Theoretical and industrial aspects of amine reclaiming unit to separate heat stable salts

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ABSTRACT

In this study, a thermal vacuum distillation amine reclaimer unit was industrially and theoretically investigated to remove HSS from a salty amine stream. The presence of ions in the salty amine solution limits application of computer simulation tools to study the process. A thermodynamic equivalent scheme was used for thermal vacuum distillation amine reclaimer, for first time and the simulation results were totally conformed to experimental and industrial data. The effect of critical parameters namely reclaimer vacuum pressure, re-circulation flow rate and HSS amount on performance of thermal amine reclaiming was investigated based on increasing amine solution quality, amine recovery, energy usage, and waste amine rate. The results showed that the required energy is mainly attributed to thermal energy rather than mechanical energies (i.e., pump equipment). It was also found that the required energy for a thermal vacuum reclaimer is lower than that for an electro-dialysis process with a value of 12 kWh/kg HSS. Therefore, the thermal vacuum reclaiming process is more economical comparing to the electro-dialysis when only energy requirement is concerned. In addition, the results showed that a decrease in reclaimer pressure leads to higher amine concentration in vapor and liquid phases and lower energy usage. Higher amine recovery can also be obtained by heating feed stream with amine-waste re-circulation and an increase in re-circulation flow rate would increase energy demand in both condenser and heat inputs.

1. Introduction

Natural gas is known as a clean fuel because of its low environmental pollution [1]. Some of the most important natural gas contaminants are hydrogen sulfide, carbon dioxide, mercaptans and etc, which are harmful to environment, human and process equipment [2,3]. Therefore, impurity removal from crude natural gas is essential to meet the pipeline standard specifications. Methyl di-ethanolamine (MDEA) solvent and other alkanolamines are usually used in natural gas sweetening for absorbing abovementioned impurities in an absorption-regeneration system [4]. An alkanolamine plant controls amount of H_2S and CO_2 in natural gas and hereby attracts increasing attention. The quality of alkanolamine solution is changed over time due to its chemical and physical degradation/decomposition [5]. High operating temperature in reboiler connected pipes of a regenerator column results in thermal decomposition of the alkanolamine solution while its chemical decomposition can be attributed to the presence of oxygen, ions,

solution pH and etc [6]. The destroyed amine leads to corrosive products [7,8] and hereby, corrosion is one of the main problems in amine gas sweetening plants leading to unscheduled outages. Some products obtained from degradation of alkanolamine solvent include heat stable salts (HSSs), non-volatile organic compounds and suspended solids [9]. Presence of heat stable salts (HSS's) and amine degradation products in amine solution are some source of corrosion causing high repair and filtration costs and environmental problems. Besides, presence of HSS declines the amount of available amine and leads to foaming tendency, heat exchanger fouling, priming and erosion [10,6]. Presence of some ions such as chloride, formate, oxalate, sulfate, acetate, and thio-sulfate results in formation of strong bonded salts [11] which could not be broken up/removed using provided heat in the regenerator column and HSS tends to accumulate in the amine solution. These acidic ions decrease pH of solution, increase solution conductivity and weaken protective layer on Fe surfaces. Therefore, HSS should be removed from amine solution in order to decrease foaming, fouling and filter

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replacement costs and improve sweetening performance of amine plant.

The contaminations of amine solution including HSS's and amine degradation products are formed from reaction of amine with constituents of feed gas or from amine thermal and chemical decomposition. The main and simplified reactions for HSS formation are as follows [12]:

$$\text{Base amine} + \text{Acid} \rightarrow [\text{Bound amine cation}^+ + \text{Acid anion}^-] \rightarrow \text{salt}$$
(1)

$$\text{Base amine} + \text{Organic acid} \rightarrow \text{Bound amine cation}^+ + \text{acid anion}^-$$
(2)

$$\text{Bound amine cation}^+ + \text{heat} \rightarrow \text{no change in stripper column}$$
(3)
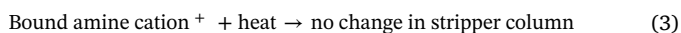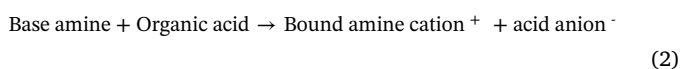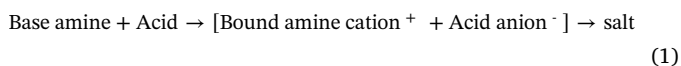
Based on Eqs. (1) and (2), non-organic acid (chloride, sulfate, phosphate and so on) or organic acids react irreversibly with available amine to form bound amine cations. According to Eq. (3), during regeneration process, the bound amine cations are not thermally regenerated and accumulated in the amine solution as HSS. For example, Eqs. (4)–(6) show three HSS formation reactions for MDEA solution.

$$\text{MDEA} + \text{H}_2\text{S} \rightarrow \text{MDEAH}^+ + \text{HS}^- \rightarrow \text{salt}$$
(4)

$$\text{MDEA} + \text{CH}_3\text{COOH} \rightarrow \text{MDEAH}^+ + \text{CH}_3\text{COO}^- \rightarrow \text{salt}$$
(5)

$$\text{MDEA} + \text{HCl} \rightarrow \text{MDEAH}^+ + \text{Cl}^- \rightarrow \text{MDEAH}^+\text{Cl}^- \rightarrow \text{salt}$$
(6)
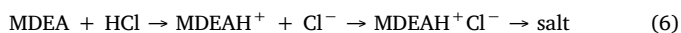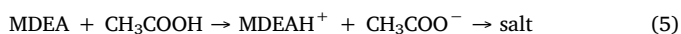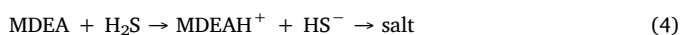
When concentration of HSS's in amine solution becomes excessive, accumulation of these contaminates creates above-mentioned operational problems. Therefore, the spent lean amine solution (salty lean amine) should be purified to increase process performance. Thermal reclaiming (vacuum distillation), ion-exchange, and electro-dialysis processes are the most applied amine purification/reclaiming methods [8]. The purpose of the amine reclaimer plant is to efficiently remove dissolved heat stable salts from a salty lean amine feed stream, generating a relatively salt-free lean amine product. An amine reclaiming unit should provide a high amine purity and recovery, less volume production of hazardous contaminates and low cost [10,13]. Sexton et al. [14] compared reclaiming technologies from amine recovery in the view of HSS removal rate and non-ionic product removal. They revealed 100% HSS and non-ionic product removal for thermal amine reclaiming. Moreover, the ion-exchange reclaiming method possessed the highest capital cost in comparison with the other techniques, while similar capital costs for thermal and electro-dialysis reclaiming methods are seen. A higher energy usage is also observed for electro-dialysis compared to thermal reclaiming method of MDEA solution [14]. However, thermal reclaiming method shows a high rate of amine loss and also produces toxic waste. The Canadian Chemical Reclaiming Ltd. (CCRL) proposed an intensified process using caustic treatment followed by vacuum distillation is frequently applied in industrial scale. Abedinzadegan Abdi and Meisen [10,13] enhanced performance of the CCRL process by replacing single stage flash drum with several tray distillation columns in the presence of inert liquid extraction. They found that an efficient separation can be obtained in multi-stage processes. Pal et al. [15] investigated HSS adsorption on different ion exchange resins and solvent-to-resin ratio was reported as major parameter affecting the process. They also fitted their results to popular isotherms and the Langmuir equilibrium isotherm better explained HSS ion exchange. Solvent-to-resin ratio was reported as major parameter affecting the process. Pal et al. [16] also examined thermal degradation of MDEA using microwave digester in a high pressure reactor. MDEA degradation obeyed first order kinetic reaction rate and acetate and glycolate formation increased with pressure. Edathil et al. [17] used Alginate based clay hybrid composites for HSS adsorption from MDEA solution. They proposed calcium alginate hybrid composite as efficient adsorbents for MDEA reclaiming. Furthermore, Alnaimat et al. [18] used electromagnetic force to separate 70% of HSS in an MDEA solution. Zain et al. [19] in continuation combined electrical and magnetic forces simultaneously to propose a novel rectangular electromagnetic setup without amine degradation. They found that proper operating conditions are the applied voltage of 3 V, feed rate of 2 ml/min and 1 T parallel magnets. Durrani et al. [20] used an activated biochar obtained from date palm in a capacitive deionization cell to remove HSS from MDEA solution. They observed a high electrosorption capacity for the electrode and proposed a pseudo-first order model for HSS adsorption. In addition, Arora et al. [21] utilized hybrid materials of CNTs-Si-Ag based electrodes for HSS electrosorption due to easy access of the ions to inner pores. Their results showed that the salt adsorption capacity of the electrode is increased from 17.3 to 21.5 mg·g^{-1} while applied voltage is varied from 0.8 to 1 V and current efficiencies increased from 16.4 to 20.4% indicating good performance of the electrode. A2-ethyl-1-hexanosolvent was used by Karnwiboon et al. [22] for HSS extraction from MDEA solution and other blends. They found that higher temperature and lower CO_2 loading increases the extraction performance of all HSS's from mixed amines. They successfully extracted 100, 85 and 81% of oxalate, formate and glycolate ions from the MDEA solution, respectively. Furthermore, Edathil et al. [23] removed 29.24% of HSS in 240 min at 25 °C using magnetic calcium alginate hydrogel composites. Advantages of their methods were its cost-effectiveness and eco-friendliness.

Due to limited existing information about the principles of thermal vacuum distillation amine reclaimer and also presence of ions in a salty amine solution (feed stream of a thermal amine reclaiming unit), application of computer simulation in study of the process performance has not been recognized yet and no comparison between simulation and industrial data has been reported yet. Moreover, the effect of critical parameters on performance of thermal amine reclaiming has not been investigated in terms of increase in amine solution quality, amine recovery, energy usage, and waste amine rate. The aim of this work is to propose a thermodynamic equivalent scheme for a thermal vacuum distillation amine reclaiming process and then the results of computer simulation are compared with experimental and industrial data. After model validation, the effect of the main operating parameters including circulation heater outlet temperature, vacuum pressure and circulation rate on performance of the unit is explained and energy usage and amine recovery rate are monitored.

2. Fundamentals of amine reclaiming and simulation strategy

There are three main technologies commonly used for amine reclaiming including thermal reclaiming, ion exchange, and electro-dialysis (ED). Thermal reclaiming, commonly used at vacuum pressures for MDEA solution, is based on heating amine solution to separate amine solvent with a lower boiling point from contaminations such as HSS's, degradation products and suspended solids. This process is commonly carried out for a slipstream from the lean amine solution leaving the regenerator reboiler. Amine thermal reclaiming can also be carried out in a non-continuous mode in a reclaiming unit. Amine thermal reclaiming occurs at different operating conditions depends on the type of amine. For a low boiling point amine like mono-ethanolamine, the amine reclaiming usually carries out at the regenerator pressure. But for secondary and tertiary amines (like di-ethanolamine and MDEA, respectively) with high boiling point temperatures, it is more helpful to reclaim them at vacuum pressures but at temperatures lower than their degradation temperatures.

Amine reclaiming process by ion exchange is used only for removal of ionic contaminants from amine solutions by exchange of ions between the ion exchange material as a solid phase and the amine solution. So, one of the major problems regarding the ion exchange amine reclaimer is that it cannot be used unlike the thermal reclaiming for removal of non-ionic contaminants like amine degradation products from the amine solution. On the other hand, ED as an amine reclaiming process uses electrical energy for separation of ionic contaminations from amine solutions. An ED system uses a stack of alternating cation
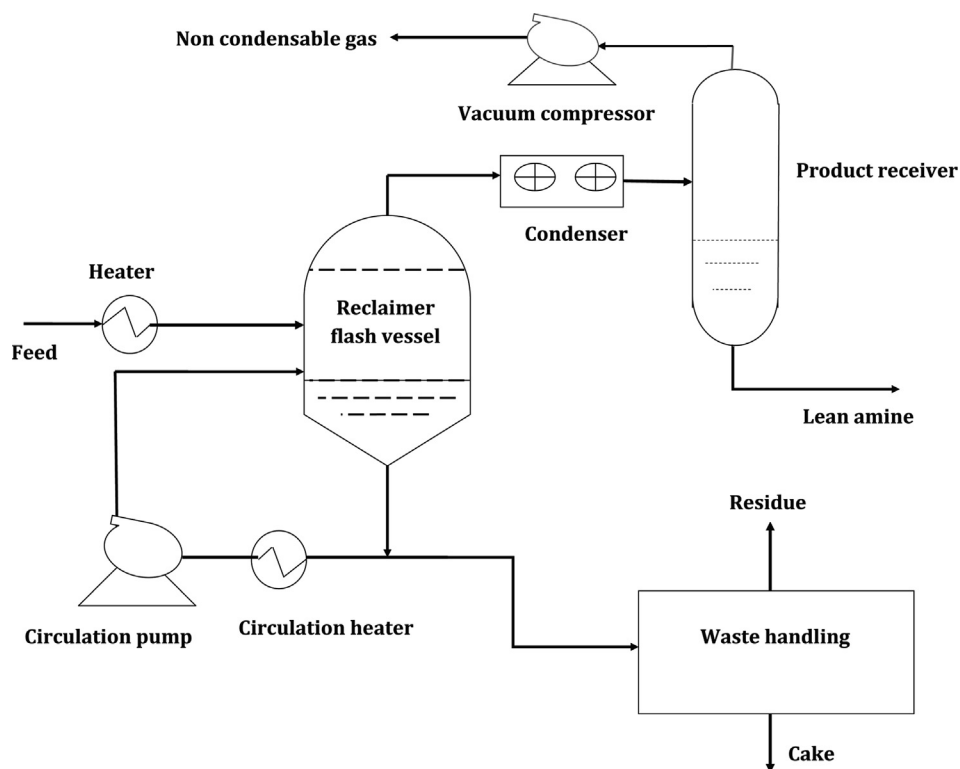
Fig. 1. Typical amine reclaiming system.

exchange membranes (CEMs) and anion exchange membranes (AEMs) located between two electrodes [24]. The ED reclaiming process like ion exchange is not capable of removing non-ionic degradation amine products from the amine solution.

Efficient removal of HSS from a salty lean amine (MDEA) feed stream results in generating a virtually salt-free lean MDEA product. As can be seen Fig. 1, the amine reclaimer contains four operating compartments namely: pre-treatment, reclamation, product handling and waste handling. Caustic solution is added in upstream of the amine reclaimer to enhance mixing and to provide relatively uniform amounts of caustic treated feed of the reclaimer. Accordingly, a caustic solution (40–50 wt%) is injected to the salty lean MDEA feed in batch-wise to ensure basic conditions with pH near to 10–12. This elevated pH protects the unit metallurgy against excessive corrosive attack whether resulting from the expected CO_2, oxygen (or air ingress into vacuum condition), or organic acids levels. The actual amount of caustic required will depend on the inorganic and organic acid content in the salty lean MDEA feed. Overall, caustic solution is injected at a rate which neutralizes any acids, and divalent cations such as Ca^{2+} and Mg^{2+}.

The reclaimer operates at vacuum pressure to decrease boiling points of the contents allowing distillation in lower temperature. Since the reclamation section operates in vacuum condition, nitrogen is added continuously to purge air that leaks into the process through leaky valves, flanges, or other connections. Regulated nitrogen purge should be adjusted by the operator to maintain < 4 vol% oxygen in the reclaimer vent. A set of vacuum compressors should be utilized to establish the intended 30 kPa vacuum in the reclaimer flash vessel. All non-condensable gases from the system are drawn into the vacuum compressors. The vacuum compressors boost the discharge pressure from about 30 kPa to 110 kPa, resulting in a net temperature rise (~69 °C).

In the reclaimer vessel, the salty lean MDEA is vaporized under vacuum pressure (i.e., 30 kPa), allowing separation of MDEA solution from the dissolved salts while the operating temperature should be well

below the degradation temperature. In order to decrease the amine amount in waste stream and enhance the amine recovery, the salty amine feed should be mixed with hot recycled stream coming from bottom of the reclaimer and the resulting stream is then pre-flashed and most of water and MDEA is evaporated. In other words, most of water, MDEA and light hydrocarbons are vaporized; however, solids, dissolved ions and heavy hydrocarbons do not pass overhead of the reclaimer. The theoretical energy required for vaporizing amine and water is equivalent to the reboiler thermal energy. The required heat to facilitate vaporization is supplied by a circulation liquid loop at the bottom of reclaimer flash vessel. Accordingly, the amount of liquid vaporized is influenced by the temperature of the circulating liquid. The residual salts accumulate within the circulation loop and reclaimer flash vessel. In addition, a constant blow-down from the system is used to remove solids. This blow-down is directed to the waste handling system for further treatment of solids (solid concentration, salt crystallization and sedimentation). On the other hand, the overhead vapors exit the reclaimer flash vessel and are directed to the product handling area. These vapors are then condensed in the product receiver drum at the temperature of approximately 60 °C. Some provisions (such as skimming) should be incorporated in presence of liquid hydrocarbons in the product receiver. Non-condensable gases exiting the product receiver enter the vacuum compressors.

Since, MDEA is reported to be thermally degraded at 182 °C [25]; hence, this temperature shall be avoided during amine reclaiming process. Accordingly, MDEA with high boiling point temperature dictates the amine reclaiming process to operate under vacuum condition [5]. So, amine reclaiming is recommended at low pressure. Moreover, a reclaimer unit can be used for other solvents such as other alkanolamines and glycols. In this paper, it is used some operating data obtained from an industrial reclaimer unit, designed originally for MEG reclaiming. This unit is also used for MDEA reclaiming after some unit modifications. So, the industrial mono ethylene glycol (MEG) reclaiming unit is firstly simulated and the obtained simulation results are compared with the existing operating data obtained from this unit.

Table 1
The properties of major components in reclaimer.

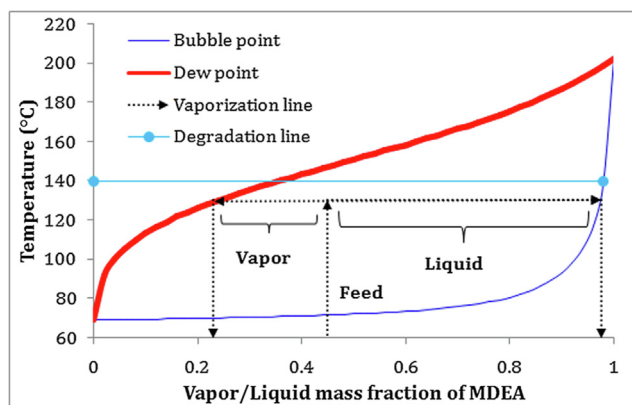| Component	Chemical formula	Molecular weight	Normal boiling point (°C)
Water	H_2O	18.02	100
MDEA	$C_5H_{13}NO_2$	119.2	247.3
Ethylene glycol	$C_2H_6O_2$	62.07	197.2

Fig. 2. The binary T-xy diagram of MDEA and water at pressure of 30 kPa.

After verification of the simulated process, MDEA reclaiming process is also simulated. Table 1 reveals properties of MDEA/water/glycol and Fig. 2 shows T-xy (vapor-liquid equilibrium) profile of MDEA/water obtained through simulation at 30 kPa, indicating wide evaporation line and no azeotrope between these components. In order to assess the progress of distillation of MDEA and water, this graph is important.

Fig. 2 shows a typical salty amine feed with 45 wt% MDEA. Since, thermal reclaiming is associated with heating, temperature of this stream is increased and reclaiming is then terminated when the operating temperature approaches to the degradation temperature. In this condition, the amount of recovered amine in vapor stream is less than its concentration in the feed stream while the residue possesses a more fraction of amine. In order to demonstrate the behavior of the amine reclaiming unit, a stream is defined and its operating temperature is gradually increased and the rate of evaporation is monitored. Fig. 3 shows two distinctive phases of recovery of water and MDEA. This figure demonstrates that with adequate increase in temperature (pressure of 30 kPa) most of water is recovered in vapor phase of the reclaimer. Once most of water is vaporized, with continuous increase in
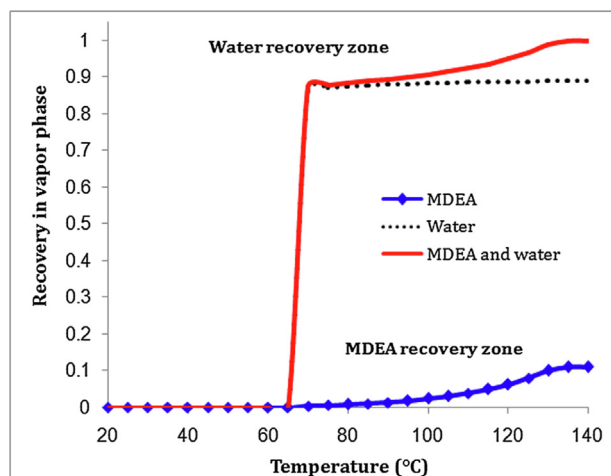

Fig. 3. The simulation results for two distinctive zones for water and amine recovery.

reclaimer temperature, MDEA vaporization is begun and the concentration of MDEA is then intensified.

In the experiments, ionic chromatography (Metrohm 861, Swiss) with the anodic column of "Metrohm S sup 5-250" is utilized for HSS analysis. MDEA content is also determined through titration with the solution of 0.1 N HCl.

3. Results and discussions

An industrial reclaimer plant of mono ethylene glycol (MEG) is here considered for simulation, which is located in phase 19 of the South Pars Gas Complex (subsidiary of National Iranian Gas Company), Assaluye, Iran. Fig. 4 shows a thermodynamic equivalent scheme for simulation of both MEG and amine reclaiming unit using Aspen HYSYS software with the acid gas thermodynamic package. The reclaimer is considered as a simple distillation column maximally with two ideal trays with no pressure drop. The "Feed" and "Recirculation" streams are introduced to the reboiler of reclaimer tower. Furthermore, Table 2 shows the operating conditions of the industrial salty lean glycol stream as the feed of the reclaimer unit. This MEG reclaiming unit was used for recovery of lean glycol stream from MEG/water system. Table 2 also compares the results of simulations with those of industrial data indicating a good agreement between them. In addition, Fig. 5 confirms the good prediction of the utilized thermodynamic model (Acid-gas chemical solvent) for vapor-liquid equilibrium of MDEA/water. This illustration clearly shows a good agreement between the simulation predictions and the experimental data [26] in terms of T-x diagram of MDEA/water at different operation pressures. To do so, ethylene glycol is removed from the feed stream and the salty amine (MDEA) is then considered as the main feed of the reclaimer unit and the results are compared to the experimental data. As can be seen in Table 3, there is a good agreement between the experimental results of vacuum distillation reclaimer with those of simulation. Hereby, Aspen HYSYS process simulator can be used to explore the effects of critical parameters on the amine reclaimer performance with high accuracy.

At constant feed properties, the important parameters of the reclaimer are pH of reclaimer circulation loop, outlet temperature of circulation heater, amine recovery, and pressure (vacuum) performance in order to have a suitable plant operation. In this study, the effect of reclaimer operating pressure, recirculation flow rate and HSS addition on energy demand of the process was investigated.

Fig. 6 demonstrates simulation results of the effect of operating pressure on MDEA/water separation. As can be seen in this figure, lower operating pressure leads to higher MDEA concentration in vapor and liquid and also more recovery of MDEA in vapor phase. According to literature [14], most of the required energy for thermal reclaiming is attributed to the thermal energies especially for reclaimer reboiler. Caustic soda is usually consumed in thermal amine reclaiming based on 1 mol NaOH/1 mol HSS ratio [27], which its cost is negligible rather than that of required thermal energy. On the other hand, the relevant costs of mechanical energies (vacuum pump and re-circulation pump) can also then be neglected. The energy demand for an amine reclaimer unit is calculated by considering the reboiler duty and re-heater duty. The reboiler thermal energy requirement is equivalent to the theoretical energy required to vaporize all amine and water in feed stream and thermal energy requirement for the re-heater is equivalent to the theoretical energy to increase sensible heat of waste stream to the operating temperature of the reclaimer. Fig. 7a shows that a lower energy demand is needed by decreasing operating pressure due to decrease in boiling points of components. This result can also be confirmed by a correlation originally proposed for estimating required energy (per kg CO_2 produced) of an amine reclaiming unit used in a post-combustion CO_2 capture system [28]:

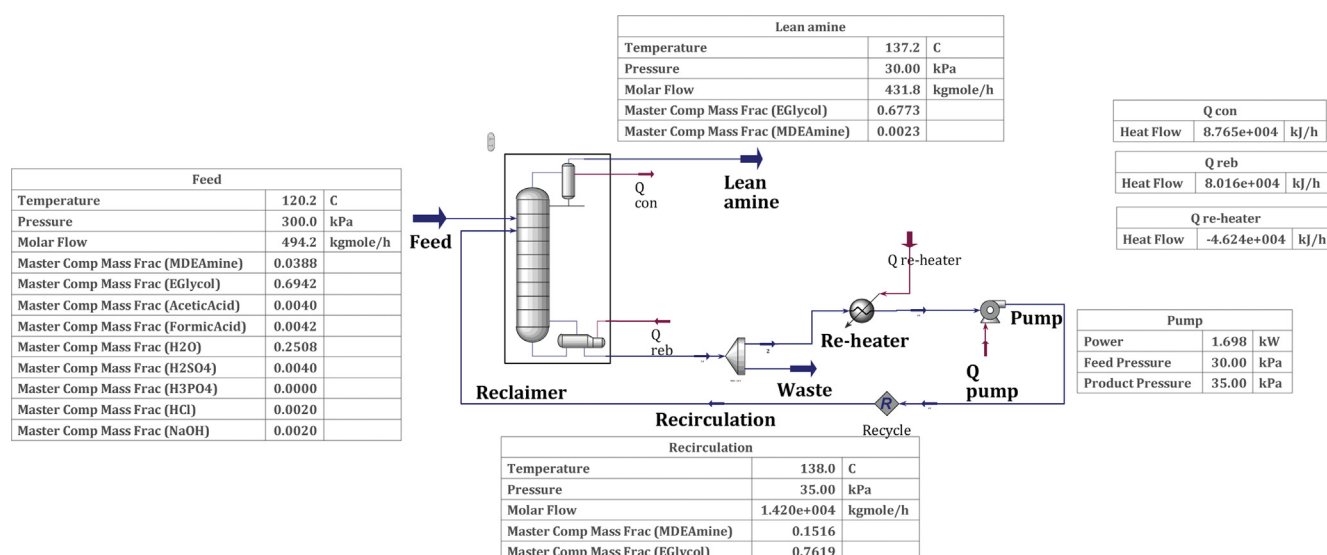$$Q_{rec} = \frac{(Cp_{amine})(T_{b_p})(F_m)}{r_{CO2 - prod}}$$

(7)

Fig. 4. The thermodynamic equivalent configuration embedded into the simulation.

Table 2
Comparison of simulation results with industrial data for MEG reclaiming.

	Feed	Lean product		Re-circulation	
		Simulation	Industrial	Simulation	Industrial
Temperature (°C)	120.2	137.2	142.5	144.2	144.2
Flow rate (kg/h)	494.2	15,040	16,123	930,800	893,264
Component	**Mass fraction**				
Ethylene glycol	0.6942	0.6773	0.6776	0.7619	0.7781
H_2O	0.2508	0.3203	0.2958	0.0044	0.0151
MDEA	0.0388	0.0023	0.02576	0.1516	0.1068
NaOH	0.0020	Trace	0	0.0080	0.0131
HCl	0.0020	Trace	0	0.0065	0.0117
Formic acid	0.0042	Trace	0	0.0225	0.032
Acetic acid	0.0040	Trace	0	0.0218	0.0238
H_2SO4	0.0040	Trace	0	0.0218	0.0146
$H_2S_2O_3$	Trace	Trace	0	0.0015	0.0008
Total salt	0.0162	0	0	0.1	0.096

In which Cp_{amine} is the specific heat capacity (kJ/kg °C) of lean amine solution, T_{bp} the atmospheric boiling point (°C) of the amine solvent in the amine solution, F_m the mass flow rate of the amine solution (kg/hr) and $r_{CO2\text{-}prod}$ is the rate of CO_2 produced (kg/hr).

This correlation can be modified based on the energy rate required for amine reclaiming unit as below:

$$Q_{rec} = (Cp_{amine})(T_{bp})(F_m) \qquad (8)$$

It can also be used the equation below in order to determine the boiling point of the lean amine solution [28]:

$$T_{bp} = \sum_{i=1}^{m} \frac{C_i}{C_T} T_{bp\text{-}i} \qquad (9)$$

where T_{bp} is the atmospheric boiling point of the lean amine solution, C_i is the concentration of the ith component in the amine solution (wt. %), C_T is the total concentration of all components in the aqueous amine solution (wt.%), and T_{bp_i} is the atmospheric boiling point of the ith component in the amine solution (°C). So, it can be concluded from Eq. (8) that the required energy rate in amine reclaimer is proportional to the rate of amine flow rate, the atmospheric boiling point of the amine solution (mainly due to that of amine solvent which has a higher boiling point temperature) and the specific heat capacity of the lean amine solution.

As a rule of thumb, the energy required for vaporizing water and

amine is much more than the energy to condense it due to presence of HSS in the salty lean amine solution. So, the condenser required duty is lower than heat inputs. Fig. 7b also depicts that the corresponding re-claimer temperature increases with operating pressure while density of re-circulation acts in reverse. The density of re-circulation stream is monitored for the sake of HSS solidification and when it increases to the target value of 1040 kg/m³, the purge stream flow rate should be in-creased in order to remove more solids from the re-circulation loop and to avoid fouling and solid deposition.

Fig. 8 shows that when a salty amine feed is mixed with a hot re-cycled stream, this would increase MDEA concentration of the entering feed to the reclaimer resulting in the higher recovery of solvent (MDEA). Accordingly, the hot re-circulated stream in the reclaimer unit plays a crucial role in amine recovery unit. Since energy requirement of thermal vacuum reclamation is not extensively studied [28], Fig. 9a shows that an increase in re-circulation flow rate would increase energy demand in both condenser and heat inputs. Fig. 9b confirms a higher pump duty with increase in re-circulation flow rate and the required energy of pump is not significant comparing to the results of Fig. 9a. Therefore, the assumption made in neglecting mechanical energies in the calculations seems reasonable. As shown in Fig. 10a, by increasing the re-circulation flow rate more amine is recovered in product while the waste stream gets concentrated in MDEA (Fig. 10b). However, the differences in lean amine flow rate and MDEA fractions for both lean and waste streams are too small. Moreover, a simple calculation shows that the threefold increasing of recirculation rate leads to increase in lean amine flow rate only by 1%. Taking into account the decreasing of the thermal reclaiming effectiveness in terms of pump duty and heat input with the increasing of recirculation rate (Fig. 9), although one can conclude that the parameter of recirculation rate should remain low, but it is not in this way. According to Fig. 8, the positive influence of the recirculation rate is increasing MDEA concentration in feed through feed pre-heating to increase MDEA recovery. In other words, the re-circulation stream helps in flashing of feed stream and the amount of vaporized liquid is influenced by the temperature of re-circulating stream. Accordingly, Fig. 10c shows that an increase in re-circulating flow rate up to 15,000 kmol/h leads to increase in MDEA recovery of 78% and further increase has not significant effect on MDEA recovery.

In the reclaimer unit, the residual salts accumulate within the re-circulation loop and a constant blow-down from the system is used to remove solids (waste stream). Fig. 11a shows that addition of HSS up to 10,000 ppm in the feed stream leads to increase in heat inputs and further increase in HSS smoothly increases heat input. Fig. 11b reveals a
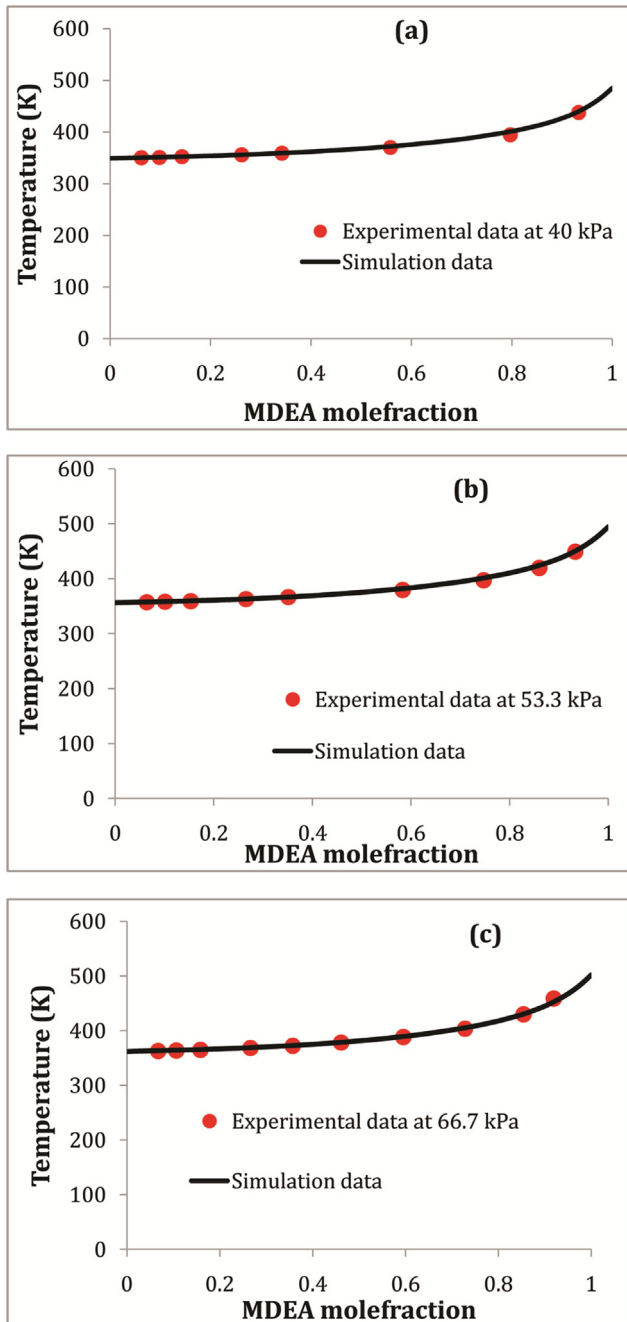
Fig. 5. The experimental and simulation T-x diagram for (a) 40 kPa, (b) 53.3 kPa and (c) 66.7 kPa.

Table 3
Comparison of simulation results with industrial data for MDEA reclaiming.

| Component | Feed | Lean product | |
		Simulation	Industrial
	Mass fraction		
H_2O	0.5664	0.7614	0.7848
MDEA	0.4245	0.2386	0.215
NaOH	0	0	0
HCl	0.0002	0	0.000024
Formic acid	0.003	0	0.000012
Acetic acid	0.0029	0	0.0001
H_2SO_4	0.0003	0	0.000015
$H_2S_2O_3$	0.0029	0	0.0001
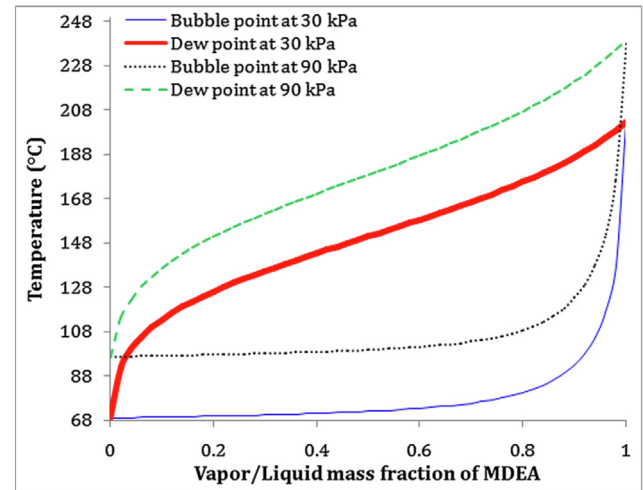
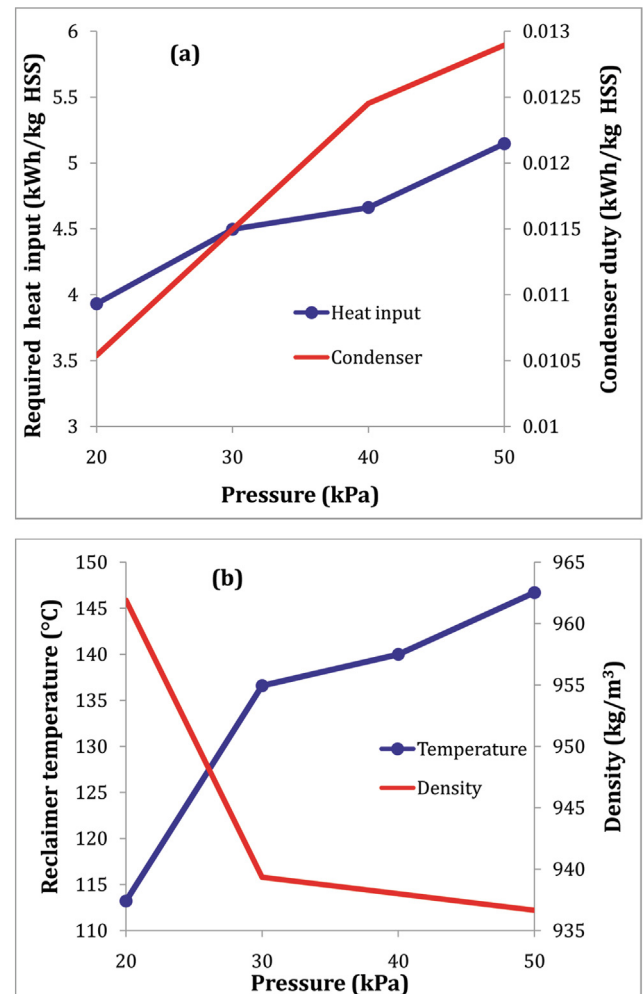**Fig. 6.** The effect of operating pressure on T-xy diagram.

Fig. 7. The effect of operating pressure on (a) energy requirement and (b) reclaimer temperature and waste density.

decreasing trend for energy input per kg of HSS in which the thermal vacuum reclaimer is more economical when energy usage of the reboiler, condenser and pump is concerned. Perhaps, reclaiming of amine by the thermal vacuum distillation technique is better suited for higher HSS's. Fig. 11cshows higher duty for pumping a re-circulation stream with higher HSS content and Fig. 11d confirms a decreasing trend for
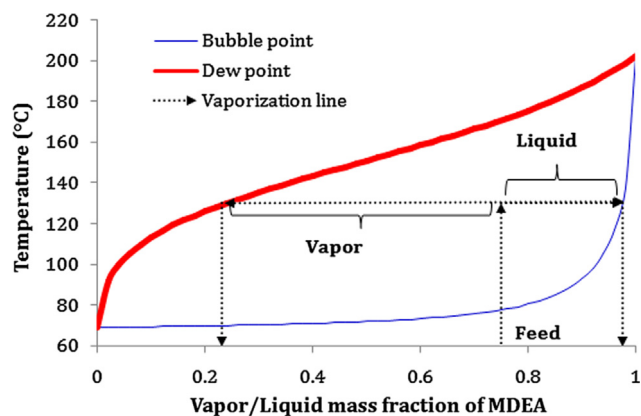
Fig. 8. The effect of feed enrichment on vapour-liquid equilibrium of MDEA/water system.
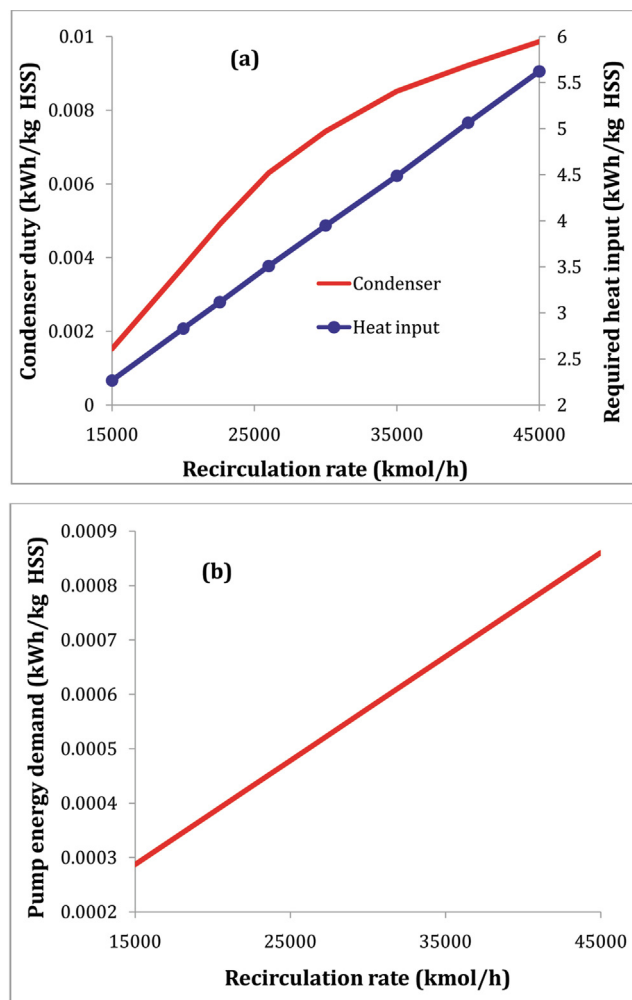

Fig. 9. The effect of re-circulation flow rate on (a) energy requirement and (b) pump duty.

Fig. 10. The effect of re-circulation flow rate on (a) lean amine rate, (b) waste rate and (c) MDEA recovery.

[14] provided a value of 12 kWh/kg HSS for electro-dialysis of MDEA solution. Our findings show that energy usage for thermal vacuum reclaimer in most of cases is lower than that of electro-dialysis. Therefore, thermal vacuum reclaimer process is more economical comparing to electro-dialysis when only energy requirement is concerned.

4. Conclusion

In this study, a thermodynamic equivalent configuration was proposed for an MDEA reclaiming unit, for the first time and a good agreement between the simulation results and industrial data was obtained. The effect of operating pressure, re-circulation flow rate and HSS content on the plant heat requirement and product composition

mechanical energy (re-circulating pump) with addition in HSS in feed. Increase in HSS also leads to more waste stream and less lean amine product as shown in Fig. 12. Fig. 13 indicates the salty lean amine is dark before reclaiming and after thermal vacuum reclaiming, its color changed and a clear liquid is observed during industrial tests implies that the obtained liquid has insignificant impurities.

In order to give a comparison of energy between the proposed method of thermal vacuum reclaimer and electro-dialysis, Sexton et al.
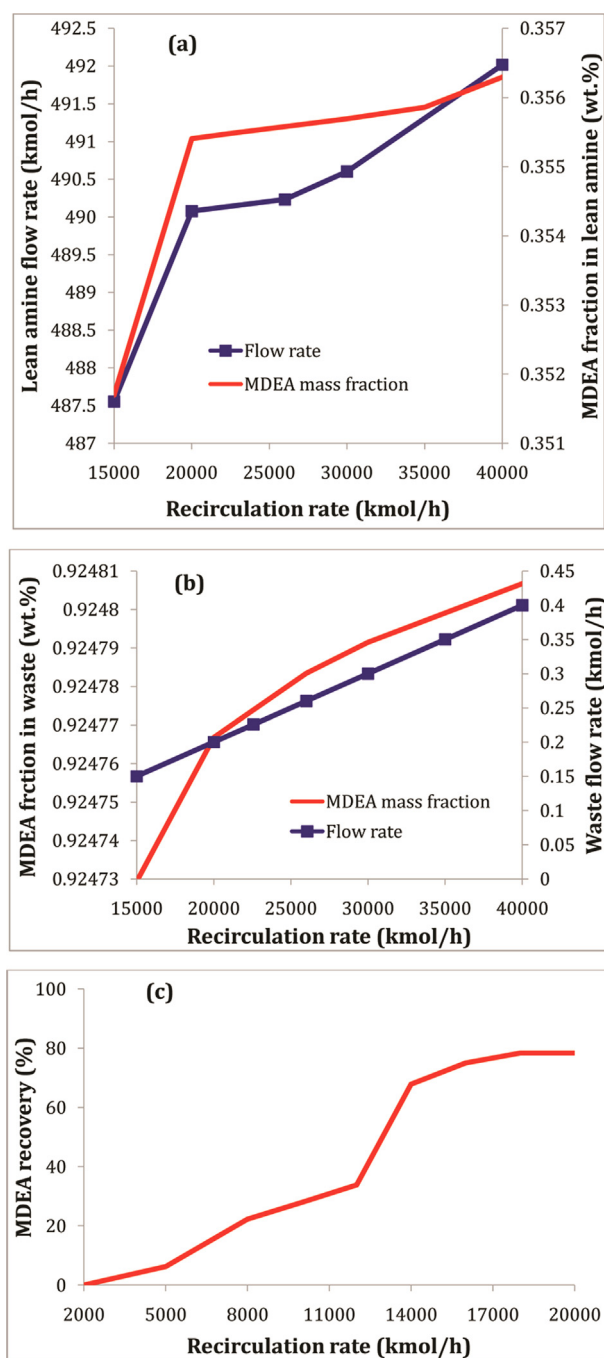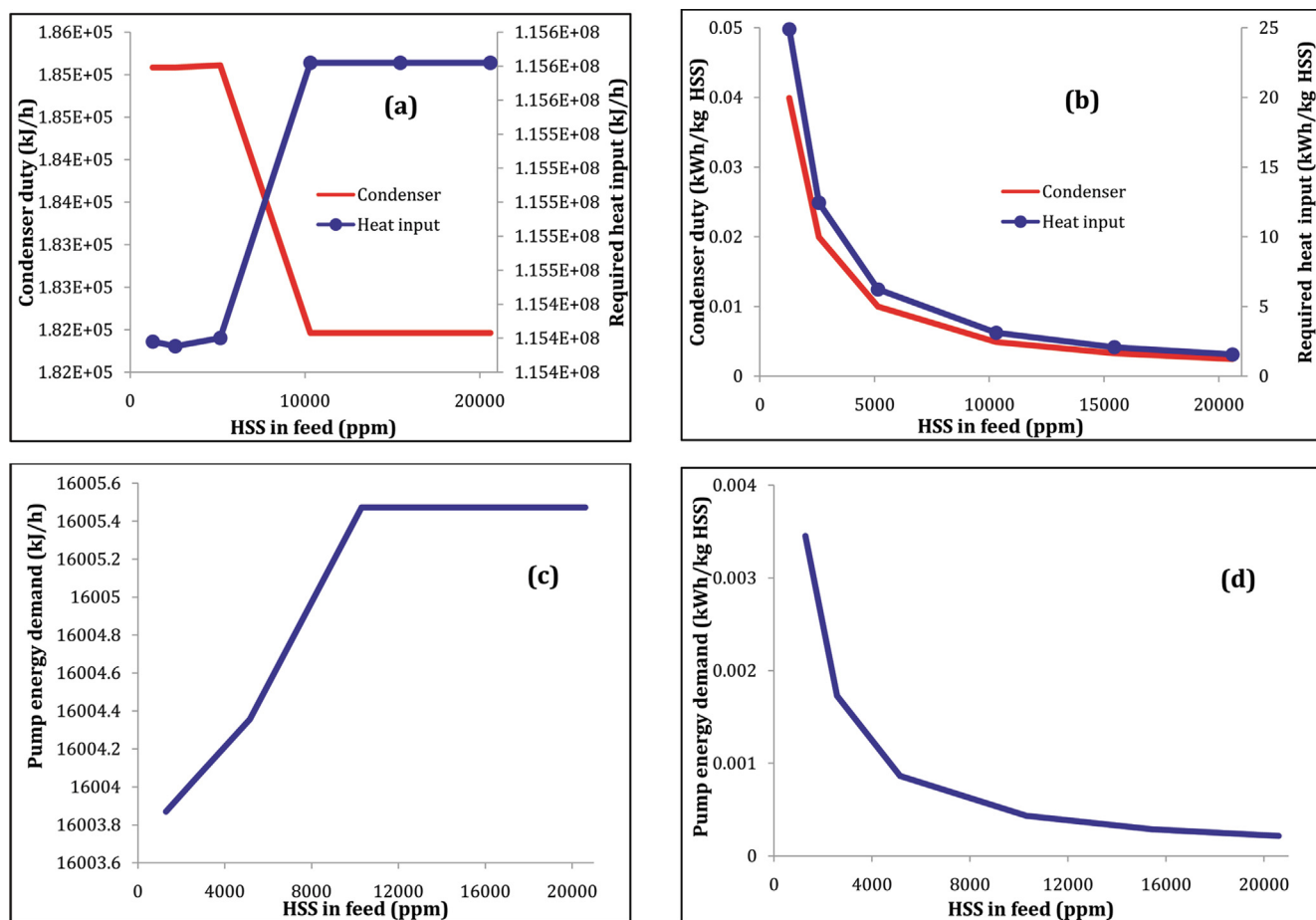
Fig. 11. The effect of HSS on (a) energy requirement with respect to kg of HSS and (b) pump duty with respect to kg of HSS.

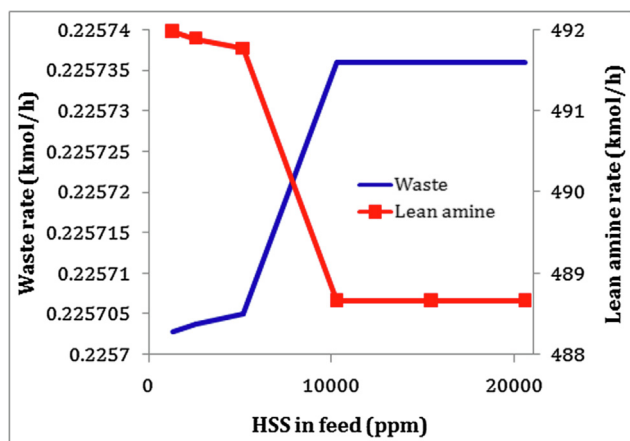**Fig. 12.** The effect of HSS on waste and lean amine rate.

Fig. 13. The color change of lean amine during thermal vacuum reclaiming from dark (salty lean amine) to clear (treated lean amine).

was analyzed. It was found that increase in operating pressure from 20 kPa to 50 kPa leads to increasing of energy requirement of the amine reclaiming unit from 1.45×10^8 kJ/h to 1.9×10^8 kJ/h, the corresponding temperature of the reclaimer increases from 111 °C to 145 °C. So, it is desired to operate in low pressures for the sake of low energy consumption. The simulation results also showed that the energy requirement for heating was much higher than that for condensing product. The binary T-xy diagram indicated that increase in amine concentration of the feed leads to a higher amine recovery and flow rate of the hot re-circulated stream in the reclaimer unit plays a crucial role in the unit. In addition, increase in the re-circulation flow rate from
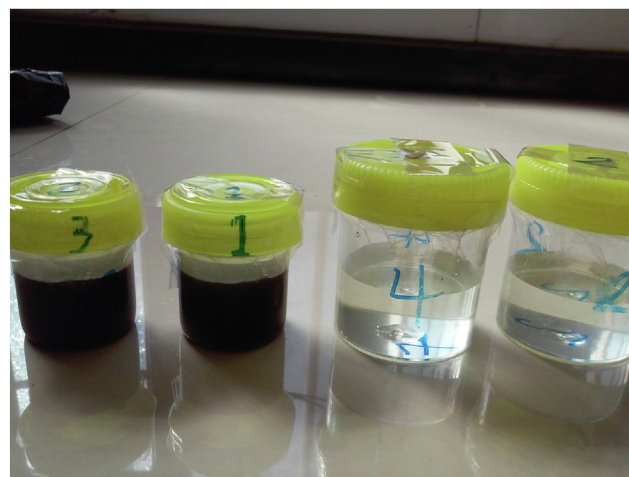
15,000 kmol/h to 45,000 kmol/h resulted in higher energy demand from 9×10^7 kJ/h to 21×10^7 kJ/h. Furthermore, the increase in re-circulation flow rate leads to more MDEA recovery in top product of the reclaimer from 487 kmol/h to 492 kmol/h. Although, an increase in heat inputs from 1.154×10^8 kJ/h to 1.156×10^8 kJ/h was observed with increase of HSS up to 10,000 ppm in the feed stream, the results showed a decreasing trend for energy input per kg of HSS. Therefore, it seems that thermal vacuum reclaimer is better suited when higher HSS's are treated.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2019.116314.

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