].

Since, the hybrid setup consists of membrane and amine absorption processes, it involves a complex set
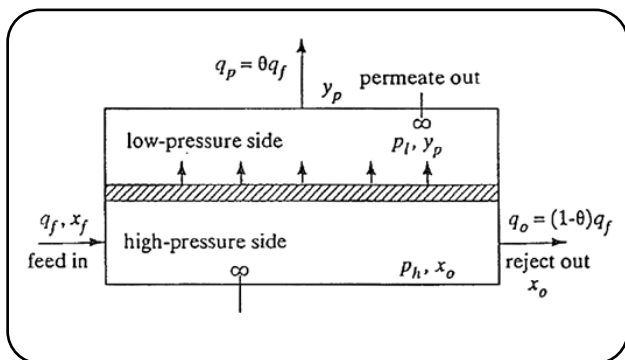
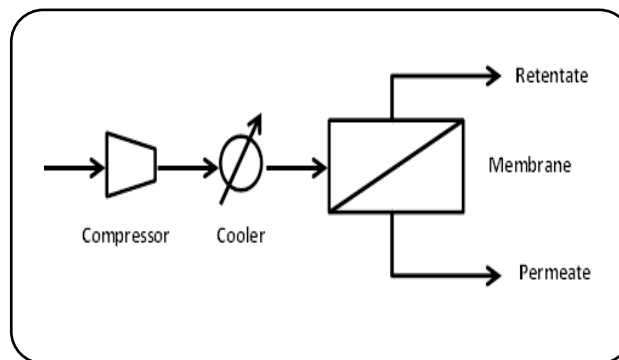*Fig. 1: Schematic of complete mixing model.*

Fig. 2: Single stage (SS) membrane configuration used.

of mathematical equations which increases the computation complexity, especially the amine absorption process due to its highly nonlinear nature, together with large recycle stream. The multi-stage permeator design pose more computational difficulties due to the complex set of differential and algebraic equations. Therefore, a simplistic approach consisting of a single stage membrane configuration is used in this work. A membrane process setup used is shown in Fig. 2, whose primary focus is the moderate purity and recovery requirement from single stage [20].

Amine base absorption process

The retentate composition from the membrane unit is further treated in the alkanolamine absorption process with amine regeneration configuration, also simulated in Aspen HYSYS V10. The composition of both CH_4 and CO_2 captured from both membrane and amine unit was compared. In amine process different solvents (in standalone or combination are used) and compared, i.e., monoethanolamine (MEA), N-methyldiethanolamine (MDEA), diethanolamine (DEA), combination of MDEA + DEA, MDEA + DEA + MEA, MDEA + MEA and MDEA+ Piperazine are studied for the treatment of acid gas, which prime focus is to vary CO_2 and CH_4 content while keeping H_2S content constant. The comparison of different solvent-based separation techniques and their effects on the reduction of the thermal energy consumption are also found elsewhere [23, 24]. For illustration purpose, the conventional MDEA process flowsheet for the removal of acid gas are shown in Fig. 3. To elaborate further, CO_2 rich natural gas enters the absorber where they are in contact with aqueous solution of MDEA flowing counter-

current to the gas stream. An exothermic reaction between a weak base (MDEA) and a weak acid (CO_2) takes place to form water soluble salts. The CO_2 rich MDEA stream exits the absorber at the bottom of the absorber, whereas, the sweet gas from the top. The bottom stream pressure is then reduced and to be further sent to separator where light hydrocarbons (HC) are separated from rest of the components. The components are then preheated in a heat exchanger by lean MDEA stream leaving the bottom of the stripper. The MDEA containing CO_2 stripped off leaves the top of the stripper column, whereas, the lean MDEA is recycled back to the absorber. As amine process encompass a substantial amount of energy for regeneration of the used solvent at the stripper reboiler, the thermal energy required at the stripper was considered as a main energy penalty in the amine process.

In order to simulate amine absorption process in Aspen HYSYS, several electrolyte-based physical property methods (EoS) are available for processes containing CO_2, H_2O and MDEA. These property methods utilize the electrolyte-NRTL (activity-based approach) to calculate the transport and thermodynamic properties in the liquid phase.

However, in this work, a new property method that is recently incorporated in Aspen HYSYS V10, for acid gas and chemical solvents based absorption systems is used. This property package is selected prior to entering the setup in the flowsheet environment. Acid Gas-Chemical solvent property package are updated and enhanced in version V10 of Aspen HYSYS. The property package is based on extensive research and development in areas such as rate-based, chemical absorption process and molecular thermodynamic models for aqueous amine solution [25].

The property package utilizes Peng-Robinson equation-of-state for vapor phase prediction and the
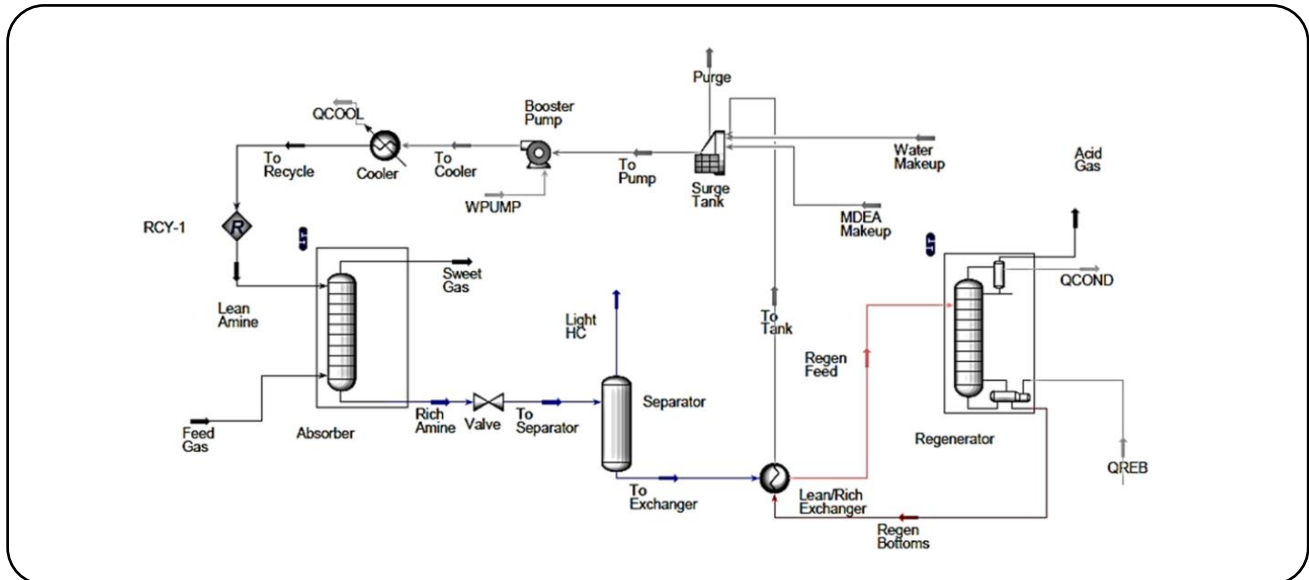
Fig. 3: Acid gas cleaning using MDEA.

electrolyte Non-Random Two-Liquid (e-NRTL) activity coefficient model for liquid phase prediction, respectively [26]. The e-NRTL model improved due to the thermodynamic and transport property model parameters which are identified by regression of extensive thermodynamics and physical property literature data for aqueous alkanolamine solutions. The e-NRTL model predictability is improved using the available VLE and heat absorption data which is used to perform the regression analysis for all supported alkanolamine solvents, commonly used in the industry [27]. Detailed information regarding the Acid Gas property package is available in Aspen HYSYS V10 help section [19]. One of the initial requirement to setup the simulation using Acid Gas property package, is that at least one amine component must be added in the component list along with CO_2, H_2O and H_2S which otherwise prompted with error.

Hybrid (amine/membrane) based approach

Amine separation technology is conventional way for the removal of acid gas from natural gas stream. Alternatively, membrane process is used for the removal of acid gases and is most commonly used prior to amine absorption process. Combination of membrane and amine process also referred as hybrid process, as shown in Fig. 4, can be used and utilizes the benefit of both the technologies. In this study, a simplistic approach for sweetening process is used. It consists of a single-stage membrane permeator combined with amine absorption process. Various solvents and their combination are used. The natural gas stream containing high concentration of acid gas is first treated by the membrane process to remove most of the acid gas before additional purification by alkanolamine absorption process. The hybrid process setup and their specified parameters used for the hybrid process are shown in Fig. 4.

RESULTS AND DISCUSSION
Membrane Model validation

The complete mixing mathematical model used in this study for the membrane process were validated using the experimental data reported by *Tranchino et al.* [28]. The data were collected using a composite hollow fibers membrane consisting of an aliphatic copolymer coated on a polysulfone support. They were tested for a binary CH_4/CO_2 mixture. The parameters such as temperature, pressure, stage-cut ($\theta = \text{permeate flow} / \text{feed flow}$) also known as degree of separation, and feed composition are studied. The feed gas contains 60% CO_2 which needs to be removed in the permeate stream to increase the recovery of CH_4 on the retentate stream. The pressure on permeate and retentate side is 405.3 kPa and 101.3 kPa, whereas, permeability of CO_2 and CH_4 used is 31.6×10^{-10} mol/m^2.s.P$_a$ and 8.81×10^{-10} mol/m^2.s.P$_a$, respectively. The experimental results along with mathematical model for permeate composition vs stage cut is presented in Fig. 5.

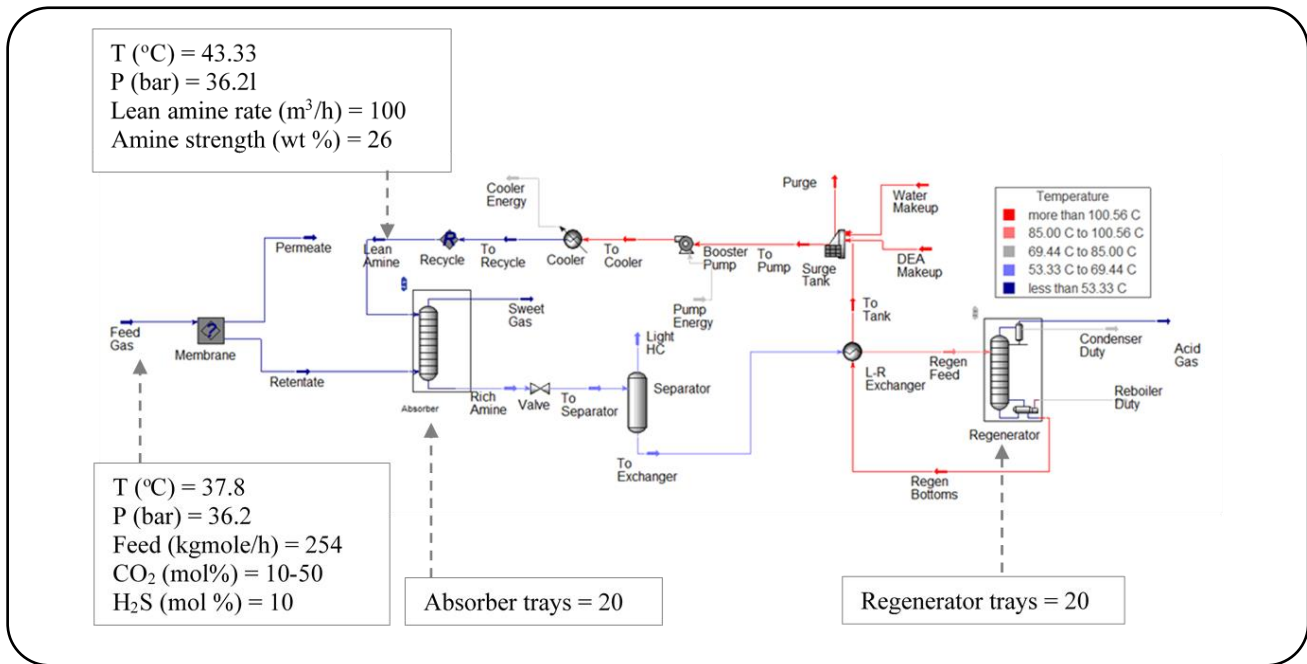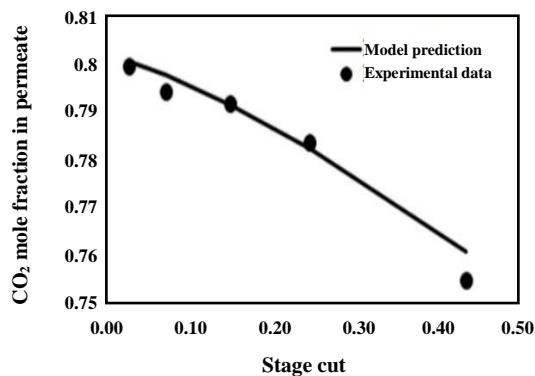*Fig. 4: Specified parameter for hybrid process.*

Fig. 5: Comparison of model and experimental data [29] for CO_2/CH_4 system.

As shown, a good agreement is obtained between mathematical model and the experimental results [28].

Sidhoum et al., investigated CO_2/N_2 and O_2/N_2 (air) separation performance using cellulose acetate hollow fibers with seep gas on the permeate side [29]. The comparison between measured and model prediction of the two systems without permeate sweeping are plotted on Fig. 6 (a) and Fig. 6 (b), respectively. For CO_2/N_2 system the composition of 40% CO_2 and 60% N_2 is used. The pressure on high and low side of the membrane is 404 kPa and 101.3 kPa, whereas, the permeability of CO_2 and N_2 used is 63.6 and 3.05×10^{-10} mol/m^2.s.P$_a$, respectively.

In case of O_2/N_2 system, the pressure on high and low side of membrane is 708 kPa and 101.3 kPa and the permeability of O_2 and N_2 used is 8.67 and 2.89×10^{-10} mol/m^2.s.P$_a$, respectively. As shown in Fig. 6 (a), the comparison shows a good agreement between experimental data and model prediction whereas, Fig. 6 (b), the model over predict with slightly higher value than the experimental results.

Similarly, data reported by *Sada et al.* [30] for the mixture of carbon dioxide and air using asymmetric fiber cellulose triacetate membranes are also compared with the model prediction as shown in Fig. 7. The gas mixture used to get experimental data consists of 50% CO_2, 10.50% O_2 and 13.10 % N_2, respectively. The pressure on high and low-pressure side of the membrane is 1570 kPa and 101.3 kPa, whereas, the permeability of CO_2, O_2 and N_2 used is 204.2, 60.2, and 13.1×10^{-10} mol/m^2.s.P$_a$, respectively. Although, the model prediction shown reasonable estimate with the experimental data, the model predicts slightly higher than measured data.

Moreover, *Pan* in 1986, reported experimental data of hydrogen recovery from ammonia plant purge gas [31]. The composition of the purge gas from ammonia synthesis consists of 63% H_2, 21% N_2, 11% CH_4, 3% Ar, and 2% NH_3. The experiments were conducted both in countercurrent and concurrent pattern and shown in Fig. 8(a). As shown, overall a good agreement was obtained between measured
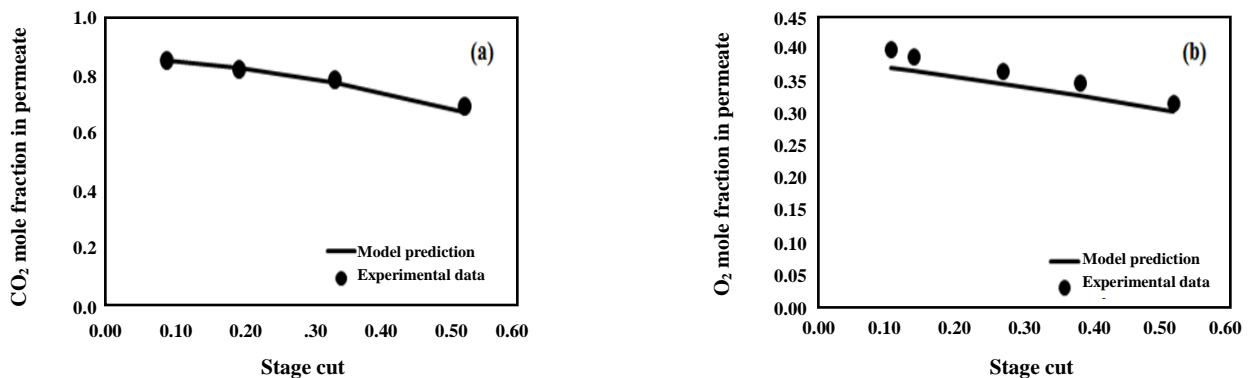
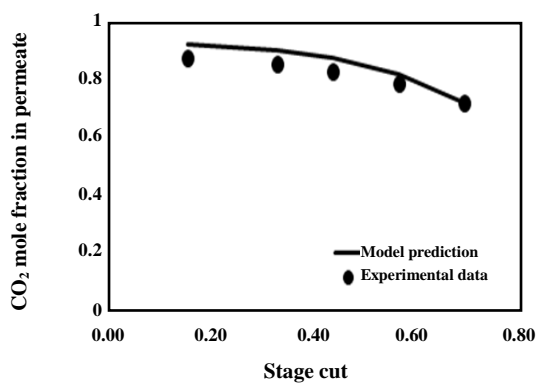*Fig. 6: Comparison of model prediction and experimental data.*

Fig. 7: Comparison of model and experimental data [31] for CO₂/Air system.

data and model prediction. For the countercurrent pattern, the results are in good agreement, while for the co-current pattern, small discrepancies are shown for higher stage cut.

Similarly, *Pan et al.*, also reported experimental data of separation of CO_2/H_2S from sour gas mixture. The feed composition of CO_2 is 48.5 % that is removed in the permeate stream, to increase the recovery of CH_4 on the retentate stream temperature and pressure conditions of $10^{\circ}C$ and the 3,528 kPa on feed stream and 92.8 kPa on permeate stream are used during the experimental findings, respectively [31]. As seen in Fig. 8(b), the results between the model prediction and the experiment result is good agreement with each other. In this study, key emphasis is on the recovery and rejection of CH_4 and CO_2, therefore, further investigate was carried out on parameters such as feed pressure, membrane area and recovery rate on permeate and retentate side.

Effect of operating charactistics on membrane
Feed pressure & recovery of CH₄/CO₂ on retentate and permeate side

The effect of feed pressure on the recovery of methane and CO_2 on the retentate and permeate side along with the area of the membrane are depicted in the Fig. 9 (a&b). As shown on Fig. 9a, as the pressure increase, the recovery of CO_2 on the permeate side also increases, since CO_2 is more permeable in the membrane. It is evident that higher feed-side pressure led to a greater pressure drop on both sides of the membrane creating a driving force for membrane separation. In contrast, as the pressure increases, the methane recovery in the retentate side is increases (Fig. 9b). As shown in the picture (zoomed) the effect of pressure on methane recovery is prominent between $0-4$ bar whereas, high pressure has negligible effect on recovery of methane. Moreover, as shown in Fig. 9b, the membrane area decreases as the pressure increases [32].

CO₂ in feed & membrane area & CH₄ recovery on retentate side

The effect of feed composition on methane recovery for the stage cut of 0.25 is illustrated in Fig. 10. As evident in Fig. 9(a&b), CH_4 recovery on retentate and CO_2 recovery on permeate side are prominent between at pressure between $(0 - 0.4)$ bar therefore, in the composition study feed and permeate side pressure is maintained at $1.20e^{-3}$ and 0.4 bar respectively. It can be observed that increase in CO_2 in the feed gas reduced the methane recovery in the permeate side.

Also, the total membrane area for effective separation of CH_4 in the retentate side decreases with increase in CO_2 concentration $(20 - 70\%)$ in the feed gas [5].
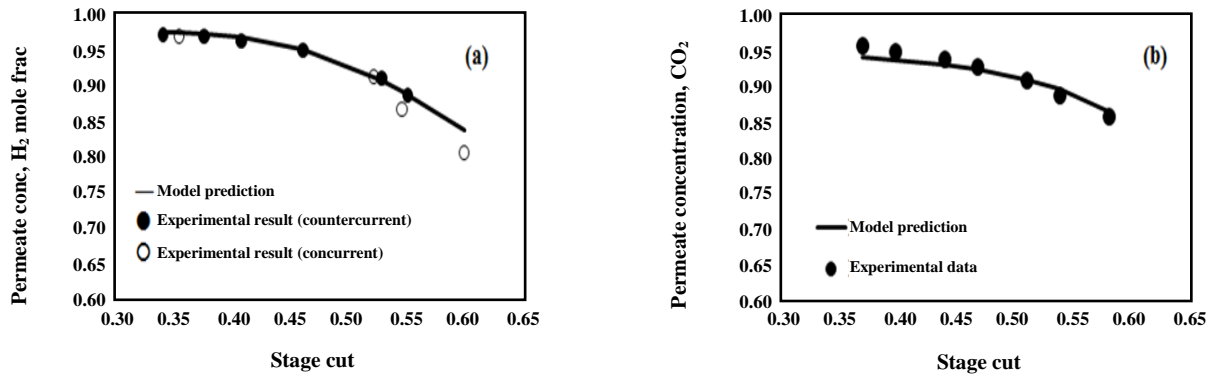
Fig. 8: Comparison of model and measured data of (a) H₂, (b) CO₂ recovery from purge gas from ammonia plant.
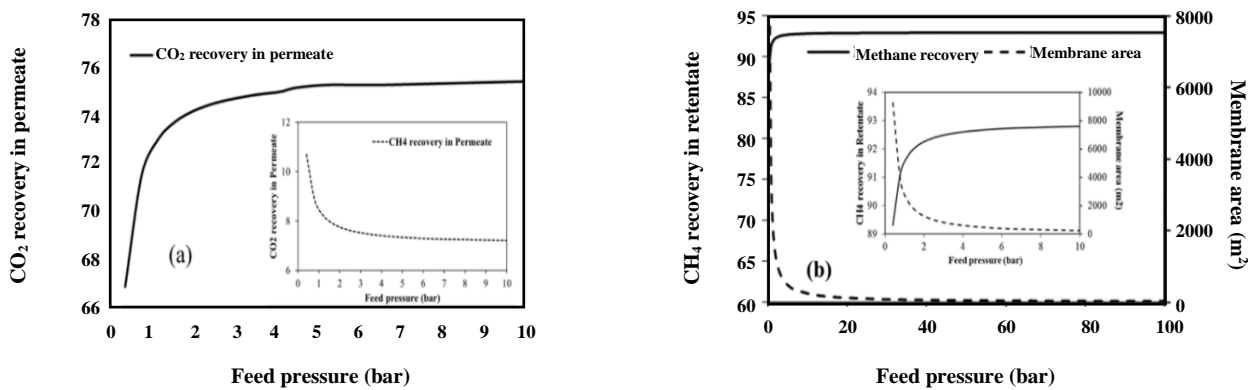

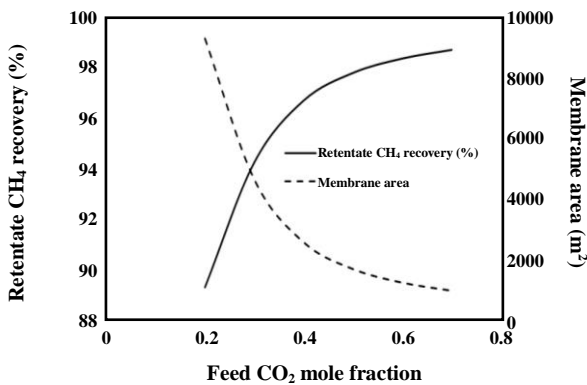**Fig. 9: Effect of pressure on (a) recovery of CO₂ and on membrane area, (b) recovery of CH₄ in the retentate side.**

Fig. 10: Effect of CO₂ mole fraction in feed on CH₄ retentate recovery and membrane area.

Analysis of Hybrid membrane and Amine absorption process

A standard process flow sheet was simulated using Aspen HYSYS V10, as shown in Fig. 4. The specification for the standard base simulation along with amine base solvent used is also shown. The amine package consisting of the non-ideal Acid Gas-Chemical Solvent equation of state was used. The package incorporated into latest version of Aspen HYSYS V10, selectively considers acid gases, mainly CO_2 and H_2S, and amines such as DEA, DGA, DIPA, MDEA, MEA, PZ, TEA, respectively. Operating conditions and amine strength are considered for all hybrid processes using different amine solutions.

Equation of State (EoS) validation with experimental data

The equation of state used in this study is validated with experimental solubility data from literature using amine as MDEA, MEA and DEA. The sources for the experimental data are shown in the Table 2 – Table 4, whereas, the comparison of experimental and predicted value from EoS is illustrated in the Fig. 11 – Fig. 13, respectively.

*Table 2: Loadings (α) values of CO_2 in MEA at different concentration (C), temperature (T) and pressure (P).*

Researcher	T/°C	C (mole/litre)	Alpha	P/kPa	NDP	Ref
Jones et al.	40, 60, 80, 100, 120, 140	15.25	0.017 - 0.728	0.00266 - 930.990	54	[34]
Lee & Mather	40, 100	15.25, 30.5	0.139 - 1.19	1.15142 - 6616	45	[35]
Lee & Mather	40, 100	30.5	0.067 - 1.00	0.068947 - 6894.7	22	[36]
Lee & Mather	25, 40, 60, 80, 100, 120	6.1, 15.25, 22.875, 30.5	0.065 - 2.152	0.1 - 10000	256	[36]
Lawson & Garst	40, 60, 80, 93.333, 100, 120, 134.44, 140	15.25, 30.5	0.11 - 0.998	1.33 - 2784.44	24	[37]
Lee & Mather	40, 100	15.25	0.074 - 1.166	0.1 - 7000	22	[36]
Nasir & Mather	100	30.5	0.004 - 0.199	0.00214 - 2.96	38	[38]
Isaacs et al.	80, 100	15.25	0.035 - 0.315	0.0066 - 1.75	19	[39]
Shen & Li	40	15.25	0.561 - 1.049	15.7 - 2550	13	[40]
Dawodu & Meisen	100	25.62	0.541 - 0.723	455 - 3863	5	[41]
Jou & Mather	0, 25, 40, 60, 80, 100, 120, 150	30	0.536 - 1.331	82 - 19954	60	[42]
Mamun & Nilsen	120	30	0.155 - 0.4182	7.354 - 191.9	19	[43]
Aronu et al.	40, 60, 80, 100	15, 30, 45, 60	0.0017 - 0.565	0.0007 - 478.99	147	[44]
Tonga et al.	40, 60, 80, 100, 120	30	0.0446 - 0.965	3.95 - 983.5	60	[45]

Table 3: Loadings (α) values of CO_2 in MDEA at different concentration (C), temperature (T) and pressure (P).

Researcher	T/°C	C (mole/litre)	Alpha	P/kPa	NDP	Ref
Jou et al.	25, 40, 70, 100, 120	23.34, 48.9	0.00037 - 1.833	0.00161 - 6380	120	[46]
Chakma & Meisen	100, 140, 160, 180, 200	19.8, 48.9	0.021 - 1.304	103 - 4930	75	[47]
Mac Gregor & Mather	40	23.34	0.124 - 1.203	1.17 - 3770	5	[48]
Shen and Li	40, 60, 80, 100	30	0.189 - 1.108	1.1 - 1979	45	[40]
Jou et al.	40, 100	35	0.002 - 0.271	0.004 - 262	37	[49]
Dawodu & Meisen	100, 120	48.9	0.123 - 0.497	162 - 3832	12	[41]
Kuranov et al.	40, 60, 100, 120, 140	18.8, 19.2, 32.1	0.184 - 1.2514	73.5 - 5036.7	78	[48]
Mathonat et al.	40, 70, 100	30	0.87 - 1.26	2000 - 10000	9	[50]
Silkenbaumer et al.	40	30	0.24 - 1.206	12.01 - 4080	10	[51]
Lemoine et al.	24.55	23.63	0.0171 - 0.2625	0.02 - 1.636	13	[52]
Park & Sandall	50, 75, 100	50	0.015 - 0.4884	0.78 - 140.4	30	[53]
Kamps et al.	40 , 70, 100	32, 48.8	0.126 - 1.243	176.5 - 7565	28	[54]
Boumedine et al.	25, 40, 65	25.73, 46.88	0.008 - 1.288	2.96 - 4560	85	[55]
Mamun et al.	55, 75, 85	50	0.1658 - 0.6898	65.75 - 813.4	37	[43]
Ermatchkov et al.	40, 70, 100	18.5 - 48.9	0.003194 - 0.7233	0.12 - 63.9	101	[56]
Derks et al.	40	23.34	0.122 - 0.81	1.25 - 93.6	10	[57]
Najibi & Maleki	25, 40, 60, 70, 80, 100, 120	23.34, 48.9	0.083 - 0.83	30.8 - 82.91	14	[58]

Table 4: Loadings (α) values of CO₂ in DEA at different concentration (C), temperature (T) and pressure (P).

Researcher	T/ºC	C (mole/litre)	Alpha	P/kPa	NDP	Ref
Lee et al.	0, 25, 50, 75, 100, 120, 140	5.25, 20.6, 35.4, 49.7, 63.7, 77.6	0.015 - 2.695	0.69 - 6894.743	322	[59]
Lee et al.	25, 50, 75, 100, 120	5.25, 20.6, 35.4, 49.7	0.022 - 2.695	0.69 - 6894.743	163	[60]
Lee et al.	50	20.6	0.04 - 1.281	0.07 - 6894.743	11	[35]
Lawson & Garst	37.78, 65.56, 79.44, 93.33. 107.22, 121.11	25	0.32 - 1.167	1.99 - 4372	37	[37]
Kennard & Meisen	100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 205	10, 20, 30	0.193 - 1.427	91 - 3746.7	133	[61]
Lal et al.	40, 100	20.6	0.005 - 0.367	0.002 - 3.34	44	[62]
Dawodu & Meisen	100	42.1	0.299 - 0.725	93 - 3742	6	[41]
Rogers et al.	50	20.2	0.006 - 0.233	0.0003 - 0.55	14	[63]
Boumedine et al.	25, 75	41.78	0 - 1.088	2.46 - 4662.7	26	[55]
Seo & Hong	40, 60, 80	30	0.404 - 0.727	4.85 - 357.3	16	[64]
Young Eun Kim et al.	40, 60, 80	30	0.279 - 0.502	115	3	[65]
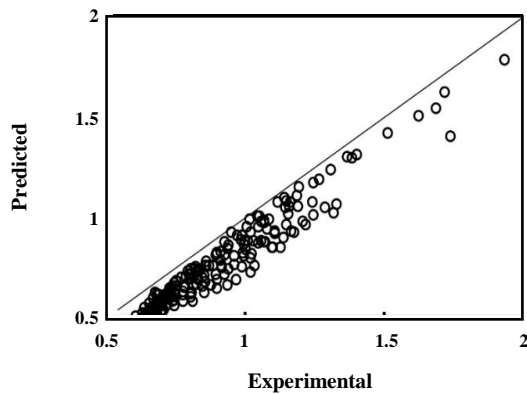
Fig. 11: Experimental vs predicted loading data (α) of CO₂ in MEA.

Analysis of Hybrid membrane and Amine absorption

The quantitative comparison between experimental data points and simulation results are made using Absolute Deviation percentage (AD %) as

$$AD\% = \left(\frac{|\alpha_{calc} - \alpha_{exp}|}{\alpha_{exp}} \right).100 \ \% \qquad (1)$$

The Mean Absolute Percentage Error (MAPE) is calculated using the following equation

$$MAPE = \frac{1}{n}\left(\frac{|\alpha_{calc} - \alpha_{exp}|}{\alpha_{exp}} \right).100 \ \% \qquad (2)$$

Where 'α' is loading of acid gas, subscripts '*cal*' and '*exp*' represents calculated and experimental values and '*n*' represent number of data points.

The literature solubility data for MEA, from various source as shown in Table 2 is compared with the EoS model prediction and illustrated on Fig. 11. Overall a reasonable agreement is obtained between EoS model prediction and the experimental, whereas, a divergence in result is attained at some data points at low pressure conditions [32, 33]. It is evident from the literature that most of the model performs poorly at low loading conditions. The mean error between experimental and calculated CO₂ loading is less than 20%.

Similarly, literature solubility data of CO₂ in MDEA are collected from different source as shown in Table 3. The literature data are used for the comparison study with the simulated result. As shown in Fig. 12, both experimental and the model (EoS) prediction shown reasonable estimation with the experimental data. The mean error between experimental and calculated CO₂ loading is less than 20%. As illustrated in Fig. 9, in combination with Fig. 12, at low pressure (0-1) bar, the deviation between experimental and simulated are large and it improves at higher pressure.

Moreover, the comparison study is further extended to the solubility of CO₂ in DEA at various conditions. The literature data is collected from different sources as shown in Table 4, is compared with the simulated result from the model (EoS) used in this work. Fig. 13, shows
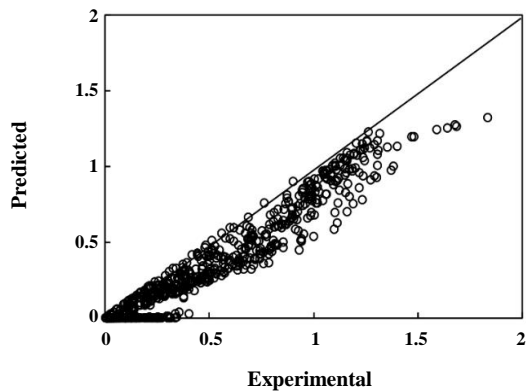
Fig. 12: Experimental vs predicted loading data (α) of CO_2 in MDEA.

Fig. 13: Experimental vs predicted loading data (α) of CO_2 in DEA.

the comparison between prediction and experimental data points. Overall, the prediction provides a reasonable estimate with the literature data. Similar to previous reported results, the mean error between experimental and calculated CO_2 loading is less than 19%.

Effect of lean loading of CO_2 on the reboiler duty

Number of stages in absorber and stripper of amine absorption process are arbitrarily chosen to be 10 and 20, respectively. The number of stages required for both the absorber and regenerator columns were optimized in simulation to minimize the reboiler duty. The effect on the reboiler duty was studied by varying the lean loading of CO_2 from $0.05 - 0.4$, for different amine solution such as MDEA, MEA, DEA, TEA, DGA, DIPA and MDEA+ MEA. Different CO_2 concentration in feed to amine unit (5, 15 and 20%) are used in the study. However, due to similar overall trends only 20 mol % of CO_2 in the feed is shown here.

Fig. 14, shows the effect of lean loading of various amines on the reboiler duty for a targeted CO_2 recovery and purity when a CO_2 concentration in the feed gas to amine unit is 20 mol%. As compared in Fig. 14, for various amines studied, the required heat duty decrease as the lean loading increases. In comparison with other amines, MEA consumed higher reboiler duty, whereas, for DEA is the lowest. Moreover, the slope of reboiler heat duty curve for MEA, are steeper between lean loadings of 0.05 to 0.25, whereas, for DEA almost invariant change in slope in curve is observed.

As shown in Fig. 14, for both MEA and DEA, the slope of the curve decreases with increase in lean loading and
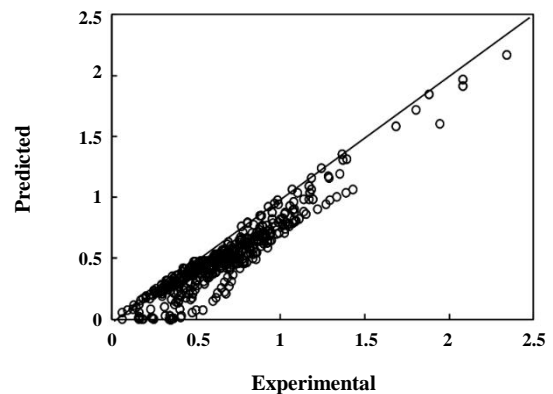
the optimized reboiler heat duty is found to be proportional to the lean loading value of 0.30, which is approximately $1.25e^5$ kW. Also at lean loading of 0.05 (mol of CO_2/mol of MEA or DEA), a large amount of heat is required (approx. 1.9e5kW) at the reboiler to separate the desired CO_2. Similarly, at low solvent circulation rate, heat energy consumed by the reboiler to separate the CO_2 is very high. Therefore, at low lean CO_2 loading, a significant amount of additional energy is required during regeneration process. As the lean loading is increases the reboiler duty start to decrease until it reaches to a plateau above 0.30. Further, increase in lean loading of CO_2, the slope of the curve become linear.

Consequently, the amine solution with a higher CO_2 loading can be regenerated more easily with low reboiler duty as compared to lower CO_2 loading with high reboiler duty. Moreover, the CO_2 loading of lean solution against reboiler duty need to be adjusted so that the energy consumption at the regeneration unit can be reduced, while keeping the target capture performance. This also helps in overall reduction in cost of the capture process. Furthermore, it is also worth to discuss the comparison between the different CO_2 lean-loading of different amines on reboiler heat duty. Due to lower heat of reaction and latent heat of vaporization, DEA, offers better energy savings than MEA [66]. Conversely, lean CO_2 loading with other solvents such as MDEA, TEA, DGA, DIPA and combination of MDEA + DEA, shows even better result of energy reduction. The get clear illustration and comparison Fig. 10 is zoomed. As shown that DGA, offers the lowest overall reduction in reboiler heat duty for regeneration.
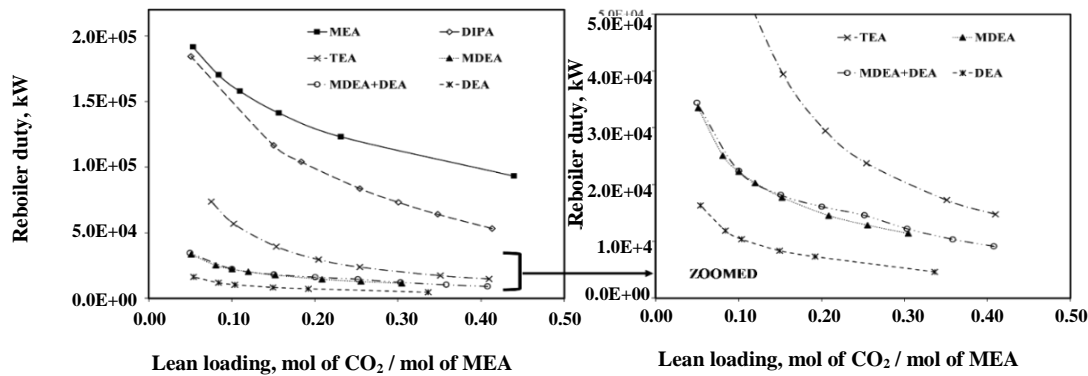
Fig. 14: Reboiler duty for the targeted CO₂ recovery and purity when lean loading varies from 0.05 to 0.40 (mol CO₂/ mol amines) for high CO₂ in feed.
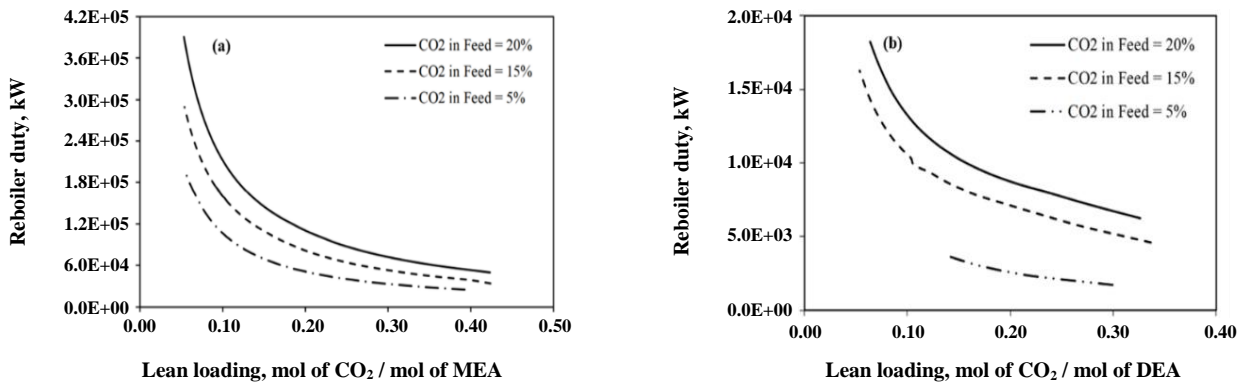

Fig. 15: Reboiler heat duties at different CO₂ concentration with lean loading (a) MEA and (b) DEA.

Moreover, the reboiler duty required to treat different gas mixture to design specification was investigated for other feed gas to amine unit with concentration of CO_2 varies to 5, 15 and 25%, respectively.

After testing all solvents and considering similar effects on the reboiler duty at the studied concentrations plotted against lean loading, only MEA and DEA are selected for illustration as shown on Fig. 15 (a) and Fig. 15 (b), respectively. As shown, the reboiler duty decreases and reaches to a plateau for a lean loading of 0.25 afterwards. It is also obvious that the MEA is more advantageous when the CO_2 content in the feed gas mixture is lower. A similar behavior is seen in case of DEA.

In literature there is no such evidence that hybrid amine membrane setup offer any advantages for the post-combustion CO_2 removal [21]. Moreover, both membrane and amine were studied as series and in parallel arrangement and it was concluded that the hybrid setup

consist of membrane and MEA might not be a good choice for post-combustion CO_2 capture.

The standalone in comparison with hybrid process utilizes the lowest energy [21, 66]. It is coherent from Fig. 15, that as the CO_2 concentration increases, the reboiler duty also increases. In the literature, membranes unit are used as multistage membrane setup with or without permeate or retentate recycle. However, to further gain insights into how the hybrid system performs, in particular using different amines used in separation process. It is preferable to arrange the configuration in a most straight forward consist of single stage membrane and Amine unit setup, as shown in Fig. 4.

Effect of CO₂ concentration in the feed on the total energy, with or without membrane unit

The total energy consumed in cooler, pump, regenerator reboiler and regenerator condenser in
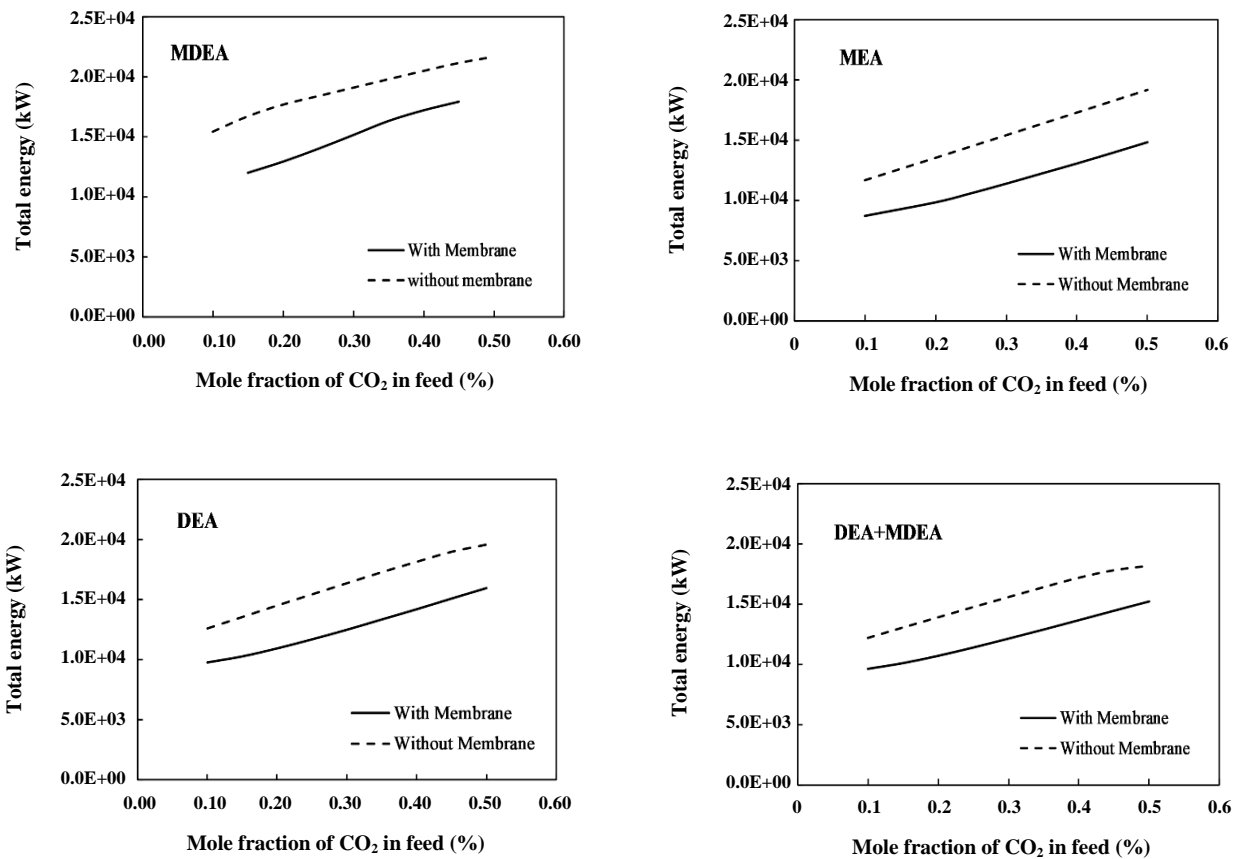
Fig. 16: Total energy consumed with/without membrane vs CO_2 composition in feed.

alkanolamine unit of hybrid unit (amine & membrane) are studied at various feed gas concentration. Different amines such as MDEA, MEA, DEA and DEA+MDEA are selected in this study along with CO_2 whose concentration varies from 0.1 – 0.5 mole %, while keeping the H_2S concentration to 0.1 mole %. The rest of the condition used in this case study is illustrated in Table 5. As shown in Fig. 16, overall the total energy consumed using standalone amine process or hybrid setup consist of amine and membrane increases with increase CO_2 composition in the feed. However, reduction in total energy is observed when hybrid setup is used as compared to amine unit as individual process.

Moreover, the comparison of total energy consumed in hybrid system, for various amine solution, and by various CO_2 concentration in the feed is also studied and illustrated in Fig. 17. The results shows, with MDEA used in amine absorption process, the total energy consumed is the highest and MEA is the lowest.
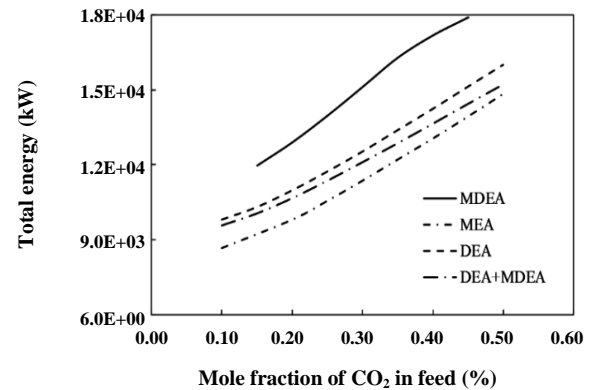

Fig. 17: Total energy consumed with different amines in hybrid setup with increase in CO_2 composition in feed.

Also, from Fig. 17, among membrane and amine unit, amine adsorption process consumes more energy unlike membrane process where no addition energy is required to boast the permeation and rejection.

CONCLUSIONS

The study focus on studying various amines used in absorption process and its effect on energy penalty, considering standalone amine process or hybrid setup consist of single stage membrane and amine process. The membrane with multi-stage configuration are always advantageous, however, single permeator setup with complete mixing model are chosen for simple and quick computation response. As different amines are tested in amines absorption process, the overall energy requirement in hybrid process was significantly reduced, whereas, the MEA capture offers more advantageous with energy penalty to its lowest as compared to other amines used. Furthermore, the new EoS in Aspen HYSYS, produced a reasonable estimate of CO_2 solubility in amines which confirms its suitability in acid gas recovery unit.

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