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Alternative solvents for post combustion carbon capture

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Abstract

The process model of post combustion chemical absorption is developed in Aspen Plus for both coal and gas fired power plant flue gas treating. The re-boiler energy requirement is considered as the most important factor to be optimized. Two types of solvents, mono-ethylamine (MEA) and di-ethylamine (DEA), are used to implement the model for three different efficiencies. The re-boiler energy requirement for regeneration process is calculated. Temperature and concentration profiles in absorption column are analyzed to understand the model behavior. Re-boiler energy requirement is considerably lower for DEA than MEA as well as impact of corrosion also less in DEA. Therefore, DEA can be recommended as a better solvent for post combustion process for carbon capture plants in fossil fuel fired power industries.

Keywords: Carbon dioxide capture; Flue gas; MEA; DEA; Re-boiler duty.

1. Introduction

Global climate change has rapidly become the most prominent environmental issue in the present day. It is a well-known fact that the main contributor for the issue is the fossil fuel based energy generation. It can be solved either by shifting to renewable energy sources (clean energy sources) or eliminating the emission of available plants with emission reduction technologies. However, green house gas emission free technologies will not be practical solution in near future. Therefore, most possible alternative is carbon capture and sequestration as it can be applied in existing power plants and industries without major modifications. The most well-established method for carbon dioxide (CO_2) capture is post combustion chemical absorption method with alkanolamine solvents. Weak base amines are reacted with CO_2 and other acid gases to form weak chemical bonds. Alkanolamine can be mainly categorized as, primary (monoethanolamine-MEA, diglycolamine-DGA), secondary (diethanolamine-DEA) and tertiary (methyldiethanolamine-MDEA, triethanolamine-TEA) amines. However, the most applicable amine among them is MEA, due to the low partial pressure of CO_2 in the flue gas of fossil fuel fired power plant [1]. The most important parameter when designing a carbon capture plant is operating cost, which is related to the energy requirement in regeneration process. Even though MEA is widely use amine for CO_2 capture, regeneration energy requirement is high for that process. Therefore, alternative solvents should be analyzed to perform the post combustion capture process with fewer energy requirements.

Both MEA and DEA are considered as highly reactive amines for gas absorption process [2]. However, secondary amines are less corrosive as well as required less heat of regeneration, due to an additional ethanol group [3]. The objective of this research was to compare the possible solvents that can be used for post combustion CO_2 capture with lower energy requirement. In this study, MEA and DEA solvents are selected to optimize the CO_2 capture process. Operating conditions are selected to avoid the main drawback of alkanolamine, which is large energy requirement. The physical properties of both amines are summarized in Table 1 [4].

Table 1. Basic information about MEA and DEA

Specification	MEA	DEA
Chemical formula	C_2H_7NO	$C_4H_{11}NO_2$
Amines category	Primary	Secondary
Molecular weight [g/mol]	61.08	105.14
Density [g/cm^3]	1.012	1.090
Boiling point[°C]	170	217

2. Model development

For the analysis of the solvent for carbon capture process, the Aspen Plus flow sheet modeling tool is used. The CO_2 removal model for both coal and gas fired flue gases is developed. According to the solvent type, parameters and operating conditions have to be selected. The most versatile property method in Aspen Plus, that is Electrolyte Non Random Two Liquid (NRTL) method, is used to implement the process optimization. The model is developed for 85%, 90% and 95% removal efficiencies. The flue gas compositions for both coal and gas fired systems are given in Table 2.

Table 2. Inlet flue gas composition and parameters used for the simulations [5, 6]

Parameter	Coal Fired	Gas Fired
Flow rate [kg/s]	673.4	793.9
Temperature [K]	313	313
Pressure [bar]	1.1	1.1
Major Composition	Mol%	Mol%
H_2O	8.18	8.00
N_2	72.86	76.00
CO_2	13.58	4.00
O_2	3.54	12.00
H_2S	0.05	0.00

The reactions used for the CO_2 capture model with MEA and DEA are tabulated in Table 3 [7]. The equilibrium and kinetic data are taken from the literatures and the Aspen Plus databanks for the calculations and given in the same table [8, 9]. The reactions 4 and 5 are only valid for coal fired flue gas reacting system.

The required operating conditions for MEA and DEA in Electrolyte NRTL property method are present in Table 4 [10]. Aspen Plus simulation tool has certain limitations and indicate below. The limitations of MEA and DEA mass fractions are 50 and 30 [w/w%] respectively.

The optimal specifications for the coal and gas processes such as amine concentration, lean loading, and solvent flow rate are summarized in Table 5 for different efficiency values. Optimum specifications are selected after the number of simulations which has been performed in previous studies [11].

The concentration of DEA has to be maintained less compared to MEA concentration. Even though in previous studies, it has shown that higher concentration will lead to lower re-boiler energy requirement, it is not accurate to perform simulation for higher concentrations due to limitations in Aspen Plus simulation tool (Table 4).

The basic process flow scheme for post combustion process is shown in Figure 1. The description of the process is given in the previous publications [12].

The most suitable column specification for model development is given in Aspen Plus [9] and Mohammad [13].

Table 3. Chemical reactions of MEA and DEA process

Reactions	Reaction number	**Thermodynamic behavior**			
		A_j	B_j	C_j	D_j
MEA+CO_2+H_2O system					
$2H_2O \leftrightarrow OH^- + H_3O^+$	(1)	132.89	-13445.9	-22.47	0
$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$	(2)	231.46	-12092.1	-36.78	0
$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$	(3)	216.05	-12431.7	-35.48	0
$H_2O + H_2S \leftrightarrow HS^- + H_3O^+$	(4)	214.58	-12995.4	-33.55	0
$H_2O + HS^- \leftrightarrow S^{2-} + H_3O^+$	(5)	-9.74	-8585.47	0	0
$MEAH^+ + H_2O \leftrightarrow MEA + H_3O^+$	(6)	-3.038	-7008.3	0	-0.00313
$MEACOO^- + H_2O \leftrightarrow MEA + HCO_3^-$	(7)	-0.52	-2545.53	0	0
DEA+CO_2+H_2O system (In addition to reactions 1-5)					
$DEAH^+ + H_2O \leftrightarrow DEA + H_3O^+$	(8)	-13.3373	-4218.70	0	0.00987
$DEACOO^- + H_2O \leftrightarrow DEA + HCO_3^-$	(9)	16.5026	-4068.76	-1.502	0
$ln\, K_j = A_j + \frac{B_j}{T} + C_j\, ln\, T + D_j T$	(10)	Equation for equilibrium constants			
		Kinetic behavior			
		k_j	n_j	E_j	T_o
MEA+CO_2+H_2O system					
$CO_2 + OH^- \rightarrow HCO_3^-$	(11)	4.32e+13	0	13249	298
$HCO_3^- \rightarrow CO_2 + OH^-$	(12)	2.38e+17	0	29451	298
$MEA + CO_2 + H_2O \rightarrow MEACOO^- + H_3O^+$	(13)	9.77e+10	0	9855	298
$MEACOO^- + H_3O^+ \rightarrow MEA + CO_2 + H_2O$	(14)	2.7963e+20	0	17229	298
DEA+CO_2+H_2O system (In addition to reactions 11-12)					
$DEA + CO_2 + H_2O \rightarrow DEACOO^- + H_3O^+$	(15)	6480000	0	5072	298
$DEACOO^- + H_3O^+ \rightarrow DEA + CO_2 + H_2O$	(16)	1.34e+17	0	11497	298
$r_j = k_j \left(\frac{T}{T_0}\right)^{n_j} exp\left[-\frac{E_j}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$	(17)	Equation for rate constants			

Table 4. Range of applicability of amine models [10]

Range of applicability	MEA	DEA
Temperature [K]	<393.15	<413.15
Concentration [w/w%]	<50	<30

Table 5. Optimum solvent conditions for both coal and gas fired power plant flue gas capture process

Specification	85% Removal Efficiency		90% Removal Efficiency		95% Removal Efficiency	
Coal fired power plant CO_2 capture						
	MEA	DEA	MEA	DEA	MEA	DEA
Amine concentration [w/w%]	40	30	40	30	40	30
CO_2 lean loading [mole CO_2/mole amine]	0.27	0.05	0.27	0.05	0.25	0.05
Solvent flow rate [tonne/hr]	7845	8698	8480	9620	8400	10825
Gas fired power plant CO_2 capture						
Amine concentration [w/w%]	40	30	35	30	30	30
CO_2 lean loading [mole CO_2/mole amine]	0.30	0.10	0.25	0.10	0.25	0.10
Solvent flow rate [tonne/hr]	3624	4053	3168	4421	3890	6000

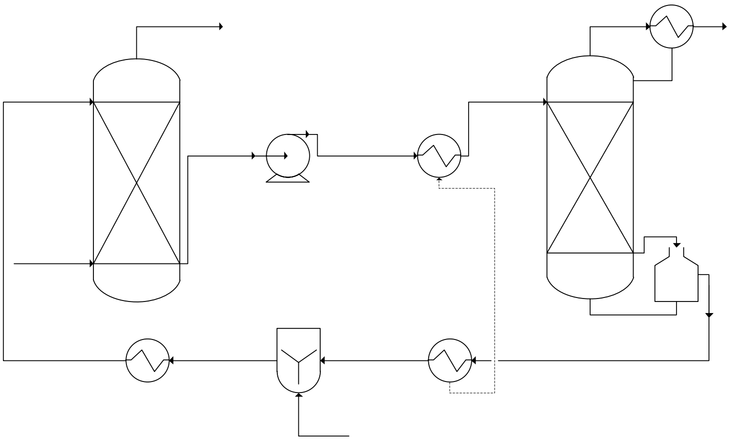

Figure 1. Process flow diagram of post combustion chemical absorption

3. Simulations

The CO_2 capture model is developed for three different efficiencies as 85%, 90% and 95% for both coal and gas fired power plant flue gases. The selected solvent conditions are used for the model implementation with recommended column parameters. Temperature profiles and CO_2 loading profiles are analyzed for both cases. Figures 2-5 represent the liquid and vapour phase temperature profiles in absorber column for coal and gas fired capture model.

According to Figures 2 and 3, maximum temperature for coal fired flue gas capture process with MEA as solvent is in the range of 347 - 352 K. However, for DEA solvent process the maximum temperature reach slightly lower values, and it is around 342 - 346 K. When efficiency is higher, temperature profiles also show higher values for both MEA and DEA. Liquid and vapor phases have almost similar patterns for both solvent cases. The absorber tends to exhibit a temperature bulge at the top of the column for both liquid and vapor phase. Temperature bulge is due to highly exothermic reactions at the top of the column.

Gas fired process show lower temperature profiles compared to coal fired system. Maximum temperature is around 330-331 K and 326-330 K for MEA and DEA solvent systems, respectively. However, maximum temperature is varying with removal efficiencies. Higher removal efficiencies have higher temperature profiles along the absorption tower. The shape of the temperature profiles has the similar patterns mentioned in the literatures even though the maximum temperature value is different [14].

Figure 6 is representing the CO_2 loading profiles in absorption column for coal fired flue gas treating system for both MEA and DEA solvents. The CO_2 loading profiles for MEA are having higher values compared to DEA. Lower efficiency process models are showing higher CO_2 loading profiles. However, rich loading values are closer for all efficiencies and slightly higher for 85% removal model. Figure 7, which is showing CO_2 loading profiles for gas fired flue gas systems, have similar patterns.

The rich loading values for different models (six models for MEA and six models for DEA for coal and gas fired systems) are given in Table 6. The required re-boiler energy duties are tabulated in the same table for all the cases with necessary solvent circulation rates.

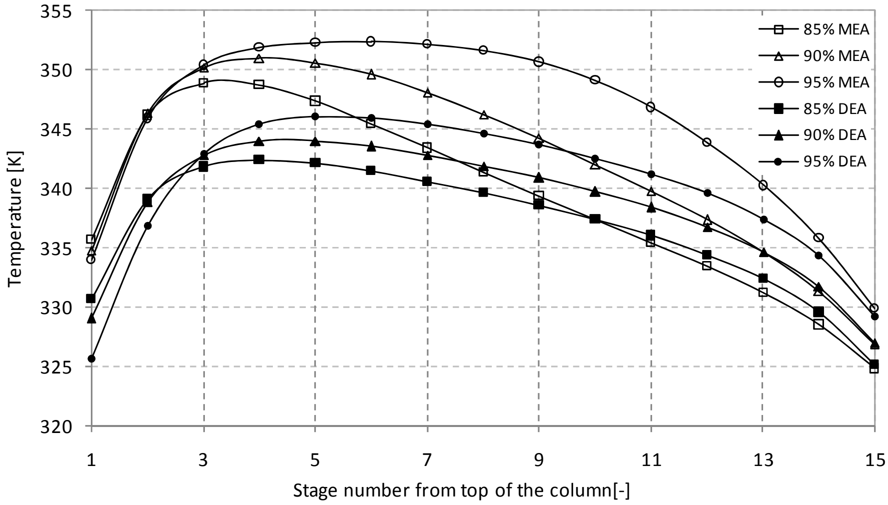

Figure 2. Liquid phase temperature profiles in absorption column for coal fired flue gas

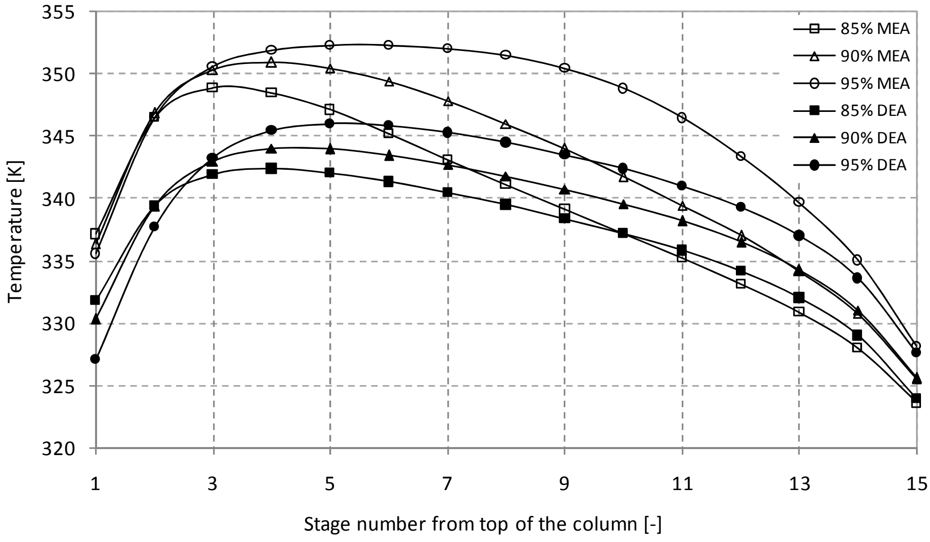

Figure 3. Vapor phase temperature profiles in absorption column for coal fired flue gas

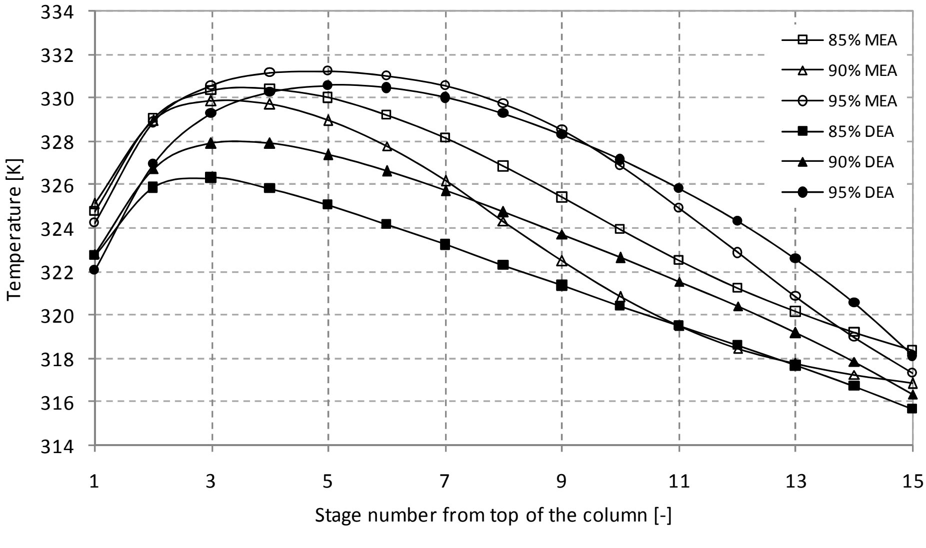

Figure 4. Liquid phase temperature profile in absorption column for gas fired flue gas

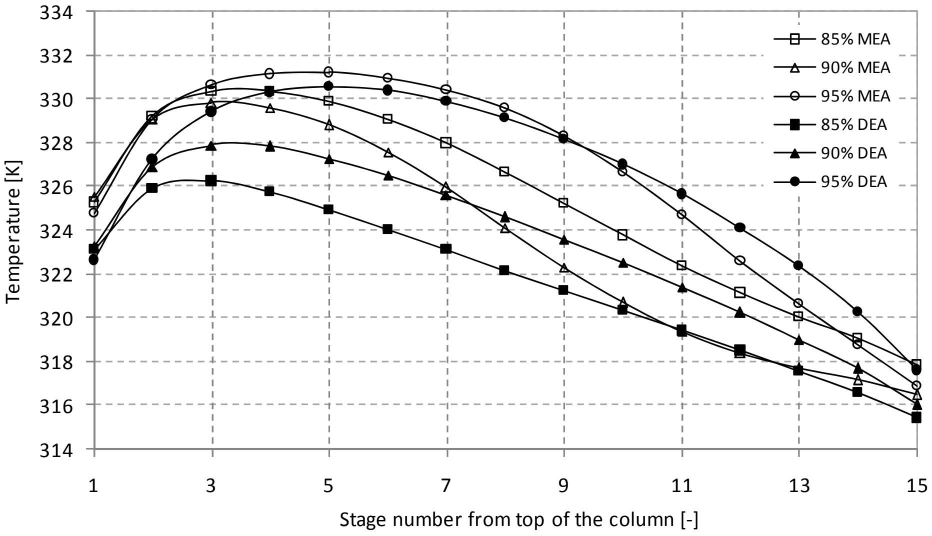

Figure 5. Vapor phase temperature profile in absorption column for gas fired flue gas

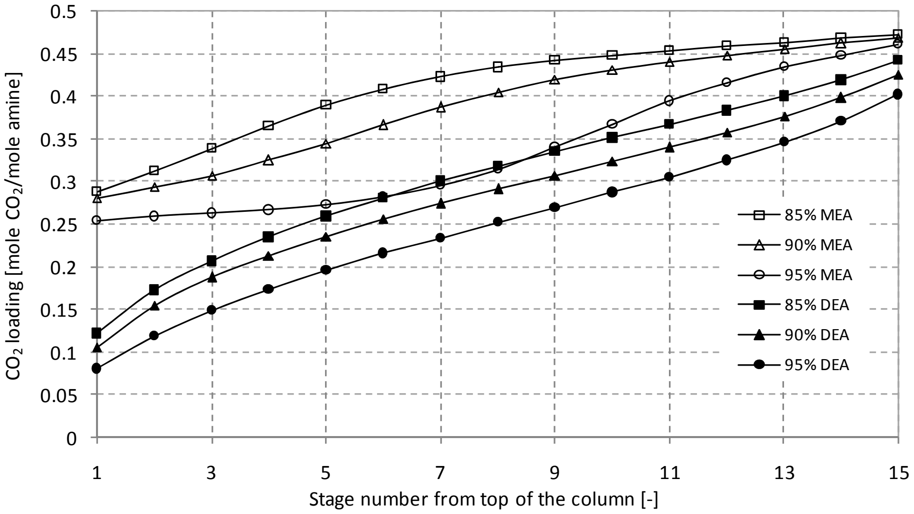

Figure 6. CO_2 loading profiles in absorption column for coal fired flue gas

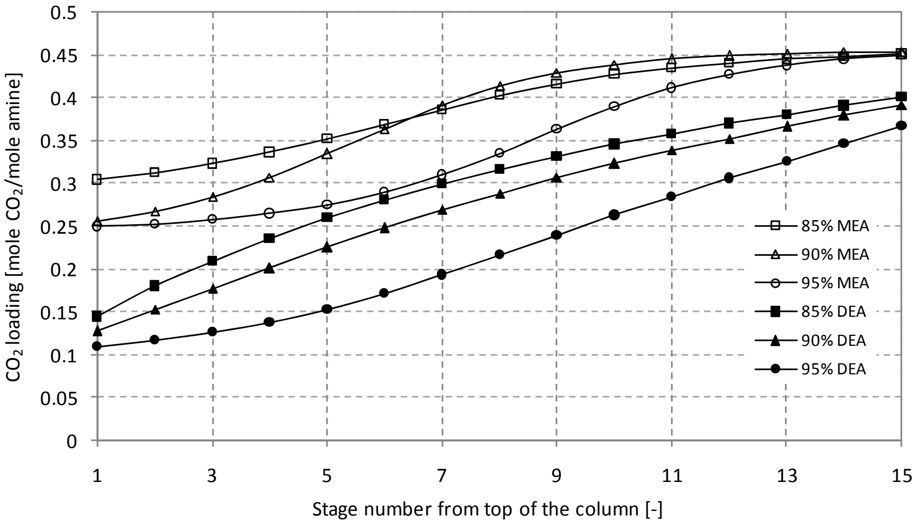

Figure 7. CO_2 loading profiles in absorption column for gas fired flue gas

Table 6. Re-boiler energy requirement, rich loading and solvent circulation flow rate for coal and gas fired processes

Specification	85% Removal Eff.		90% Removal Eff.		95% Removal Eff.	
Coal fired power plant CO_2 capture						
	MEA	DEA	MEA	DEA	MEA	DEA
Re-boiler duty[kJ/kg CO_2]	3507	3371	3581	3462	3914	3747
CO_2 rich loading [mole CO_2/mole amine]	0.473	0.442	0.469	0.425	0.461	0.402
Solvent flow rate [tonne/hr]	7845	8698	8480	9620	8400	10825
Gas fired power plant CO_2 capture						
Re-boiler duty[kJ/kg CO_2]	3641	3381	3982	3471	4100	3756
CO_2 rich loading [mole CO_2/mole amine]	0.451	0.400	0.454	0.392	0.449	0.367
Solvent flow rate [tonne/hr]	3624	4053	3168	4421	3890	6000

As it can be seen from the Table 6, DEA processes have lower re-boiler energy demand for all the cases. Gas fired processes have a slightly higher re-boiler energy requirement than coal fired system. Reason for that is, gas fired flue gas consist of less amount of CO_2. Therefore, a large amount of liquid flow has to be purified in the stripper. Therefore, energy requirement to heat the solvent is high for gas fired process. When removal efficiency is increasing, re-boiler energy requirement also increases. Reason for that is, to capture a higher amount of CO_2, it has to process higher solvent in the stripper. DEA process shows lower re-boiler duties for all the models. The 85% removal model of DEA process has 3371 kJ/kg CO_2 for coal fired system and 3381 kJ/kg CO_2 for gas fired system. This is lower value compared to 3507 kJ/kg CO_2 and 3641 kJ/kg CO_2 for coal and gas fired MEA solvent systems, respectively. Similar to that, all the efficiency models show lower re-boiler duties for DEA processes. This is an agreement with the literatures, that Veawab et al. [15] reported that solvent regeneration energy is decreasing in the order MEA>DEA>MDEA. Reason behind that is, DEA has lower heat of reaction compared to MEA process. The overall re-boiler energy requirement mainly consists of three major parts. The energy needed to liberate the CO_2 from amines, heat required to increase the solvent temperature and energy uses for water evaporation process. DEA has lower CO_2 loading efficiency than MEA solvent, and that will cause for a higher amount of solvent circulation rate. Even though DEA solvent circulation rate is higher compared to MEA process, DEA has less heat of reaction. Therefore, heat of reaction or heat required to liberate the attached CO_2 will dominate to have less re-boiler duty for all these cases.

When we consider about corrosions, Veawab [16] noted that corrosion takes place in almost every section of the capture plant. The impact of corrosion depends mainly on few factors, including CO_2 loading, amine type and concentration, temperature and degradation products [17]. The corrosivity of amines decrease in the order of MEA>AMP>DEA>MDEA [18]. Therefore, DEA is better compared to the MEA in the sense of that.

4. Conclusion

Using DEA will reduce the corrosive effect and required less amount of energy in the regeneration process. The 85% removal model of DEA process has 3371 kJ/kg CO_2 for coal fired system and 3381 kJ/kg CO_2 for gas fired system. This is lower value compared to 3507 kJ/kg CO_2 and 3641 kJ CO_2 for coal and gas fired MEA solvent systems, respectively. Similar to that, all the efficiency models show lower re-boiler duties for DEA processes. However, circulation rate is high in DEA model compared to MEA process because of low reactivity. That will cause for increasing operational cost. Typical temperature profiles for liquid and vapour phase in the absorber model is analyzed together with CO_2 loading profiles. Temperature profiles are important to understand since it shows the reaction behavior. The shape, value and the point of maximum temperature bulge depend upon where in the column the bulk of the acid gas is absorbed into lean solvent as well as heat of reactions, evaporation and amount of vapour and liquid flow rate. Finally, DEA can be recommended for coal and gas fired flue gas capture for removal efficiencies.

Nomenclature

K	equilibrium constant for thermodynamic model	R	gas constant [J/mol K]
A, B, C, D	constants	k	reaction rate coefficient
T	temperature [K]	j	component name
E	activation energy [J/mol]	r	reaction rate

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