

SIMULATION-ASSISTED STUDY OF TEMPERATURE, PH, ENERGY CONSUMPTION AND SEPARATION PERFORMANCE FOR DIFFERENT AMINES AND AMINE MIXTURES IN CO₂ REMOVAL UNIT OF AMMONIA PLANT

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Abstract

Design of CO₂ removal unit of an ammonia plant of one Iranian petrochemical complex is based on Mono Ethanol Amine (MEA). Corrosion problems have been shown to be highly problematic in operation of this unit. In this article, after a brief review of the process and solvents, HYSYS process simulator is utilized to simulate the process. First of all current operational conditions and solvent were simulated. The simulation results are compared to data obtained from the plant, and are proofed to be satisfactory correct. Secondly six other systems containing other amine or mixture of amines were simulated to find whether or not it is possible to change amine solution while maintaining same operation conditions and equipments specifications (e.g. tower diameter and circulation rate). Simulation results show that among all solutions only DGA can be substituted. Finally simulations of DGA/MEA mixtures were done. Simulation results show that mixture of 10% wt. DGA and 15% MEA can be utilized in this plant. This mixture can both lower corrosion problems and power required in process.

Key words: MEA Corrosion, Mixed Amine, DGA, Acid gas, HYSYS, Process Simulation.

1. Introduction

It has been decades since amines are utilized for removal of CO₂ or H₂S in gas refineries or other gas sweetening applications [1,2]. Many researchers have been explored for optimum amine or amine mixtures for a specified application to obtain better performance [3,4]. Corrosion is one of the major concerns facing the main equipments, after some years of working in this units, thus, is one of criteria's in solvent selection [5,6]. Computer based process simulations, have been proofed to be useful in selecting amines or a mixture of amines for different feed conditions [7,8,9].

Aim of this research is to find an amine or mixture of amines to help corrosion problems of a working plant, while maintaining circulation hydraulic design and absorption and stripping tower design (solvent change with no capital expenses). With change of Amine solution, process can move toward less corrosion problems. For this new solvent following items should be noticed: This new solvent should be as powerful as MEA in absorption of CO₂, It should be readily accessible and should not cause any change in equipments.

2. Process and solvents characteristics

2.1. Process

Process flow of CO₂ separation from feed gas is illustrated in Figure 1. For absorption of CO₂ from feed gas containing about 17% molar CO₂, in an ammonia unit in a petrochemical complex, 25 % wt. MEA is utilized in two steps of absorption and stripping. High pressure absorption of acid gas in absorption tower (T-101) and stripping with pressure reduction in (T-102 A/B) towers are achieved. CO₂, after separation from feed gas is sent to urine unit. Feed gas enters the absorption tower bottom and lean amine is introduced from top. CO₂ is absorbed by solvent through physical or chemical or a combination of both. As solvent becomes rich with acid gas, it needs to be recovered. Rich solvent after leaving

absorption tower pass through E-101 heat exchanger (known as L/R exchanger) and is heated. After passing through pressure reduction valve, some of the acid gas is stripped and enters reboiled stripper T-102 A/B. In this tower all acid gas is stripped and lean solvent goes into L/R exchanger and then pumped back to the top of the absorption tower.

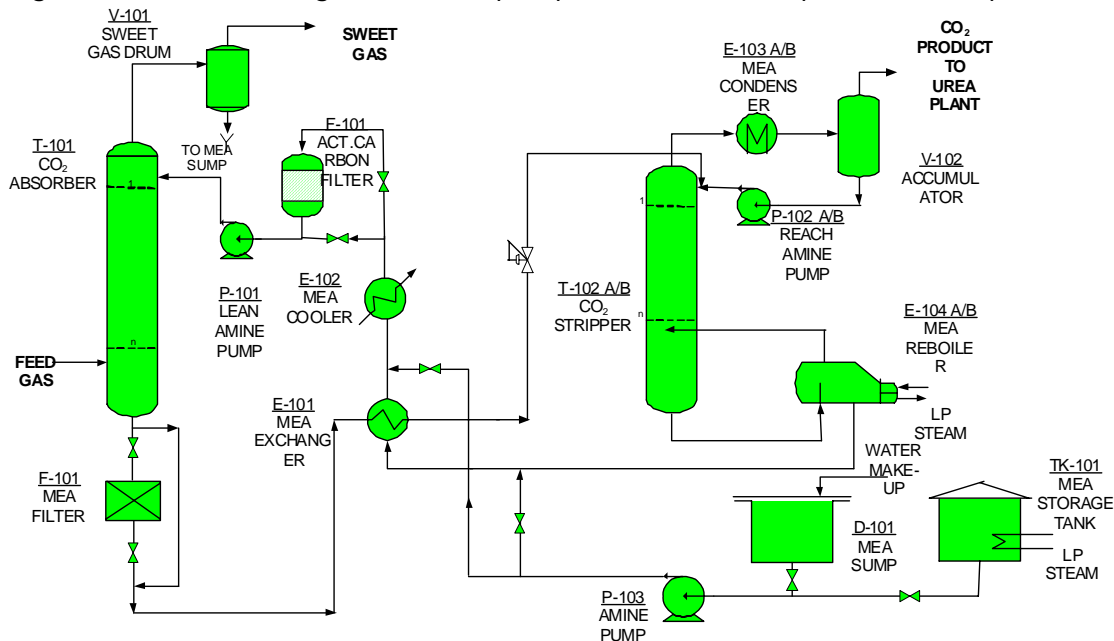
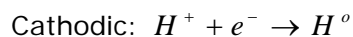
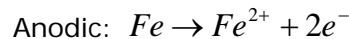


Fig. 1 CO₂ acid gas removal process flow

2.2. Corrosion problems

According to corrosion reports, sever corrosion is seen in some of the main process equipments. Stripping tower, reboiler, L/R heat exchanger and bottom of absorption tower are typical corrosion locations. Figure 2, 3 and 4, show corrosion problems at different equipments in the plant. Corrosion in these equipments takes place in two ways:

A) Carbon steel corrosion because of wet acid gas reaction with iron in aqueous phase in presence of Amine. B) Rich amine corrosion. Anodic, cathodic and overall reactions are as follows:



Most of hydrogen atoms generated by corrosion reaction combine to produce hydrogen molecules (H₂), but some atomic hydrogen penetrates into metal network. Corrosion reaction is irreversible and its rate depends upon temperature and concentration of reactants (corrosion rate increases with increasing temperature and H⁺ concentration). Also because of electrochemical nature of reaction, conductivity of aqueous phase plays a major role, in reaction kinetics. CO₂ concentration in water (or increase of partial pressure of CO₂ in gas phase) increase in concentration of H⁺ ion and consequently increases corrosion in accordance to overall oxidation/reduction reaction. Critical operational factors effecting corrosion rates are as follows:



Fig. 2 Pitting Corrosion in L/R amine heat exchanger shell



Fig. 3 AISI 1018 carbon steel coupon after exposure in upper side of L/R amine heat exchanger

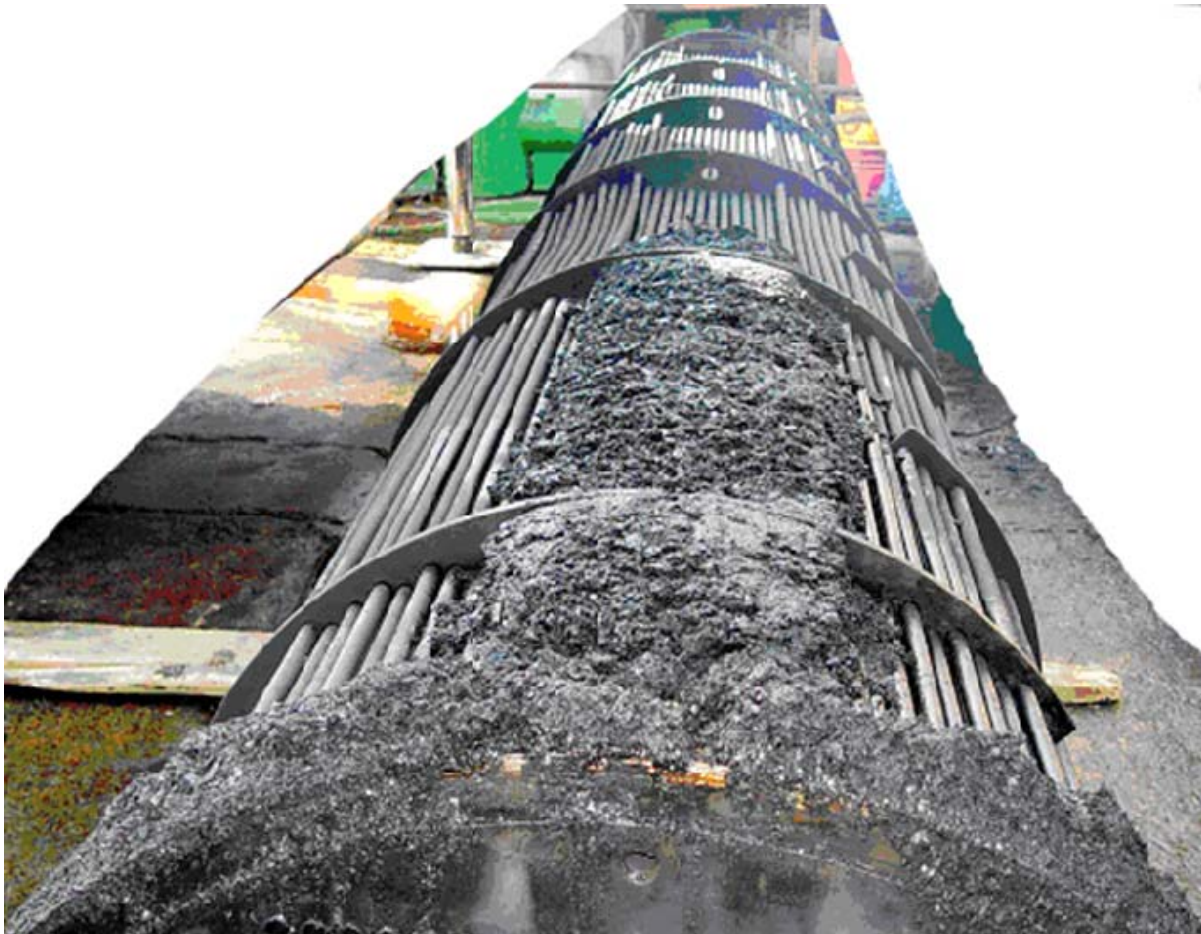


Fig. 4 Corrosion and sediments in L/R amine heat exchanger tubes

2.2.1. CO₂ Loading

CO₂ loading is the molar ratio of solved acid gas to amine. Pure amine is not inherently corrosive, but a mixture of amine, CO₂ and water is corrosive. CO₂ solved in Amine is a primary cause of corrosion in amine units. Corrosion reports show that corrosion in equipments which rich amine pass through them, is always more severe than equipments for lean amine. Maxi-mum gas loading in rich amine is 0.25-0.4 mol gas/mol amine for MEA, 0.33-1.00 for DEA, 0.45-0.5 for MDEA and 0.25-0.45 for DGA.

2.2.2. Amine Type and amine concentrations

Different types of amines, used in CO₂ and/or H₂S removal units are as follows:

MEA (Mono Ethylene Amine): MEA is the most common amine. It is highly alkaline, has highest separation capacity and can be recovered easily. Although MEA is suitable in many ways, but due to corrosive nature, concentration should be low, maximum relative concentration is 25% wt.; as a result, MEA needs high solvent rate (high pump power consumption) and steam rate in stripping tower.

DEA (Di Ethanol Amine): DEA is an amine of second type. DEA is a weaker amine solution and can not absorb CO₂ with a rate as high as MEA, but because it is not as corrosive as MEA, concentrations can be up to 35%. DEA circulation rate and demand for steam is relatively lower, but due to higher viscosity, power consumption in pump is higher. This solvent acts selectively in absorption of acid gases and in cases which H₂S and CO₂ both are present, absorbs H₂S relatively more, thus, is more suitable for natural gas refining purposes.

TEA (Tri Ethanol Amine): TEA is an amine of third type. It has a lower absorptive property relative to the both MEA and DEA.

DGA (Di Glycol Amine): DGA is a first type amine, it is highly absorptive. Since it has low corrosion problems and is completely miscible thus, it can be used at concentration up to 70% by weight. As a result needs lower circulation and steam rates.

DIPA (Di Iso Propanol Amine): is an amine of second type. It is used at concentration up to 50%. Problem with this amine is its high freezing point (45 C°), which can be problematic (the pipes and fittings blockage).

MDEA (Methyl Di Ethanol Amine): MDEA is a third type amine, with a low absorption rate, but it has no corrosion problem. This solvent can be used at concentrations up to 50% W/W. Demand for energy is low for this solvent. This solvent acts selectively in absorption of acid gases (absorbs H₂S more). General properties of different Amines are presented in Table 1.

Table 1 Properties of common solvents for CO₂ removal

Property	MEA	DEA	TEA	MDEA	DIPA	DGA
Mol.weight	61.09	105.14	149.19	119.17	113.19	105.14
Spgr 20/20°C	1.0179	1.0919	1.1258	1.0418	0.9890	1.055
Boiling point, °C						
76.mmHg	171	decomp	360	247.2	248.7	221
50mmHg	100	187	244	164	167	
10mmHg	69	150	208	128	133	
Vapor pressure, mmhg at 20°C	0.36	0.01	0.01	0.01	0.01	0.01
Freezing point, °C	-10.5	-28.0	21.2	-21.0	42	-9.5
Solubility in water (% weight) at 20°C	Completely miscible	96.4	Completely miscible	Completely miscible	87	Completely miscible
Absolute Viscosity (CPS)	24.1(at 20°C)	380(at 30°C)	1.013(at 20°C)	101(at 20°C)	198(at 30°C)	26(at 24°C)
Heat of vaporization (Btu/lb at 1 atm)	355	288	230	223	184.5	219.1

2.2.3. Operating Temperature

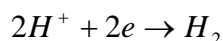
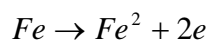
Temperature in CO₂ absorption is one of the most important parameters and has direct effect on the corrosion rate. The most temperature sensitive equipment in the process is R/L Amine heat exchanger. Temperature in reboilers is also very important.

2.2.4. Solution Velocity

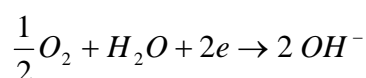
Solution velocity has impact on Erosion corrosion. This corrosion becomes more sever if the solution has solid particles. It's noteworthy that if filming inhibitor is not used, corrosion control is possible by the magnitude of the solution velocity. (Filming inhibitors, reduce corrosion by producing a film on the surface of the metal and disconnecting surface from the solution.) In the case when solid particles are present and the solution velocity is high, erosion corrosion cause protection film to be destroyed.

2.2.5. Amine Degradation

Amine degradation decreases the ability of solution to perform separation and increase corrosion rate [10,11]. Amine aqueous solution degrades in the pressure of O₂ & CO₂. MEA degradation is much more than amines like DEA. Electrons generated by metal oxidation are absorbed by H⁺ and increase corrosion rate as follows:



It should be noticed that hydrogen is not the only element that absorb electrons. In alkaline environments (as ammonia) oxygen also reacts as follows:



It should be noticed that degradation of amine by oxygen also increases rate of corrosion additionally. Oxidation of amine by oxygen produce heat stable Amine Salts (HSAS). In case HSAS concentration is more than 2%, corrosion becomes more severe. From amine solution oxidation (primary step in degradation) formic acid is produced. Formic acid reacts with amine to produce amide which attacks carbon steel and increase corrosion rate.

3. Simulation

A process simulator should meet two requirements. First, it should have capability to trace effective parameters and their variations, throughout the unit. Secondly, perform amine thermodynamic calculation with high accuracy. To meet the described conditions, for feasible solvent change studies in specified plant we used HYSYS process simulator. Following models are used for mathematical modeling of absorption/stripping systems [12-16]:

1. Kent/Eisenberg model: This model states the equilibrium solubility of acid gas and amine solution. Although we cannot see activity factor in this model, but this parameter is implied in equilibrium constants and Henry constant and no assumption, based on ideality of liquid phase is considered. This model is useful for molar loadings from 0.0001 to 1.2.
2. Lee/Mather model.
3. Electrolyte NRTL model: is completely compatible with NRTL equation and molecular mutual effects factors are accurately calculated as in NRTL method. This model is used for the calculation of activity coefficients for aqueous electrolytic systems and several different solvents. Activity coefficients for ions and molecules in solution can be calculated by this model. EL-NRTL model uses extremely lean aqueous solutions as a reference state for ions. In this model Born equation is used for transfer from reference state of extremely lean solution of solvents mixtures to extremely lean aqueous state.

In this research, thermodynamic calculations we carried out using Electrolyte NRTL model (E-NRTL) and also Amine package models. Simulation results are compared to data extracted from one of Iranian ammonia plants CO₂ removal units. Accuracy of simulation in predicting temperature and pH which are very important parameters in indicating corrosion rate to select the proper amine solvent or a mixture of amines. Diameter of tower, heat load of L/R amine heat exchanger (E-101) and amine condenser (E-103) are considered as important parameters in selecting solvent.

4. Results and discussion

First simulations were carried out at designed plant specifications and MEA as solvent. Specifications of feed gas are presented in Table 2. For MEA Comparison between simulation result of thermodynamic models AMINES, EL-NRTL and collected plant data are summarized in table 3 and 4. Results show that both thermodynamic models predict streams specifications and required duties for condensers and reboilers perfectly well. Comparing results of simulation using two models and plant data show that EL- NRTL model gives more accurate results. Also this model has capability of predicting some important properties of the process such as pH on trays. One of the important advantages of this model is that it has no limitations on concentrations of amine solutions. Simulated pH profile for both absorption and stripping tower are shown in figure 5. Figure 6 shows pH change in different process locations, at specified operating condition. From simulated pH and temperature profiles, predicted corrosion locations are absorber bottom and stripper top. This prediction is approved by plant over hall reports.

Table 2 Specifications of feed gas for CO₂ removal unit

Component	Feed Gas
	% Molar, Dry basis
Hydrogen	61.26
Nitrogen	20.01
Methane	0.4
Oxygen	0
CO ₂	17.69
CO	0.4
Argon	0.24
Total Dry	6693.8 moles
Total	6755.2 moles
Temperature (°C)	63
Pressure (bar _a)	27.7

Table 3 Simulation results for Sweet Gas stream specifications using thermodynamic models AMINES and EL- NRTL compared to data from operating plant

Description	Sweet Gas stream specification				
	Plant data	Simulation Results			
	Molar Flow	Amines Model Molar Flow	± %Error	EL-NRTL Model Molar Flow	± %Error
Hydrogen	4088.2245	4100.30408	0.30	4088.25212	0.00
Nitrogen	1335.47776	1339.39767	0.29	1335.46722	0.00
Methane	26.91815	26.7748171	0.53	26.5731468	1.28
Oxygen	0	0	0.00	0	0.00
CO ₂	0.54935	0.54914343	0.04	0.54899467	0.06
CO	26.91815	26.7734311	0.54	26.7565197	0.60
H ₂ O	21.6	20.6108219	4.58	21.6395055	0.18
Argon	15.93115	16.0650718	0.84	16.0379138	0.67
Total Dry	5494.019				
Temperature (°C)	46	46	0.00	45.981563	0.04
Pressure (bar a)	27.4	27.4	0	27.4	0.00
<i>Average deviation from plant data</i>			<i>0.79%</i>		<i>0.31%</i>

Description	CO ₂ Product				
	Plant data	Amines Model	± %Error	EL-NRTL Model	± %Error
<i>Total Dry (kmol/h)</i>	1180.2	1183.65344	0.29	1182.19522	0.17
H ₂ O (kmol/h)	222.7	225.943623	1.46	220.975835	0.77
Total(kmol/h)	1402.9	1409.5971	0.48	1403.171055	0.02
Temperature (°C)	60	60.3716165	0.62	59.9660312	0.06
Pressure (bar a)	1.3	1.3	0	1.3	0.00
<i>Average deviation from real data</i>			<i>0.57%</i>		<i>0.204%</i>

Table 4 Simulation results for energy consumptions using thermodynamic models AMINES and EL- NRTL compared to data from operating plant

	plant data	Simulation Results			
		Amines Model	± %Error	EL-NRTL Model	± %Error
Duty of Heat Exchanger (E-101), Gcal/h	21.83	21.63	0.9	21.76	0.3
Cooler Duty (E-102), Gcal/h	37.9	36.3	4	37.2	1.85
Condenser Duty (E-103), Gcal/h	19.66	19.66	0	19.66	0
Reboiler Duty (E-104), Gcal/h	56.63	56.63	0	56.63	0

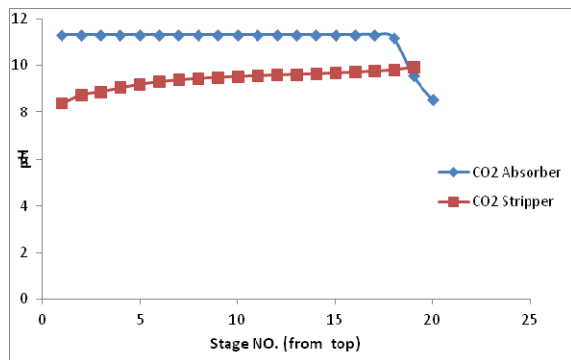


Fig. 5 simulated pH profile on trays for absorption and stripping towers

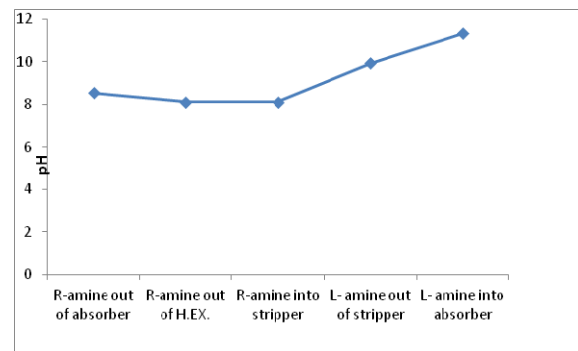


Fig.6 Simulated pH change in the path of absorption tower to stripping tower and vice versa

Table 5 Simulation Results for MEA vs. DGA/MEA solutions

Description	Sweet Gas (simulated)			\pm %Diff. (5-0)	\pm %Diff. (10-0)
	MEA Molar Flow	5% wt DGA Molar Flow	10% wt DGA Molar Flow		
Hydrogen	4088.25212	4087.75575	4087.34305	0.012141	0.022236
Nitrogen	1335.46722	1335.29281	1335.15066	0.01306	0.023704
Methane	26.5731468	26.5565065	26.540833	0.062621	0.121603
Oxygen	0	0	0	0	0
CO ₂	0.54899467	0.554696361	0.57506428	1.038569	4.748609
CO	26.7565197	26.7550885	26.7537015	0.005349	0.010533
H ₂ O	21.6395055	21.7607058	22.0032396	0.560088	1.68088
Argon	16.0379138	16.0358469	16.0338568	0.012888	0.025296
Total Dry	5493.104202	5492.412283	5491.834497	0.012596	0.023115
Total	5514.743708	5514.172989	5513.837737	0.010349	0.016428
Temperature	45.981563	46.0092693	45.9881347	0.060255	0.014292
Pressure(bar)	27.4	27.4	27.4	0	0

Description	CO ₂ Product (simulated)			\pm %Diff. (5-0)	\pm %Diff. (10-0)
	MEA	5% wt DGA	10% wt DGA		
Total Dry (kmol/h)	1182.19522	1182.18	1182.12	0.001287	0.006363
H ₂ O (kmol/h)	220.975835	216.54	216.04	2.007385	2.233654
Total(kmol/h)	1403.171055	1398.72	1398.16	0.317214	0.357124
Temperature (°C)	59.9660312	59.18	59.12	1.310794	1.410851

4.1. Feasibility study of solvent change

Using HYSYS simulator and Keneth Aisenberg model, diameter of absorption tower and amount of solvent in circulation are simulated for 6 systems of other alkano Amines and their mixtures. These systems are: 1) DGA 60%, 2) DEA 30%, 3) DIPA 40%, 4) mixture of MDEA/ MEA (45%, 5%), 5) MDEA/ DEA (45%, 5%), 6) MDEA 50%. Same Temperature and pressure of lean Amine, pressure at the top and bottom of absorption tower and conditions, and same specifications of feed gas to absorption tower were considered for all solvents. Simulation results are shown in figure 7 and 8. Plant designed solvent circulating rate and absorption tower diameter are 897000 kg/h and 11 ft. Simulation results show that for all solvents, except DGA 60%, considerable higher flow rate and tower diameter are needed. Thus, substitution amount of MEA by other amines is not technically feasible.

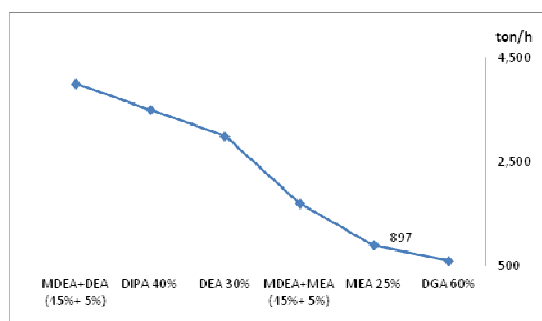


Fig. 7 solvent circulation rate for different solutions at the same operation conditions.

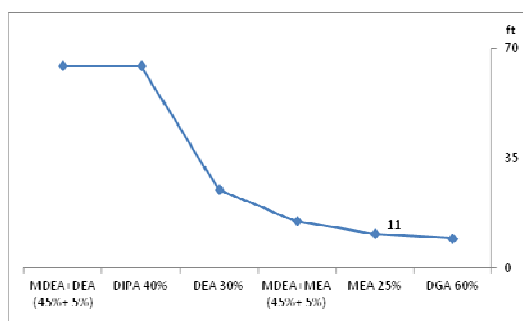


Fig.8 Diameter of absorption tower for different solvents at same operating conditions

4.2. Mixture of solvents instead of MEA

Referring to described simulations, among the alkanoamines only DGA can approximately absorb CO₂ similar to MEA with same tower diameter and circulation rate. Two mixtures of (MEA 20% + DGA 5%) and (MEA 15% + DGA 10%) have been simulated using EL-NRTL

model. The goal for these second series of simulations was to find a system which can work at designed operation conditions (circulation rate and tower diameter). Table 5, summarize simulation results for MEA system vs. MEA/DGA solutions. These simulation results show that both systems bring no considerable changes in sweet gas specifications. Table 6, summarizes energy consumption results for MEA vs. DGA/MEA solutions. It is noteworthy that in case of substitution of MEA with MEA/DGA mixture, considerable decrease in duty for reboilers and condensers is predicted. Figure 9, 10 and 11 show pH change in absorption and stripping tower trays and other process equipments. In figure 12 and 13, temperature profile in absorption and stripping towers for three simulated solvent systems are shown.

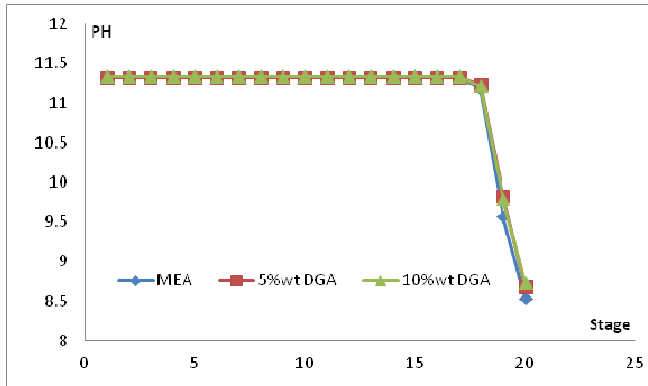


Fig. 9 pH change in Absorption tower trays for different solvents

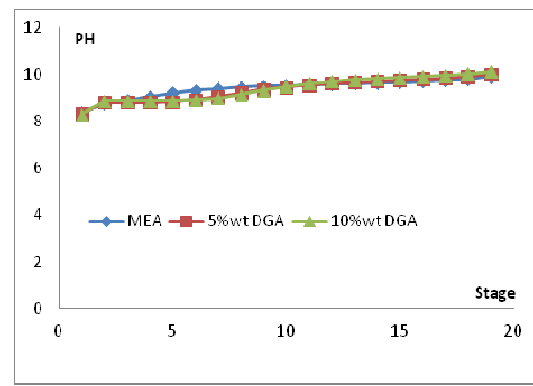


Fig. 10 Simulated pH change in stripping tower trays

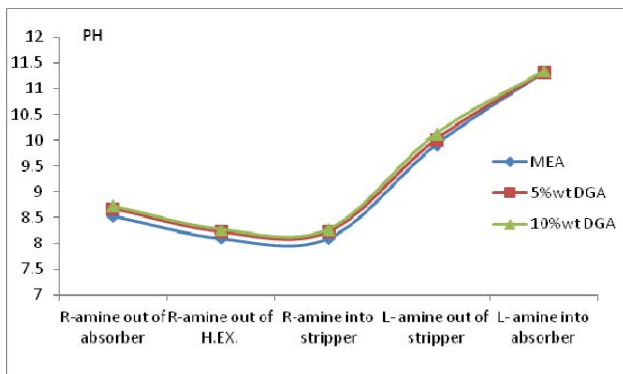


Fig. 11 Simulated pH change in path between absorption and stripping tower and vice versa.

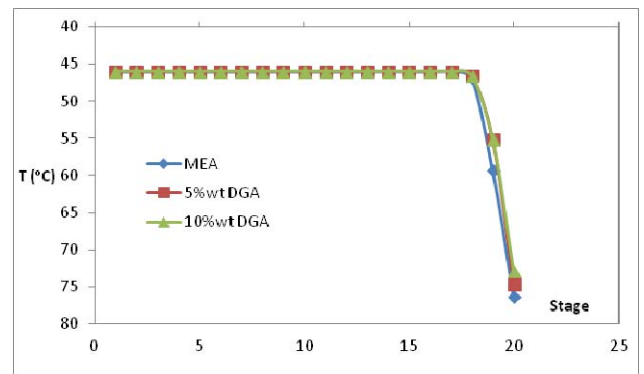


Fig. 12 Simulated temperature change, in absorption tower trays for different solvents

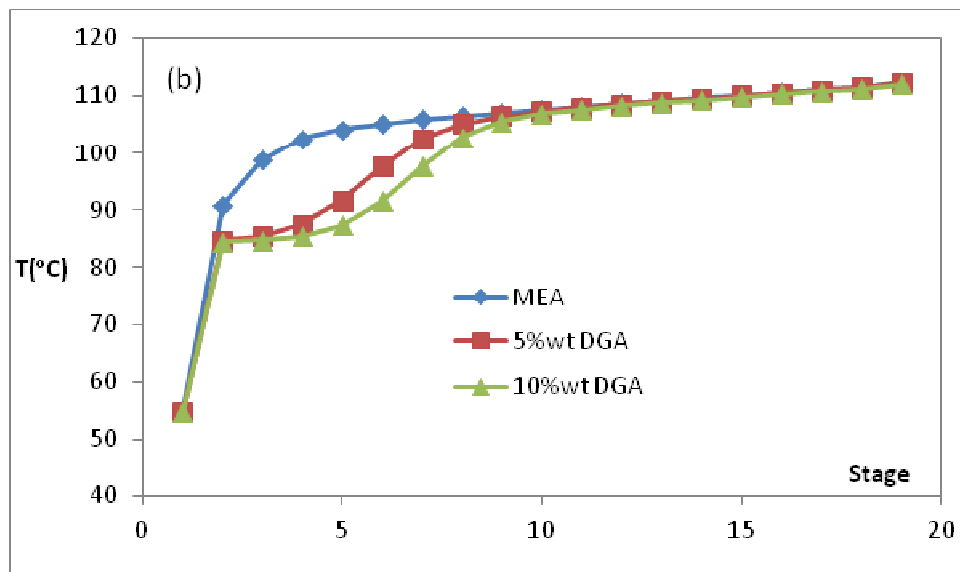


Fig.13 Simulated temperature change in stripping tower trays, for different solvents

Table 6 Simulation energy consumption results for MEA vs. DGA/MEA solutions

	25% MEA	20% MEA+5% DGA	15% MEA+10% DGA
Total Dry(kmol/h)	1184.20	1184.19	1184.12
H ₂ O	220.98	216.54	216.04
Total	1421.75	1418.00	1418.00
Temperature (°C)	59.57	59.18	59.12
Pressure(bar a)	1.3	1.3	1.3
Condenser Duty (Gcal/hr)	19.66	10.77	10.76
Reboiler Duty (Gcal/hr)	56.63	45.7	43.87

5. Summary and conclusions

In this research, 3 series of simulations were carried out to find an amine or a mixture of amines, which can yield same CO₂ separation while maintaining all operation conditions and equipments (e.g. circulation rate and tower diameter).

Results of this study show that solvent substitution with DGA can improve corrosion problems, reduce circulation solvent flow (considerable reduction in utility consumption) and system losses and need no change in the equipments. Using other solvents is not technically feasible. Using MEA and DGA mixture (MEA 15% + DGA 10%) could slightly increase pH in absorption tower trays and amine streams and reduce pH in stripping tower trays, but because of improvement in corrosion this method could be one of the strategies which could be employed in ammonia unit for solving corrosion problems.

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