

# Journal Pre-proof



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PII: S1004-9541(19)30936-X

DOI: <https://doi.org/10.1016/j.cjche.2019.12.004>

Reference: CJCHE 1598

To appear in: *Chinese Journal of Chemical Engineering*

Received date: 22 October 2019

Revised date: 21 November 2019

Accepted date: 3 December 2019

Please cite this article as: A.A. Abd, S.Z. Naji and A. Barifcani, Comprehensive evaluation and sensitivity analysis of regeneration energy for acid gas removal plant using single and activated-methyl diethanolamine solvents, *Chinese Journal of Chemical Engineering*(2019), <https://doi.org/10.1016/j.cjche.2019.12.004>

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# Comprehensive evaluation and sensitivity analysis of regeneration energy for acid gas removal plant using single and activated-Methyl diethanolamine solvents

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## Abstract

The absorption of acid gas using reactive amines is among the most widely used types of capturing technologies. However, the absorption process requires intensive energy expenditure majorly in the solvent regeneration process. This study simultaneously evaluated the regeneration energy of MDEA and PZ/MDEA solvents in terms of heat of absorption, sensible heat, and vaporization heat. Aspen Hysys version 8.8 simulation tool is applied to model the full acid gas removal plant for the chemical absorption process. The new energy balance technique presents around the absorption and desorption columns to bring a new perspective of energy distribution in the capturing of acid gas plants. Sensitivity analysis of regeneration energy and its three contributors is performed at several operations parameters such as absorber and stripper pressures, lean amine circulation rate, solvent concentration, reflux ratio, and CO<sub>2</sub> and H<sub>2</sub>S concentrations. The results show that the heat of absorption of PZ/MDEA system is higher than that for MDEA system for the same operating conditions. The sensible heat is the main contributor in the required regeneration energy of MDEA solvent system. The simulation results have been validated against data taken from real plant and literature. The product specifications of our simulation corroborate with real plant data in an

excellent approach, additionally the profile temperature of the absorber and the stripper columns are in good agreement with literature. The overall results highlight the direction of the effects of each parameter on the heat of absorption, sensible heat, and vaporization heat.

**Keywords:** Heat of absorption; sensible heat; vaporization heat; regeneration energy; acid gases capturing; piperazine; activated-Methyl diethanolamine.

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## 1. Introduction

Global warming due to anthropogenic greenhouse gas emissions considers as the main challenge in the likely future scenario of increasing the demand for energy because of the continued increases in population and prosperity. CO<sub>2</sub> is arguably the main contributor in greenhouse gases which accounts up to 80% of the total emissions [1]. The oil and gas industry supplies a wide range of energy products while requires intensive energy in the extraction process, besides huge amounts of gas emissions mainly CO<sub>2</sub>. In 2015, the energy consumption in the oil and gas industry was almost 42.7 million tons of standard coal in China only [2]. This amount of consumed energy is accompanied by 100.8 million tons of CO<sub>2</sub> emissions, divided into direct emissions with 47 tons from fuel combustion, 31.6 million tons of indirect emissions from electricity consumption, and 22.2 million tons from the process. Globally, there are almost 15 carbon capture and storage plants executed having a cumulative capturing capacity of 28 million tons per year [3].

Out of the 15 plants, 8 projects shown in **Table 1** installed on natural gas sweetening plants. Various techniques presented to capture acid gases, namely absorption using alkanolamine, membrane technique, oxy-combustion carbon capture, and adsorption. Absorption by alkanolamine considers as a viable option for minimizing the greenhouse gases. The main challenge of using this process is the intensive energy requirements in the capturing process, especially the energy requires to regenerate the solvent that accounts for almost 50% of the whole process energy [4]. **Li et al. (2012)** stated that the required energy to regenerate rich amine solvent is typically 3 to 4 MJ/kg CO<sub>2</sub> [5]. Various modifications have been proposed to solve the problem of high energy consumption. The modifications follow two paths: optimization of process flowsheet and deployment of new solvents. Many attempts have been introduced different modifications in the process flowsheet, **Freguia, and Rochelle (2003)**, **Tobiesen et al. (2007)** discuss the feature of solvent cooling in the middle of the stripper [6][7]. Precooling of the sour gas before the absorber is another strategy to improve the process of capturing and reducing the energy requirements [7][8]. **Jassim and Rochelle (2006)** presented a multi pressure configuration to operate the stripper at different pressures which increases the possibility of recovery of stripping steam at high-pressure levels [9]. Steam heat losses from the stripper consider as one of the direct reasons that the amine scrubbing is inefficient, where the vaporized water emitted with CO<sub>2</sub> from the top of the absorber. The absorber overhead process can be minimized using a cold bypass that recovers the heat and saves energy for later uses [10]. **Arnaiz and co-workers (2019)** presented chemical looping

combustion as a promising technology to reduce the energy penalty [11]. Where chemical looping combustion suggests the use of oxygen carriers to exist the combustion of fuel without nitrogen. A series of investigations have been performed at DONG Energy's pilot to advance CO<sub>2</sub> capturing, the results observed 7% energy saving from the stripper inter-cooling process. While improving the configuration of the lean vapor recompression can result in saving up to a 20% reduction in energy requirements for reboiler in the MEA process [12]. Furthermore, several other modifications have been proposed like using absorber condenser and feed stream back to the absorber, optimization of the rich solvent injection in the stripper, and deploy multi absorber to achieve efficient regeneration of the solvent. **Karimi et al. (2011)** reported that the vapor recompression configuration is the best choice regarding CO<sub>2</sub> loading capacity and the total energy requirements [13]. **Romeo et al. (2008)** proposed a new design of low-pressure heater to take advantage of the compression cooling of CO<sub>2</sub>. Alkanolamines such as MEA, MDEA, DEA, DGA, and AMP are most solvents that use to absorb CO<sub>2</sub> in the industry [14]. **Raynal et al. (2011)** mentioned that The CASTOR EU project proved that the using of alkanolamine solvents can meet the requirements of removal 90% of CO<sub>2</sub> from sour gas [15]. **Naji and Abd (2019)** reported that the advantages of using alkanolamine solvents are cost-effectiveness, ability to absorb high concentrations of acid gases, and the possibility of re-use of the solvents [16]. On the other hand, their study mentioned that the energy penalty is the main problem facing absorption by alkanolamine solvents. **Zhao et al. (2017)** mentioned that monoethanolamine (MEA) solvent is widely used due to its high reactivity with

carbon dioxide, some other studies [18, 19, 20] support this trend [17]. However, the regeneration of the MEA solvent needs high energy up to 70-80 % from the capturing plant cost [4][5]. **Zhang et al. (2016)** concluded that the regeneration energy requires to regenerate MEA from the rich solvents is 4.2 GJ/ton CO<sub>2</sub> for their study system [22]. The high regeneration energy is attributed to the high enthalpy of MEA with carbon dioxide [17]. **Gupta et al. (2013)** presented that the enthalpy of solution considers as a crucial property in the design of capturing plants [23]. Where the amount of steam requirements in the amine regeneration section relates directly to the enthalpy of solution. **Li and Smith (2016)** stated that the absorption heat of reaction is 95 kJ/mol CO<sub>2</sub> for MEA and it is difficult to change by process improvements [24]. Methyl-diethanolamine (MDEA) is a tertiary amine usually used to absorber acid gases in the traditional absorption capturing process. The reaction heat of produced bicarbonate from the reaction of MDEA and CO<sub>2</sub> is 61 kJ/mol CO<sub>2</sub> which is much lower than that 95 kJ/mol CO<sub>2</sub> of MEA/CO<sub>2</sub> [25, 26]. MDEA itself comes with a low absorption rate towards CO<sub>2</sub> which limits its application in acid gas separation, piperazine presented as an absorption activator that can promote the absorption rate [27]. Blend solvents (PZ/MDEA) have much lower heat of reaction (70 kJ/mol CO<sub>2</sub>) compare to 95 kJ/mol CO<sub>2</sub> heat of reaction for MEA [26]. These improvements in the capacity of the solvent made great strides in terms of reducing energy for instance ~0.4 MW h/ton CO<sub>2</sub> to ~0.3 MW h/ton CO<sub>2</sub> based on MEA solvent process [28]. **Nwaoha et al. (2016)** demonstrated that tri-solvent amine requested lower regeneration energy compared to a single amine solvent, other studies [30, 31] confirmed this finding [29]. Phasic solvents are phase change

solvents as a new breed of systems to capture acid gases. **Pinto et al. (2014)** demonstrated that the process with phase change solvents can operate with low energy demand around 2.1 GJ/ton of CO<sub>2</sub> [32]. The concept is that the single-phase solvent stream splits into two-stream one drawback direct to the absorber and only the rich CO<sub>2</sub> stream sends to the stripper which reduces the required energy of regeneration due to low flowrate [ 33, 34, 35]. The regeneration energy is a combination of three types of heats 1) heat of absorption 2) sensible heat is the heat required to bring up the temperature of the solution close to the stripper conditions 3) the vaporization heat is the required heat to generate steam in the stripper to serve the regeneration process [36, 37]. Out of the mentioned heats, absorption heat considers as the main contributor in the regeneration energy. **Kim and Svendsen (2011)** presented the heat of absorption as the sum of heat of reaction and the heat of dissolution [38]. The heat of absorption can be determined by dividing the total heat duty by the total amount absorbed of carbon dioxide [39]. Several studies executed in estimating the heat of absorption for tertiary amines solvents is reported in Table 2. **Conway et al. (2014)** conducted that to reduce the sensible heat, the specific heat capacity and the density of rich solution should be small, correspondingly the cyclic capacity should be high [40]. **Aronu and co-workers (2011)** reported that high cyclic capacity results in low sensible heat and low amine solvent recirculation rate [41]. Sensible heat in a typical system of aqueous MEA accounts for up to 40% of the regeneration heat due to the high amount of water. **Nwaoha et al. (2017)** described the vaporization heat as the required heat that can generate the required vapor to desorption acid gases

from the solvent [42]. The heat of vaporization depends on the rate of water in the solvents solution where low water content comes with low heat of vaporization [43].

Number of questions regarding the regeneration energy consumption remain to be addressed. Additional studies to understand more completely the key tenets of regeneration energy are required. The aim of this paper extends the knowledge of regeneration energy by investigation of various parameters that have direct and/or indirect effects on the heat of absorption, sensible heat, and vaporization heat. New energy balance technique has been introduced around the absorber and stripper columns to estimate energy demand. The study baseline specifications are taken from Habshan acid gas removal plant in Abu Dhabi and data of this work collect using Aspen HYSYS simulation tool. The paper seeks to investigate the effects of absorber and stripper pressures, lean amine circulation rate, lean amine temperature, solvent concentration, reflux ratio, and CO<sub>2</sub>/H<sub>2</sub>S concentrations on the three heats elements of the regeneration energy. This paper presents a good opportunity of understanding the regeneration energy in terms of the main contributors and the operation parameters.

Table 1: Carbon capture and storage plants on natural gas units around the world. [44, 45]

Project	Capture Technique	Capacity (Mt/year)
Val Verde Unit	Selexol	1.3
Shute Creek Facility	Selexol	7
Sleipner CCS Plant	MDEA	0.9
Snøhvit CCS Plant	MDEA	0.7
Century Project	Selexol	8.4
Lost Cabin Gas project	Selexol	0.9
Petrobras Lula Oil Field CCS Project	Membrane	0.7
Uthmianiyyah CO <sub>2</sub> -EOR Project	DGA	0.8

Table 2: some of previous studies about heat of absorption.

Authors	Amine Solvent	Temperature, k	Pressure, kPa
Merkley, K. (1987) <sup>[46]</sup>	MDEA (20,40,60%)	288.7, 333, 388, 422	156, 225, 570, 1121
Oscarson, et al. (2000) <sup>[47]</sup>	MDEA (20,35,50%)	299.9, 349.9, 399.9	1380, 3450, 6900
Mathonat, et al. (1997) <sup>[48]</sup>	MDEA (30%)	313.2, 353.2, 393.2	2000, 5000, 10 000
Kierzkowska- Pawlak, et al. (2002) <sup>[49]</sup>	MDEA (10,20,30%)	293.2, 313.2, 333.2	100, 300
Carson, et al. (2000) <sup>[50]</sup>	MDEA (10,20,30%)	298.2	265
Arcis, et al. (2008) <sup>[51]</sup>	MDEA (15, 30%)	322.7	200–5000
Kim, et al. (2011) <sup>[38]</sup>	MDEA (30, 40%)	313.2, 353.2, 393.2	300

## 2. Energy analysis scope and method

The regeneration energy has a crucial impact on the total cost of acid gas capturing plants and therefore considers the main criterion in the economic evaluation of CO<sub>2</sub> capturing. Accurately estimation of the enthalpy of feed to the stripper is difficult due to the amine/amine heat exchanger which increases the temperature and resulting in vaporized part of the absorbed acid gases. It has therefore been assumed that there is no vaporization of the absorbed acid gases in the amine/amine heat exchanger. In addition, all the heat that releases from the lean solvent solution taken up by the feed solution where this heat will increase the temperature of feed and decreases the reboiler duty. The amount of vapor stream leaving at the top of the flush drum has a molar rate of 46.23 Kmol/h which is less than 0.03% from the feed and can be neglected. Finally, the temperature difference between sour feed gas and the solvent is small. The regeneration heat consists of three elements: the heat of absorption, sensible heat, and vaporization heat. The reaction between CO<sub>2</sub>/H<sub>2</sub>S and solvent is exothermic and relates to the change in enthalpies. The change in enthalpy is mostly due to the change in the specific heat capacity and the temperatures. It has therefore been used the differences in the heat capacities and temperature to predict the heat of absorption. Similar to the heat of the absorption, increasing the sensible heat leads to increasing in the total regeneration heat. The sensible heat is obviously relating to the total recirculation of the amine solvents and the type of amine. The heat of vaporization in this simulation estimated for water only due to the boiling point of water 100 °C much lower that of amines 145-170 °C which makes water

more susceptible than amines. To estimate the total regeneration heat for CO<sub>2</sub>/H<sub>2</sub>S capturing plant from natural gas, energy balance deployed for absorption and desorption columns. Fig. 1 displays the bounded region around the absorber to illustrate the feed stream in and out. Applying the energy balance around the absorber can give the total heat of absorption as shown in equation 1.

$$\text{Heat of absorption} = \dot{m}_{sweet}(H_{sweet} - H_{sour}) + \dot{m}_{lean}(H_{lean} - H_{rich}) \quad (1)$$

Where,  $\dot{m}_{sweet}$  and  $\dot{m}_{lean}$  are the molar flow rate of clean gas and amine respectively, and H represents the enthalpy for sweet and sour gases, and lean and rich solutions. This heat should be applied to the reboiler to separate the dissolved acid gases and will be called dissolution heat as in equation 2.

$$\text{Heat of absorption} = -\text{Heat of dissolution} \quad (2)$$

While the energy balance on the stripper columns can be illustrated as in equation 3:

$$Q_{reboiler} + \dot{m}_{lean}(H_{lean} - H_{rich}) = Q_{condenser} + \dot{m}_{acid\ gas} * H_{acid\ gas} \quad (3)$$

Where,  $Q_{reboiler}$  and  $Q_{condenser}$  are the heat duty of reboiler and condenser respectively.  $\dot{m}_{acid\ gas}$  and  $H_{acid\ gas}$  are molar flowrate and molar enthalpy.

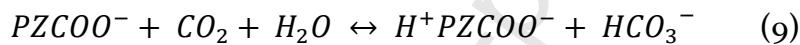
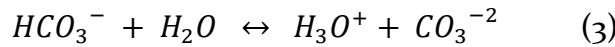
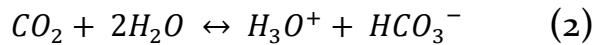
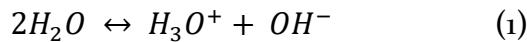
$Q_{condenser}$ ,  $\dot{m}_{acid\ gas}H_{acid\ gas}$ , and  $\dot{m}_{lean}(H_{lean} - H_{rich})$  represented vaporization heat, the heat of absorption, and sensible heat respectively. It is observed that the summation of the sensible, vaporization, absorption heats equals to the required reboiler energy. The total enthalpy of the reaction of the solution is the summation of every single element. The heat of absorption counts the largest contributor for the regeneration energy. Increasing the concentration of solvent and rich acid gas loading results in reducing the heat

of absorption. Reducing the temperature difference and minimizing the mass flow rate of the solvent lead to reduce the sensible heat. While the amount of energy required to vaporized steam in the stripper depends mainly on the temperature of the solution before entering the condenser. To conclude, the total energy required for regeneration of the solvent is the sum between the heat of absorption and heat of reaction.

### **3. Simulation basis and process mechanism**

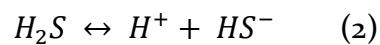
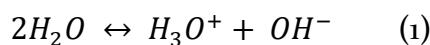
As a baseline case, the specifications of the study have been taken from Habshan natural gas stream as shown in Table 3. Carbon dioxide and hydrogen sulfide in the feed stream are 3.29% and 0.55% which are absorbed by single or piperazine-MDEA solvents with total amine concentration fixed to 45%. The simulation deployed piperazine to MDEA solvent to compare the results with the MDEA solvent specifications (Habshan unit uses 45% MDEA only). The process is shown in Fig. 1 has been simulated using Aspen HYSYS program version 8.8 which is widely used in the oil and gas industry. Aspen HYSYS offers various types of thermodynamics fluid packages like Peng-Robinson, SRK, Glycol Package, and Acid Gas. Acid Gas fluid package is recommended for hydrocarbons; it has therefore been chosen [16]. To simplify the process complexity, some assumptions made i.e. all the heat exchangers flow in counter current mode, the liquid and vapor leave each tray in equilibrium, the vaporization of amine is negligible, no degradation and corrosion of solvent and no heat losses in the absorption/desorption columns.

Various reactions proposed between the PZ/MDEA solvent and CO<sub>2</sub> in presence of water as below [27, 52, 53, 54, 55, 56, 57]:



Reactions 1,2, and 3 represent the typical process of ionization of the aqueous solution. **Sartori and Savage (1983)** stated that the reaction between MDEA solvent and CO<sub>2</sub> comes with very low absorption rate which generates HCO<sub>3</sub><sup>-</sup> instead of MDEACOO<sup>-</sup> as shown in reactions 4 and 5 [55]. Therefore, piperazine activator is important to promote the absorption rate. The rest of reactions display the process of formation of deprotonated and dicarbamate as a result of CO<sub>2</sub> and PZ reaction.

Correspondingly, H<sub>2</sub>S reacts with MDEA solvent instantaneously and involve proton transfer:





Reactions 1 and 2 present the ionization of water and dissolved H<sub>2</sub>S, while reaction 3 shows the protonation of MDEA and reaction 4 is the overall reaction. The absorption process is carried out applying chemical amine solvent includes mass transfer through several exothermic reactions. The target here is to accelerate the mass transfer rate and presents a higher solvent loading capacity. For the regeneration, the reaction in the stripper is endothermic and favors high temperature and low pressure as an operating condition. Therefore, more heat of reaction of amine solvent means more regeneration energy required to regenerate the solvent. The tray spacing is chosen to be 0.6096 m in the range 0.5 to 0.76 based on recommendations from previous studies [58, 59] and the other columns input specification is shown in Table 4. To avoid the possibility of foaming, the system factor for both absorber and stripper specified to be 0.8 [59]. High concentration of piperazine leads to precipitation, it has been therefore limited the piperazine concentration below 7% [59, 60].

Table 3. Real plant specifications.

Sour Feed Gas Stream	
Pressure, bar	67.5
Temperature, °C	55
Feed gas flowrate, MMSCFD	610
Compositions	Mole fraction
C <sub>1</sub>	0.766
C <sub>2</sub>	0.0643
C <sub>3</sub>	0.0353
H <sub>2</sub> S	0.0055
CO <sub>2</sub>	0.0329
N <sub>2</sub>	0.0913

Lean Amine Stream	
Solvent	0.45
H <sub>2</sub> O	0.55
Pressure, bar	67.5
Temperature, °C	60
Flowrate, m <sup>3</sup> /h	360

Table 4: Absorber/Stripper input data [58].

Absorber Column	
Trays number	25
Sour gas feed stage	2
Lean amine feed stage	21
Tray type	Valve
Absorber diameter	2.8 m

Stripper Column	
Trays number	25
Feed stage	25
Tray type	valve
Reboiler type	shell and tube heat exchanger
Condenser type	Air cooled

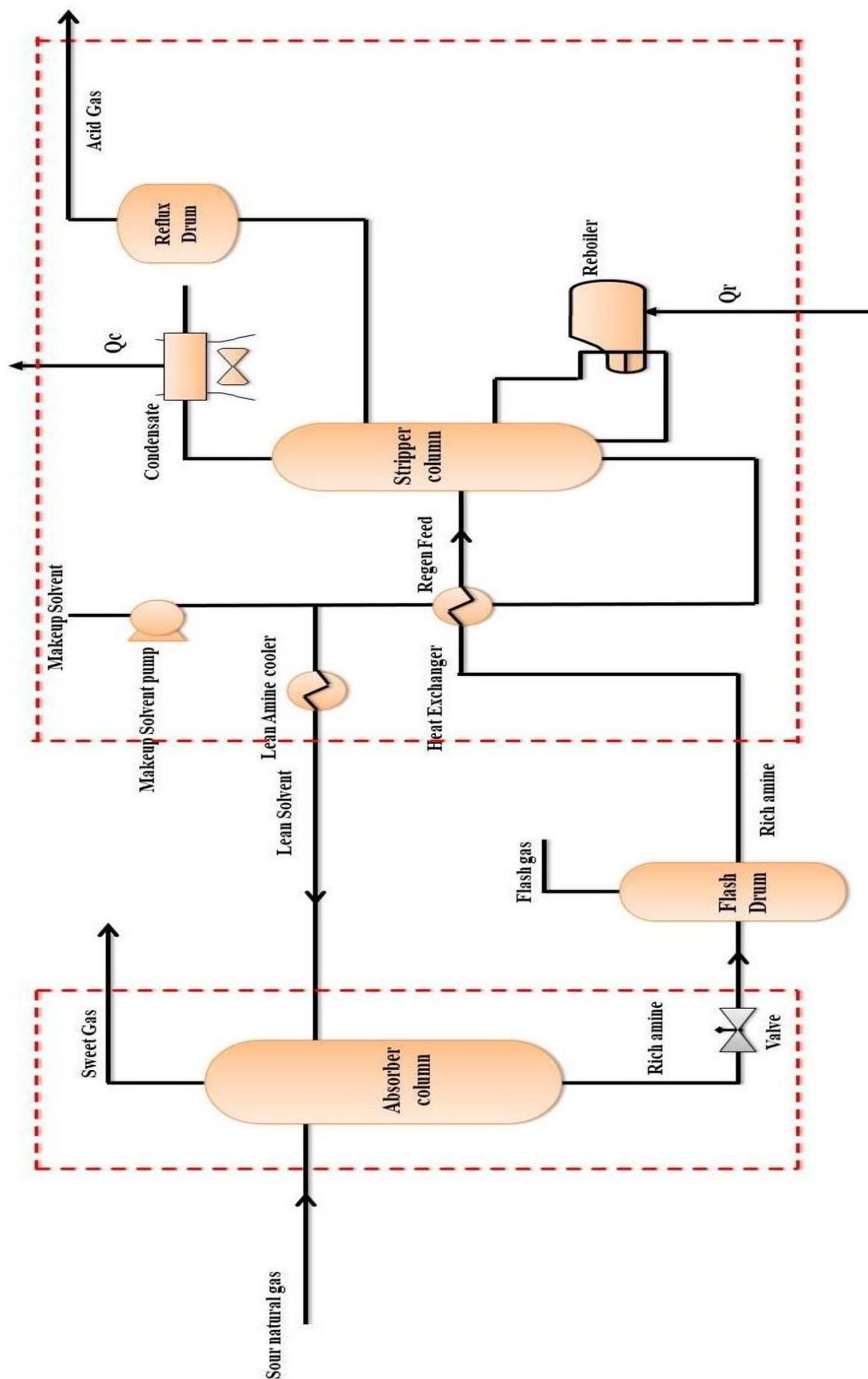


Fig. 1: Process flow diagram for the acid gases removal plant.

#### 4. Simulation validation

Firstly in this work is the validation of the simulation results with real plant and literature as a baseline so that the simulation is capable to accurately estimate the plant specifications over a various range of conditions. The temperature profile for both the absorber and stripper column is the best approach to validate the process [61]. The CO<sub>2</sub>/amine reaction is exothermic and the temperature increases as the absorption rate increases [62]. The absorber temperature profile for a high concentration of MDEA solution (> 30%) usually starts increasing and then drops to the outlet temperature at the bottom of the absorber [63, 64, 65]. In addition, the stripper temperature profile is usually high at the bottom of the columns (almost linear from the center of the column to the bottom) due to the reboiler energy [3, 66]. Our simulation results bear a close resemblance to literature findings in regards of absorber and stripper temperature profile for both solvents MDEA and PZ/MDEA as shown in Fig 2.

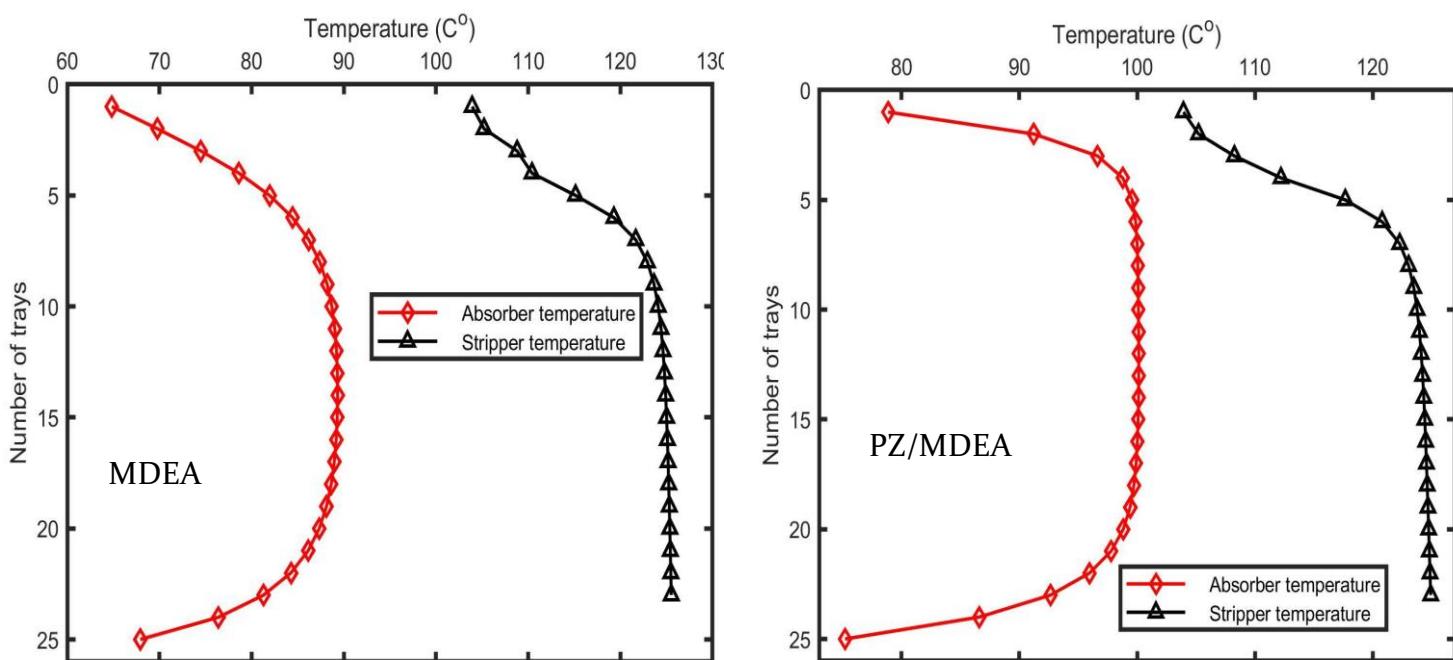


Fig.2: Temperature profile for Absorber/Stripper columns.

The other results of the simulation plant and the actual plant are compared to validate the reliability and the accuracy of the simulation results. Table 5 displays the comparison between the simulation results and the actual plant data from Habshan acid gas removal plant.

Table 5: Comparison between simulation data and actual plant specifications.

Parameter	Actual Plant 45% MDEA	Simulation 45% MDEA	Simulation 5% PZ/ 45% MDEA
<b>Feed gas</b>			
CO <sub>2</sub>	1133 kmol/h	1133 kmol/h	1133 kmol/h
H <sub>2</sub> S	170.11 kmol/h	170.13 kmol/h	170.13 kmol/h
Temperature	54.5 °C	54.5 °C	54.5 °C
Pressure	67.5 bar	67.5 bar	67.5 bar
<b>Sweet gas</b>			
CO <sub>2</sub>	676 kmol/h	442.3789 kmol/h	55.936 kmol/h
H <sub>2</sub> S	0.60 kmol/h	0.81 kmol/h	0.3109 kmol/h
Temperature	60 °C	64 °C	67 °C
Pressure	66.5 bar	66.5 bar	66.5 bar
Total flow	29835 kmol/h	29661.55 kmol/h	29406.44 kmol/hr
<b>Acid gas</b>			
CO <sub>2</sub>	456.6 kmol/h	647.07 kmol/h	1021.445 kmol/h
H <sub>2</sub> S	169.6 kmol/h	161.98 kmol/h	178.4959 kmol/h
Temperature	57 °C	51.43 °C	53
Pressure	2 bar	2 bar	2 bar
Total flow	686.66 kmol/h	1244 kmol/h	853.9 kmol/h

## 5. Results and discussion

A common absorption/desorption acid gases removal process adopted for simulation Fig.1. The sour natural gas fed to the absorption to the bottom of the absorber column and contacts the downward amine solvent stream known as a lean amine stream. The rich amine solution leaves the absorber column and enters the flash drum to vent the generated vapor before entering the lean/rich heat exchanger. After the exchanging of heat between the rich amine stream and the regenerated solvent from the stripper, the rich amine enters the stripper at the bottom. The stripper is working at a higher temperature than that for absorber and a pressure more than the atmospheric pressure. The process simulation conducted by using Aspen HYSYS with aiming of comparison between MDEA and PZ/MDEA systems in terms of regeneration energy. For accurate comparison, both systems have been simulated at the same feed conditions that mentioned in Table 3 with different solvents. Fig. 3 reveals that the absorption heat of PZ/MDEA is the main contributor to the regeneration energy. Correspondingly, the regeneration energy is mainly

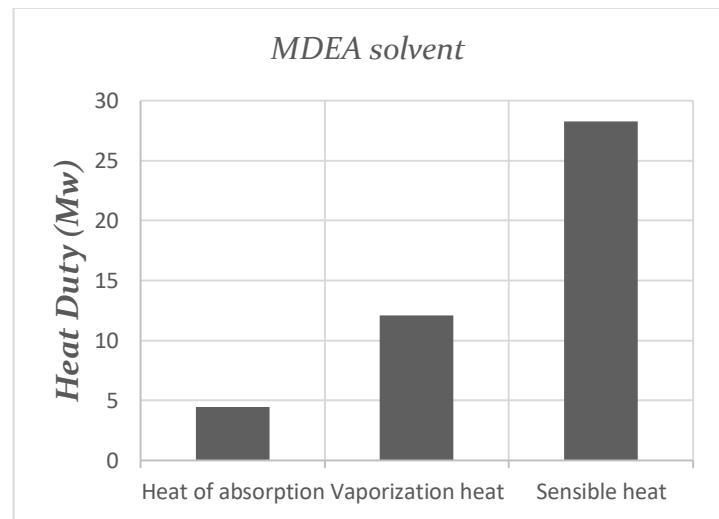
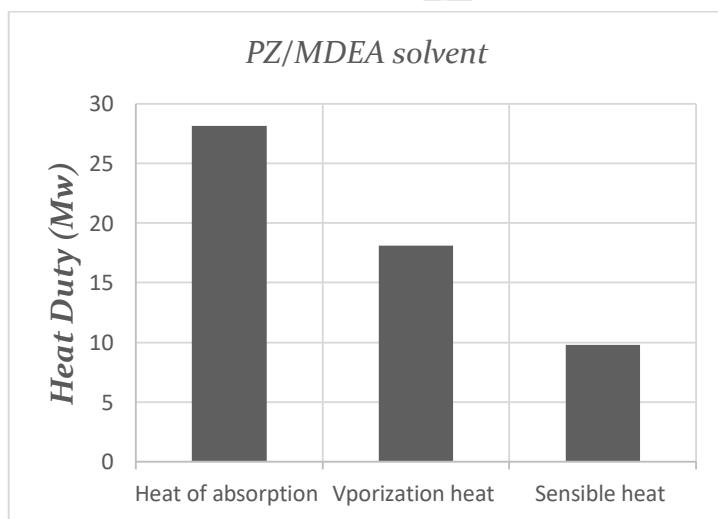


Fig. 3: comparison of heats distribution for MDEA and PZ/MDEA solvents.

### 5.1. *Absorber/stripper pressure*

Absorber pressure has been considered to be a critical parameter that is not likely to change significantly during the operation. **Mudhasakul et al. (2013)** reported that applying high pressure in the absorber column can help the absorption process in terms of carbon dioxide capturing [67]. In order to test the effects of absorber column pressure on the regeneration energy, analysis study has been executed to investigate a various range of pressures. Fig. 4 illustrates the effects of absorber pressure on the regeneration energy in terms of its three heats duties. The results observe that high absorber pressure is highly energy consumption for both solvents types. Increasing the absorber pressure will increase the driving force for the absorption resulting in increases the rich solution loading. This causes a reduction in the required solvent flowrate. Correspondingly, piperazine volatility increases by reduction of absorber pressure [25]. Therefore, this dual effect should be considered in estimating the optimum absorber pressure. The effects of regenerator pressure on the regeneration energy in terms of heat of absorption, sensible heat, and vaporization heat have been evaluated. The three heats slightly increase with increasing the stripper pressure. Generally, high pressure of stripper enhances the carbon dioxide desorption, while high pressure increases the water vapor in the outlet acid gases stream thereby reducing the useless energy [68]. It is important to notice that the transferred heat in the Lean/Rich heat exchanger increases significantly due to increasing the temperature difference between the absorber and the stripper when increasing the stripper pressure. For the

latter, the absorber and stripper operation pressures are a critical issue and should be subjected to future technical optimization.

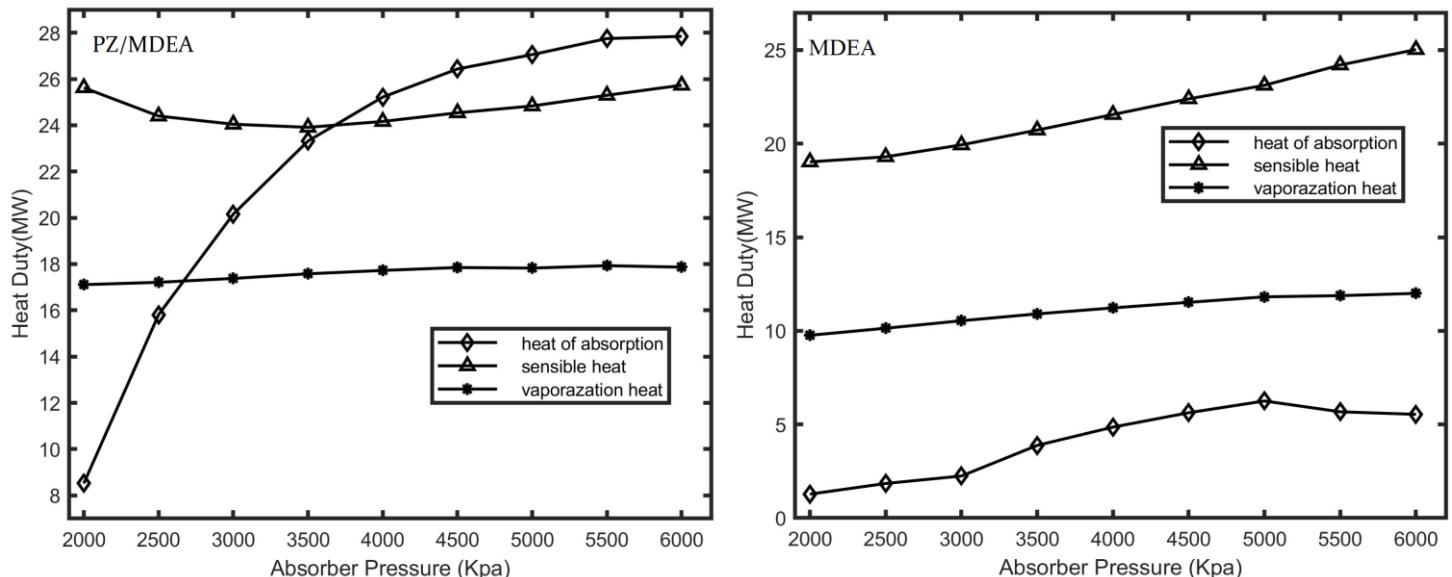


Fig.4: Effects of Absorber/Stripper pressure on the energy distribution.

### 5.2. Lean amine circulation rate

The amine circulation rate has a close bearing on the energy requirements for the acid gases capturing plant. The solvent circulation rate is a crucial issue because it influences directly the regeneration energy and the absorber column size. **Raksajati and co-workers (2013)** investigated the effect of the solvent properties, solvent concentration, and solvent loading on the regeneration energy for their system [69]. In their study conducted that the regeneration energy increases as the solvent circulation rate is increased. The increase of amine solvent circulation rate can be used to enhance the absorption performance in terms of providing more solvent-free molecules that can capture CO<sub>2</sub> and enlargement of the gas/liquid interface active area. A corresponding major heat requires to pump the solvent and extra energy to

heat a rich amine stream to the proper temperature for the regeneration column. Analysis study has been performed to examine the effect of amine circulation rate ranging from 350 to 500  $m^3/h$  on the sensible, absorption, and vaporization heats. The results are in good agreement with literature where three types of heats increase as the amine circulation rate is increased and the regeneration energy as a result. The most remarkable result to emerge from the data is that the heat of absorption for the PZ/MDEA solvent is significant compared to the heat of absorption of MDEA solvent for the same operating conditions as shown in Fig. 5. Interestingly, the sensible heat requires for the PZ/MDEA solvent system is low compared to MDEA solvent system while the vaporization heat requires for the PZ/MDEA system is low compared to MDEA system. Therefore, it might not necessary that an increase in the amine circulation rate improves the overall system performance.

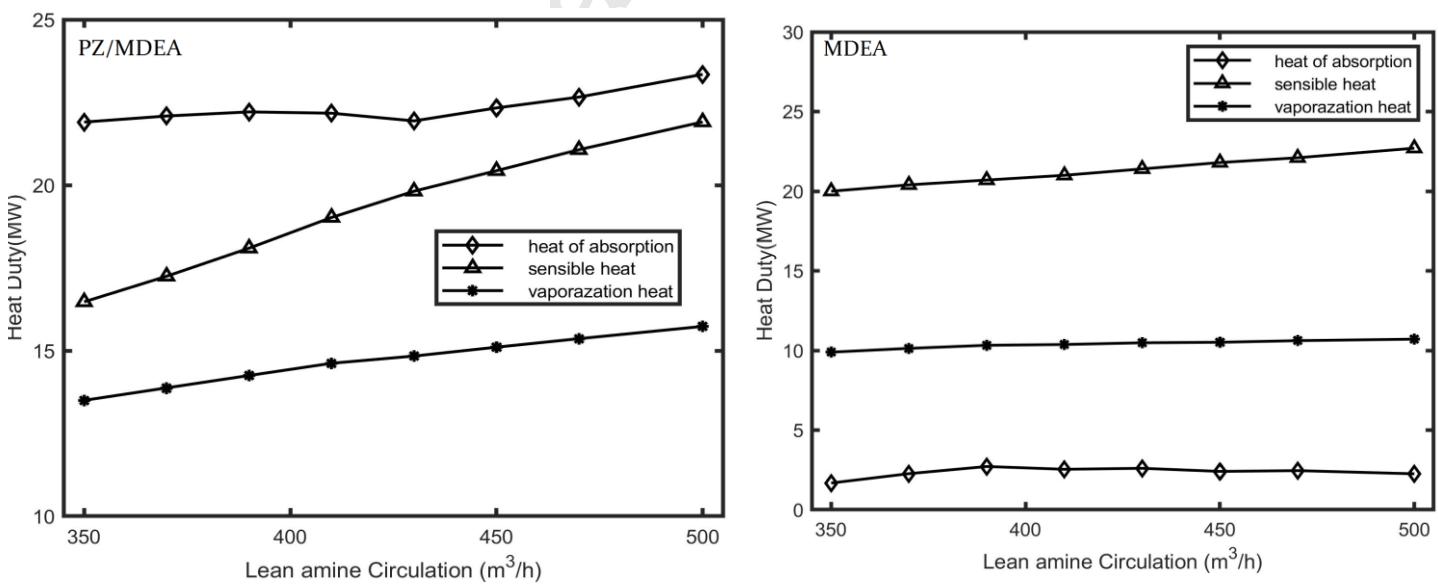


Fig.5: Effects of lean amine circulation rate on the energy distribution.

### 5.3. Solvent concentration

Piperazine is an effective activator for MDEA solution where it absorbs CO<sub>2</sub> quickly and transfers the absorbed molecules to the MDEA [25]. Carbon dioxide preferentially reacts with piperazine to form carbamate instead of consisting bicarbonate as a result of reacting with MDEA due to higher stability of carbamate. Ghalib et al. (2017) conducted that the piperazine concentration impact is dependent on the acid gas partial pressure and temperature [70]. They revealed, increasing piperazine concentrations have a positive impact on the acid gas loading at high acid gas partial pressure. Correspondingly, increasing temperature has a negative impact on the acid gas loading, where Dashti et al. (2019) stated, the best working range temperature is between 45 °C to 55°C [71]. Analysis study has been executed to investigate the effects of increasing piperazine concentrations on the sensible, vaporization, absorption heats. The results demonstrate that the three types of heats depend on piperazine concentration in a great extent. The heat of absorption for mix solvents is not always estimated as the average value of heat of absorption for separate solvents due to the fact that carbon dioxide/hydrogen sulfide will not react in equal rate with every single solvent. Both vaporization heat and heat of absorption increase as piperazine concentration increases. At high piperazine concentration, the reaction rate will increase, and this may result to fast the absorption equilibrium that leads to an increase in the heat of absorption. In addition, increasing piperazine content in the solvent solution will reduce the water content which turns in reducing the amount of vaporized water. On the contrary, sensible heat for the PZ/MDEA solvent decreases as the PZ

concentration increases as shown in Fig. 6. The enthalpy of the solution increases as the PZ loading increases which reduces the amount of vaporized water that required to reach the separation specifications. A higher concentration of PZ loading absorbs more CO<sub>2</sub>, which causes a reduction in enthalpy and as a result reduction in sensible heat. For single MDEA system, Fig. 6 shows the effect of varying MDEA concentration on the heat distribution. As the MDEA concentration increased a sharp decline in sensible heat can be noticed together with increasing in the absorption heat, while the vaporization heat is almost constant or varying in small scale.

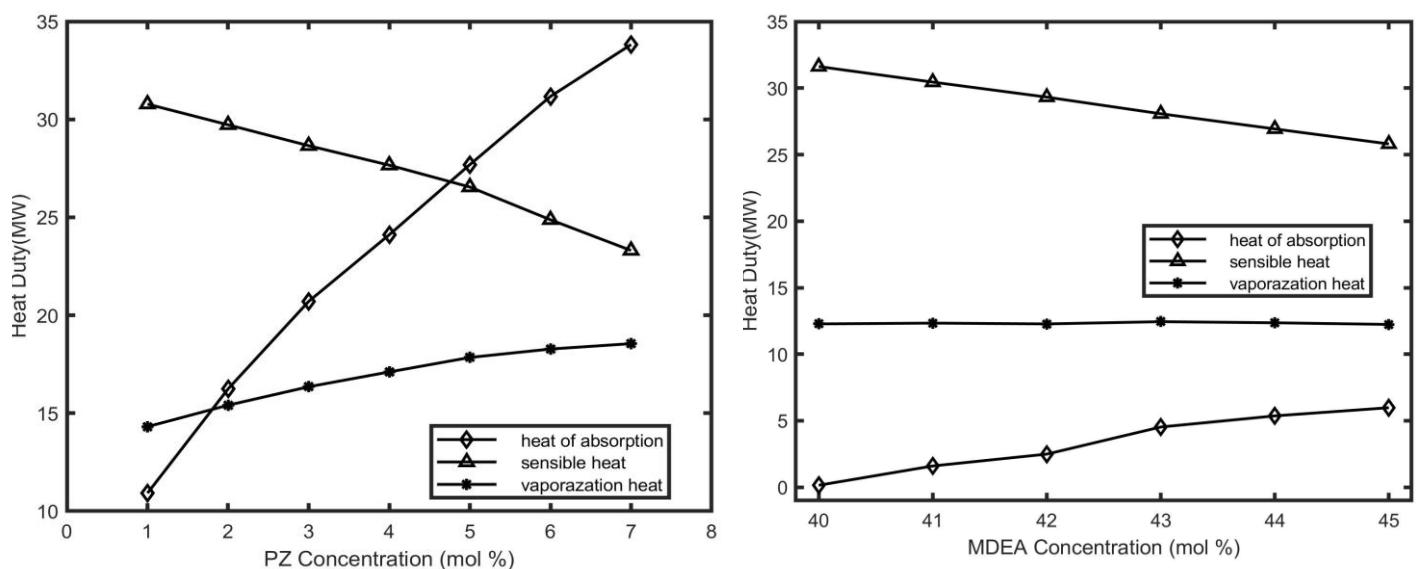


Fig.6: Effects of piperazine concentration on the energy distribution.

#### 5.4. Lean amine temperature

Lean amine temperature can be deployed to control the temperature of the absorber and its reaction kinetics. Lean amine effects on the distribution of three energy parts have been studied for PZ/MDEA and MDEA systems. Generally, reduction of the absorber temperature enhances the column performance and due to the difficulty of manipulating the feed sour gas

temperature, lean amine temperature plays a pivotal role in controlling the absorber temperature. **Addington and Ness (2010)** advised maintaining the temperature difference between the sour feed gas stream and the lean amine stream in range 5 to 10 °C [72]. The results show that the vaporization and sensible heats decrease as the lean amine temperature increases for both systems as shown in Fig. 7. On the contrary, the heat of absorption increases as the lean amine temperature increases for both solvents. It is interesting to note that the heat of absorption starts increasing sharply up to 60 °C and then decreases. The possible reason is that more CO<sub>2</sub> reacts with PZ/MDEA solvent results in more generated energy as the reaction here is exothermic. The generated energy will increase the temperature of the stream that enters the stripper column. As a consequence, the solubility of CO<sub>2</sub> decreases, therefore low sensible heat required to regenerate the solvent. Correspondingly, reducing the solubility of CO<sub>2</sub> in the solvent increases the heat of absorption.

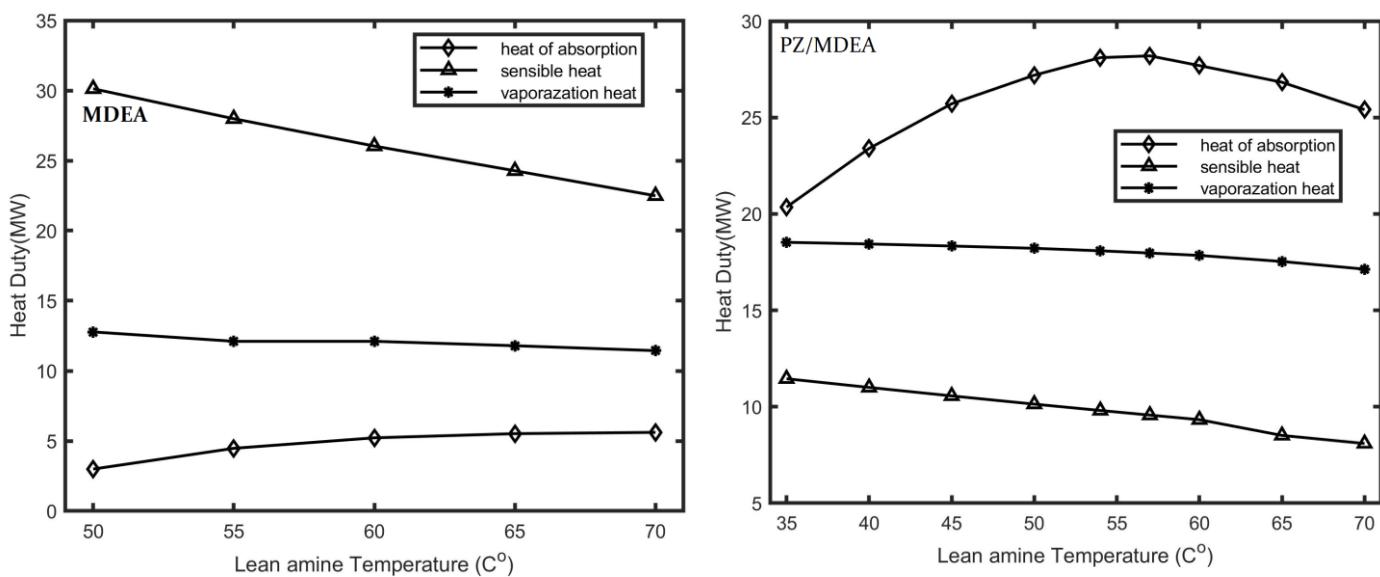


Fig.7 : Effect of lean amine temperature on the energy distribution.

### 5.5. Reflux ratio

The reflux ratio defines as a part of the distillate stream to feedback to the stripper column. **Jung et al. (2015)** stated that the reflux ratio has a direct effect on the stripper operation and the overall process efficiency [73]. They mentioned that reducing the reflux ratio results in a reduction of the reboiler duty, this fits well with **Younas and Banat (2014)** [74]. **De Figueiredo and co-workers (2014)** specified that a minimum reflux ratio comes with minimum energy consumption [75]. The effect of the reflux ratio in the regenerator column has been studied in a range of 1 to 1.8 for both solvents. Results reveal a significant increase in vaporization heat for both solvents however, the vaporization heat for the PZ/MDEA system is higher than that for MDEA system as shown in Fig. 8. In regards to sensible heat and heat of absorption almost constant or increases slightly.

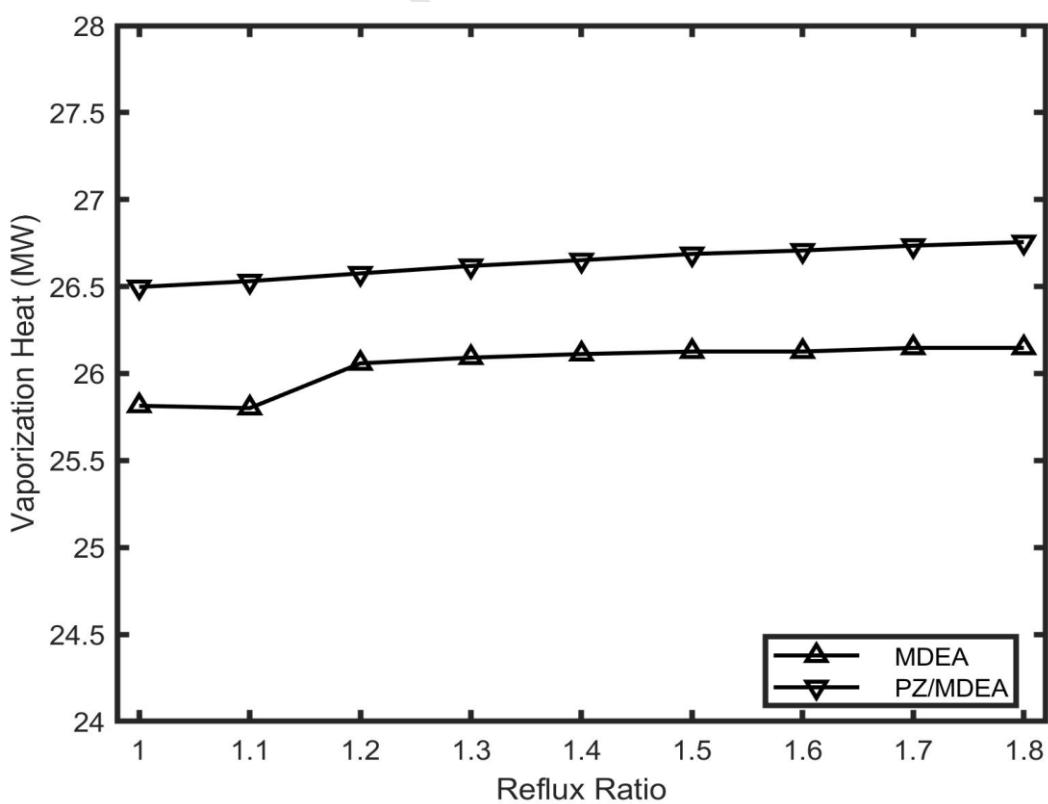


Fig.8: Effects of reflux ratio on the energy distribution.

### 5.6. Carbon dioxide/hydrogen sulfide concentrations

Effects of carbon dioxide and hydrogen sulfide concentrations in the inlet stream in terms of vaporization, sensible, and absorption heats have been evaluated. In regards to CO<sub>2</sub> concentration is ranging from 3% to 10%, while H<sub>2</sub>S concentrations in the range between 0.001% to 0.01%. It has been noticed that at low CO<sub>2</sub> concentrations, the sensible heat is the main contributor in the total energy demand with MDEA solvent system. While both vaporization and absorption heats are noticeable as the CO<sub>2</sub> concentration is increased as shown in Fig. 9. For PZ/MDEA solvent system, contrary to the findings with MDEA solvent that the total energy requirement is impacted by the heat of the absorption as shown in Fig. 9. The sharp increase in heat of absorption is due to the high heat of reaction for CO<sub>2</sub> and PZ solution. As far as the increase in H<sub>2</sub>S concentration is concerned, a sharp decline in heat of absorption as the H<sub>2</sub>S concentration increase from 0.2% to 0.6%. Beyond 0.6% H<sub>2</sub>S concentration, the heat of absorption becomes insensitive with MDEA solvent system. On the other hand, the heat of absorption with PZ/MDEA system records a sharp decrease as the H<sub>2</sub>S increases over the changing range. **Fouad and Berrouk (2013)** reported that the amine favors carbon dioxide products which are controlled by irreversible reactions [75]. **Haghtalab and Izadi (2014)** reported that piperazine reduces the absorption rate of H<sub>2</sub>S in the absence of CO<sub>2</sub> [76]. For sake of simplicity, increase acid gas concentration means more molecules that will contact the solvent molecules and as the solvent concentration stays constant that resulting in low absorption rate. The possible reason behind this decrease in heat of absorption follows the fact that CO<sub>2</sub>

reaction rate is high enough to prevent H<sub>2</sub>S buildup. High carbon dioxide reaction rate will capture more free solvent molecules these facts well agreements with Fig. 10.

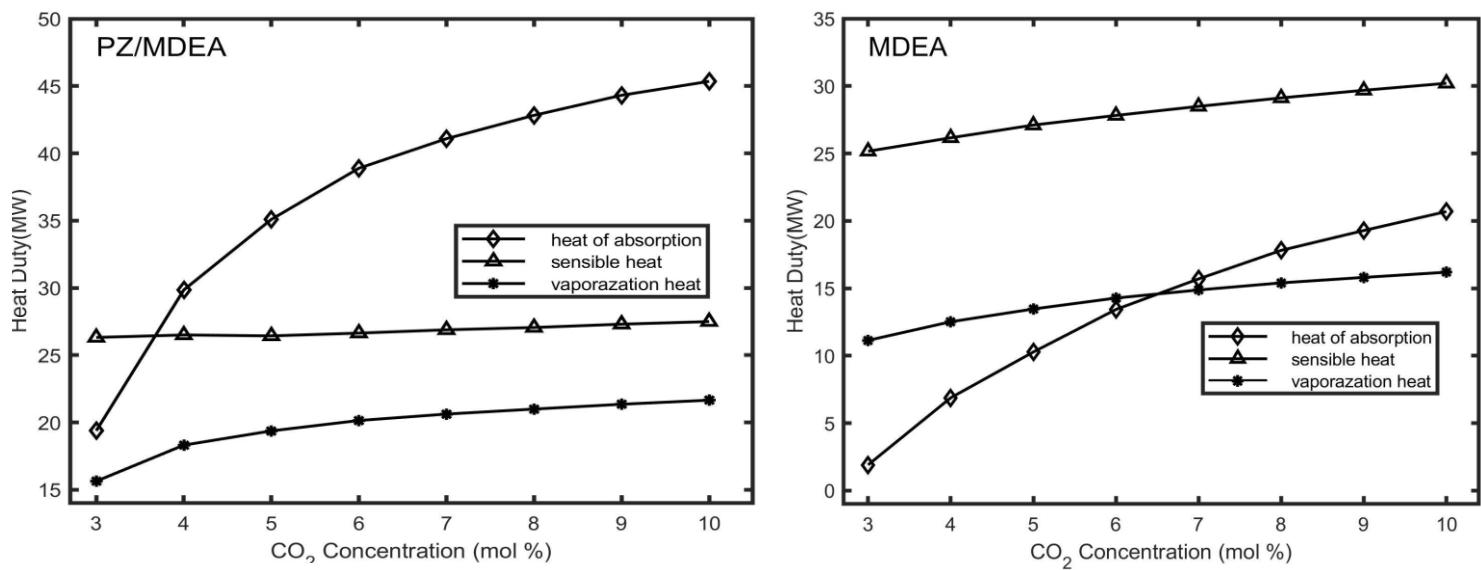


Fig.9: Effects of CO<sub>2</sub> concentration on the energy distribution.

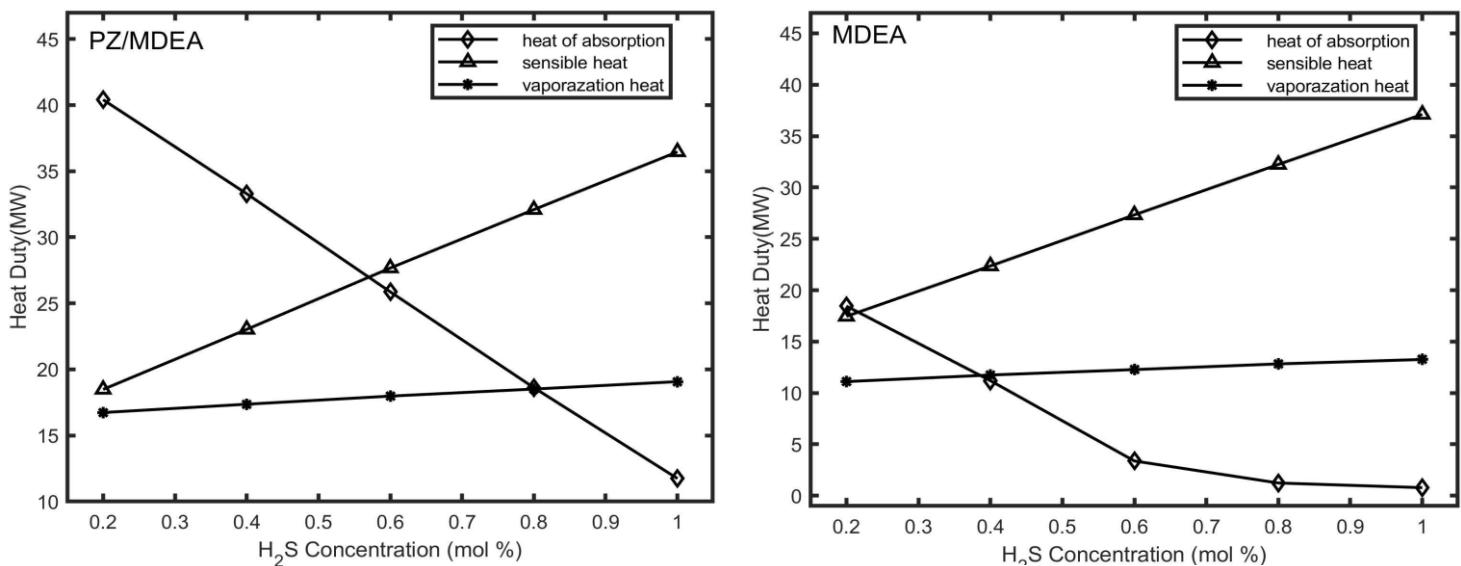


Fig.10: Effects of H<sub>2</sub>S on the energy distribution.

## Conclusion

Analysis study has been performed on Habshan unit gas cleaning by the implementation of Aspen HYSYS tool to investigate the energy requirements in the regeneration process applying alternative amines solvents like single MDEA and activated-MDEA with piperazine. A new energy balance technique around absorption and desorption columns was proposed. The proposed balance divided the regeneration energy into three elements namely heat of absorption, sensible heat, and vaporization heat. The simulation results have been successfully validated with Habshan gas unit in terms of product specifications and with literature in terms of column's temperature profile. The simulation results are close to the actual plant specifications in regards of acid gases removal and conditions as shown in Table 5. Sensitivity analysis has been presented to evaluate the effects of absorber/stripper pressures, lean amine circulation rate, lean amine temperature, solvent concentration, reflux ratio, and CO<sub>2</sub>/H<sub>2</sub>S concentrations on the energy distribution have been evaluated. The results reveal that increasing absorber pressure is an intensive energy requirement for both the solvents systems. Increase lean amine temperature results in reducing the sensible heat and vaporization heat while the heat of absorption slightly increases. Increase solvent concentrations result in an increase in heat of absorption and vaporization heat for both solvents systems with slight decreases in sensible heat. The solvent circulation rate mainly influences the sensible heat where increasing the amine circulation rate increases the sensible heat with slightly increases in absorption and vaporization heats as well. In addition, increasing reflux ratio produces a high

quality of sweet gas besides more heat for vaporization for both solvents. The future prospects of this simulation will be interesting on the proposing new alternative where various possibilities of energy and cost savings will be explored.

## References

- [1] A. Hussain, *A Single Stage Membrane Process for CO<sub>2</sub> Capture from Flue Gas by a Facilitated Transport Membrane*, SEP. SCI. TECHNOL. 47(13) (2012) 1857–1865, doi:10.1080/01496395.2012.661013.
- [2] D.-Q. Sun, B.-W. Yi, J.-H. Xu, W.-Z. Zhao, G.-S. Zhang, Y.-F. Lu, *Assessment of CO<sub>2</sub> emission reduction potentials in the Chinese oil and gas extraction industry: From a technical and cost-effective perspective*, J. CLEAN. PROD. 201 (2018) 1101–1110, doi: 10.1016/j.jclepro.2018.08.044.
- [3] U. Zahid, F. N. Al Rowaili, M. K. Ayodeji, U. Ahmed, *Simulation and parametric analysis of CO<sub>2</sub> capture from natural gas using diglycolamine*. INT. J. GREENH. GAS CON. 57 (2017) 42–51, doi: 10.1016/j.ijggc.2016.12.016.
- [4] D. Aaron, C. Tsouris, (2005). *Separation of CO<sub>2</sub>from Flue Gas: A Review*, SEP. SCI. TECHNOL. 40(1-3) (2005) 321–348, doi:10.1081/ss-200042244.
- [5] H. Li, J. Yan, P. E. Campana, *Feasibility of integrating solar energy into a power plant with amine-based chemical absorption for CO<sub>2</sub> capture*, INT. J. GREENH. GAS CON. 9 (2012) 272–280, doi: 10.1016/j.ijggc.2012.04.005.
- [6] S. Freguia, G. T. Rochelle, *Modeling of CO<sub>2</sub> capture by aqueous monoethanolamine*. AIChE J. 49(7) (2003) 1676–1686, doi:10.1002/aic.690490708.
- [7] F. A. Tobiesen, H. F. Svendsen, T. Mejell, *Modeling of Blast Furnace CO<sub>2</sub>Capture Using Amine Absorbents*, IND. ENG. CHEM. RES. 46(23) (2007) 7811–7819, doi:10.1021/ie061556j.
- [8] H. M. Kvamsdal, J. P. Jakobsen, K. A. Hoff, *Dynamic modeling and simulation of a CO<sub>2</sub> absorber column for post-combustion CO<sub>2</sub> capture*, CHEM. ENG. PROCESS. 48(1) (2009) 135–144, doi: 10.1016/j.cep.2008.03.002.

- [9] M. S. Jassim, G. T. Rochelle, *Innovative Absorber/Stripper Configurations for CO<sub>2</sub>Capture by Aqueous Monoethanolamine*, IND. ENG. CHEM. RES. 45(8) (2006) 2465–2472, doi:10.1021/ie050547s.
- [10] G. Soave, J. A. Feliu, *Saving energy in distillation towers by feed splitting*. APPL. THERM. ENG. 22(8) (2002) 889–896, doi:10.1016/s1359-4311(02)00006-6.
- [11] C. Arnaiz del Pozo, S. Cloete, J. H. Cloete, A. Jiménez Álvaro, S. Amini, *The potential of chemical looping combustion using the gas switching concept to eliminate the energy penalty of CO<sub>2</sub> capture*, INT. J. GREENH. GAS CON. 83 (2019) 265–281, doi: 10.1016/j.ijggc.2019.01.018.
- [12] J. N. Knudsen, J. Andersen, J. N. Jensen, O. Biede, *Evaluation of process upgrades and novel solvents for the post combustion CO<sub>2</sub> capture process in pilot-scale*, ENERG. PROCEDIA 4 (2011) 1558–1565, doi: 10.1016/j.egypro.2011.02.025.
- [13] M. Karimi, M. Hillestad, H. F. Svendsen, *Capital costs and energy considerations of different alternative stripper configurations for post combustion CO<sub>2</sub> capture*, CHEM. ENG. RES. DES. 89(8) (2011) 1229–1236, doi: 10.1016/j.cherd.2011.03.005.
- [14] L. M. Romeo, S. Espatolero, I. Bolea, *Designing a supercritical steam cycle to integrate the energy requirements of CO<sub>2</sub> amine scrubbing*, INT. J. GREENH. GAS CON. 2(4) (2008) 563–570, doi: 10.1016/j.ijggc.2008.03.002.
- [15] L. Raynal, P. A. Bouillon, A. Gomez, P. Broutin, *From MEA to demixing solvents and future steps, a roadmap for lowering the cost of post-combustion carbon capture*. CHEM. ENG. J. 171(3) (2011) 742–752, doi: 10.1016/j.cej.2011.01.008.
- [16] S. Z. Naji, A. A. Abd, Sensitivity analysis of using diethanolamine instead of methyldiethanolamine solution for GASCO'S Habshan acid gases removal plant, FRONT. ENG. 13(2) (2019) 317–324, doi:10.1007/s11708-019-0622-2.
- [17] B. Zhao, F. Liu, Z. Cui, C. Liu, H. Yue, S. Tang, B. Liang, Enhancing the energetic efficiency of MDEA/PZ-based CO<sub>2</sub> capture technology for a 650 MW power plant: Process improvement, APPL. ENERG. 185 (2017) 362–375, doi: 10.1016/j.apenergy.2016.11.009.

- [18] K. Li, W. Leigh, P. Feron, H. Yu, M. Tade, *Systematic study of aqueous monoethanolamine (MEA)-based CO<sub>2</sub> capture process: Techno-economic assessment of the MEA process and its improvements*. APPL. ENERG. 165 (2016) 648–659, doi: 10.1016/j.apenergy.2015.12.109.
- [19] C. Biliyok, A. Lawal, M. Wang, F. Seibert, *Dynamic modelling, validation and analysis of post-combustion chemical absorption CO<sub>2</sub> capture plant*. INT. J. GREENH. GAS CON. 9 (2012) 428–445, doi: 10.1016/j.ijggc.2012.05.001.
- [20] A. Lawal, M. Wang, P. Stephenson, G. Koumpouras, H. Yeung, *Dynamic modelling and analysis of post-combustion CO<sub>2</sub> chemical absorption process for coal-fired power plants*, FUEL 89(10) (2010) 2791–2801, doi: 10.1016/j.fuel.2010.05.030.
- [21] S. Zhang, M. Du, P. Shao, L. Wang, J. Ye, J. Chen, J. M. Chen, *Carbonic anhydrase enzyme-MOFs composite with a superior catalytic performance to promote CO<sub>2</sub> absorption into tertiary amine solution*, ENVIRON. SCI. TECHNOL. (2018) doi: 10.1021/acs.est.8b04671.
- [22] W. Zhang, H. Liu, Y. Sun, J. Cakstins, C. Sun, C. E. Snape, *Parametric study on the regeneration heat requirement of an amine-based solid adsorbent process for post-combustion carbon capture*, APPL. ENERG. 168 (2016) 394–405.doi: 10.1016/j.apenergy.2016.01.049.
- [23] M. Gupta, E. F. da Silva, A. Hartono, H. F. Svendsen, *Theoretical Study of Differential Enthalpy of Absorption of CO<sub>2</sub> with MEA and MDEA as a Function of Temperature*, J. PHYSIC. CHEM. 117(32) (2013) 9457–9468. doi:10.1021/jp404356e.
- [24] B. H. Li, N. Zhang, R. Smith, *Simulation and analysis of CO<sub>2</sub> capture process with aqueous monoethanolamine solution*, APPL. ENERG. 161 (2016) 707–717, doi: 10.1016/j.apenergy.2015.07.010.
- [25] A. Y. Ibrahim, F. H. Ashour, A. O. Ghallab, M. Ali, *Effects of piperazine on carbon dioxide removal from natural gas using aqueous methyl diethanol amine*, J. NAT. GAS SCI. ENG. 21 (2014) 894–899, doi: 10.1016/j.jngse.2014.10.011.
- [26] H. Svensson, C. Hulteberg, H. T. Karlsson, *Heat of absorption of CO<sub>2</sub> in aqueous solutions of N-methyldiethanolamine and piperazine*, INT. J. GREENH. GAS CON. 17 (2013) 89–98, doi: 10.1016/j.ijggc.2013.04.021.

- [27] S. Bishnoi, G. T. Rochelle, *Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility*, CHEM. ENG. SCI. 55(22) (2000) 5531–5543. doi:10.1016/s0009-2509(00)00182-2.
- [28] K. Li, K. Jiang, T. W. Jones, P. H. M. Feron, R. D. Bennett, A. F. Hollenkamp, *CO<sub>2</sub> regenerative battery for energy harvesting from ammonia-based post-combustion CO<sub>2</sub> capture*, APPL ENERG. 247, (2019) 417–425. doi: 10.1016/j.apenergy.2019.04.057.
- [29] C. Nwaoha, C. Saiwan, T. Supap, R. Idem, P. Tontiwachwuthikul, W. Rongwong, A. Benamor, *Carbon dioxide (CO<sub>2</sub>) capture performance of aqueous tri-solvent blends containing 2-amino-2-methyl-1-propanol (AMP) and methyldiethanolamine (MDEA) promoted by diethylenetriamine (DETA)*, INT. J. GREENH. GAS CON. 53, (2016) 292–304, doi: 10.1016/j.ijggc.2016.08.012.
- [30] R. Zhang, X. Zhang, Q. Yang, H. Yu, Z. Liang, X. Luo, *Analysis of the reduction of energy cost by using MEA-MDEA-PZ solvent for post-combustion carbon dioxide capture (PCC)*, APPL. ENERG. 205, (2017) 1002–1011, doi: 10.1016/j.apenergy.2017.08.130.
- [31] X. Zhang, R. Zhang, H. Liu, H. Gao, Z. Liang, *Evaluating CO<sub>2</sub> desorption performance in CO<sub>2</sub>-loaded aqueous tri-solvent blend amines with and without solid acid catalysts*, APPL. ENERG. 218 (2018) 417–429, doi: 10.1016/j.apenergy.2018.02.087.
- [32] D. D. D. Pinto, S. A. H. Zaidy, A. Hartono, H. F. Svendsen, *Evaluation of a phase change solvent for CO<sub>2</sub> capture: Absorption and desorption tests*, INT. J. GREENH. GAS CON. 28 (2014) 318–327, doi: 10.1016/j.ijggc.2014.07.002.
- [33] L. Raynal, P. Alix, P. A. Bouillon, A. Gomez, M. F. de Nailly, M. Jacquin, J. Trapy, *The DMX™ process: An original solution for lowering the cost of post-combustion carbon capture*, ENERG. PROCEDIA 4 (2011) 779–786. doi: 10.1016/j.egypro.2011.01.119.
- [34] J. Zhang, O. Nwani, Y. Tan, D. W. Agar, *Carbon dioxide absorption into biphasic amine solvent with solvent loss reduction*, CHEM. ENG. RES. DES. 89(8) (2011) 1190–1196, doi: 10.1016/j.cherd.2011.02.005.
- [35] J. Zhang, D. W. Agar, X. Zhang, F. Geuzebroek, *CO<sub>2</sub> absorption in biphasic solvents with enhanced low temperature solvent regeneration*, ENERG. PROCEDIA 4 (2011) 67–74, doi: 10.1016/j.egypro.2011.01.024.

- [36] K. Sobala, H. Kierzkowska-Pawlak, *Heat of absorption of CO<sub>2</sub> in aqueous N, N-diethylethanolamine + N-methyl-1,3-propanediamine solutions at 313 K*, CHINESE J. CHEM. ENG. (2018), doi: 10.1016/j.cjche.2018.11.027.
- [37] H. Kim, S. J. Hwang, K. S. Lee, *Novel Shortcut Estimation Method for Regeneration Energy of Amine Solvents in an Absorption-Based Carbon Capture Process*, ENVIRON. SCI. TECHNOL. 49(3) (2015) 1478–1485, doi:10.1021/es504684x.
- [38] I. Kim, H. F. Svendsen, *Comparative study of the heats of absorption of post-combustion CO<sub>2</sub> absorbents*, INT. J. GREENH. GAS CON. 5(3) (2011) 390–395, doi: 10.1016/j.ijggc.2010.05.003.
- [39] H. Svensson, V. Zejnullahu Velasco, C. Hulteberg, H. T. Karlsson, *Heat of absorption of carbon dioxide in mixtures of 2-amino-2-methyl-1-propanol and organic solvents*, INT. J. GREENH. GAS CON. 30 (2014) 1–8.doi: 10.1016/j.ijggc.2014.08.022.
- [40] W. Conway, Q. Yang, S. James, C. C. Wei, M. Bown, P. Feron, G. Puxty, *Designer Amines for Post Combustion CO<sub>2</sub> Capture Processes*, ENERG. PROCEDIA 63 (2014) 1827–1834, doi: 10.1016/j.egypro.2014.11.190.
- [41] U. E. Aronu, K. A. Hoff, H. F. Svendsen, *CO<sub>2</sub> capture solvent selection by combined absorption–desorption analysis*, CHEM. ENG. RES. DES. 89(8) (2011) 1197–1203.doi: 10.1016/j.cherd.2011.01.007.
- [42] C. Nwaoha, R. Idem, T. Supap, C. Saiwan, P. Tontiwachwuthikul, W. Rongwong, A. Benamor, *Heat duty, heat of absorption, sensible heat and heat of vaporization of 2-Amino-2-Methyl-1-Propanol (AMP), Piperazine (PZ) and Monoethanolamine (MEA) tri-solvent blend for carbon dioxide (CO<sub>2</sub>) capture*, CHEM. ENG. SCI. 170 (2017) 26–35, doi: 10.1016/j.ces.2017.03.025.
- [43] A. Chakma, *CO<sub>2</sub> capture processes — Opportunities for improved energy efficiencies*, ENERG. CONVERS. MANAGE. 38 (1997) S51–S56, doi:10.1016/s0196-8904(96)00245-2.
- [44] GCCSI, *Global Status of CCS: Special Report, Introduction to Industrial Carbon Capture and Storage*, (2016).

- [45] A. Muhammad, Y. GadelHak, *Simulation based improvement techniques for acid gases sweetening by chemical absorption: A review*, INT. J. GREENH. GAS CON. 37 (2015) 481–491, doi: 10.1016/j.ijggc.2015.03.014.
- [46] K. Merkley, *Enthalpies of Solution of CO<sub>2</sub> in Aqueous MDEA Solutions*. M.S. Thesis, (1987) Brigham Young University, Provo, UT, USA.
- [47] J. L. Oscarson, H. K. Grimsrud, S. E. Gillespie, *Heats of mixing of gaseous CO<sub>2</sub>/CH<sub>4</sub> mixtures with aqueous solutions of methyldiethanolamine and diethanolamine*, THERMOCHIM. ACTA 351(1-2) (2000) 9–20, doi:10.1016/s0040-6031(99)00513-4.
- [48] C. Mathonat, V. Majer, A. E. Mather, J. P. E. Grolier, *Enthalpies of absorption and solubility of CO<sub>2</sub> in aqueous solutions of methyldiethanolamine*, FLUID PHASE EQUILIBR 140(1-2) (1997) 171–182, doi:10.1016/s0378-3812(97)00182-9.
- [49] H. Kierzkowska-Pawlak, R. Zarzycki, *Calorimetric Measurements of CO<sub>2</sub> Absorption into Aqueous N-Methyldiethanolamine Solutions*, CHEM. PAP. 56 (2000) 219.
- [50] J. K. Carson, K. N. Marsh, A. E. Mather, *Enthalpy of solution of carbon dioxide in (water + monoethanolamine, or diethanolamine, or N-methyldiethanolamine) and (water + monoethanolamine +N-methyldiethanolamine) at T= 298.15 K*, J. CHEM. THERMODYN. 32(9) (2000) 1285–1296, doi:10.1006/jcht.2000.0680.
- [51] H. Arcis, L. Rodier, K. Ballerat-Busserolles, J. Y. Coxam, *Enthalpy of solution of CO<sub>2</sub> in aqueous solutions of methyldiethanolamine at T=322.5K and pressure up to 5 Mpa*, J. CHEM. THERMODYN. 40(6) (2008) 1022–1029, doi: 10.1016/j.jct.2008.01.028.
- [52] M. Kundu, S. S. Bandyopadhyay, *Solubility of CO<sub>2</sub> in water + diethanolamine + N-methyldiethanolamine*, FLUID PHASE EQUILIBR 248(2) (2006) 158–167, doi: 10.1016/j.fluid.2006.08.001.
- [53] T. L. Donaldson, Y. N. Nguyen, *Carbon Dioxide Reaction Kinetics and Transport in Aqueous Amine Membranes*, IND. ENG. CHEM. 19(3) (1980) 260–266, doi:10.1021/i160075a005.

- [54] A. Samanta, S. S. Bandyopadhyay, *Kinetics and modeling of carbon dioxide absorption into aqueous solutions of piperazine*, CHEM. ENG. SCI. 62(24) (2007) 7312–7319, doi: 10.1016/j.ces.2007.08.022.
- [55] G. Sartori, D. W. Savage, *Sterically hindered amines for carbon dioxide removal from gases*, IND. ENG. CHEM. 22(2) (1983) 239–249, doi:10.1021/i1000010a016.
- [56] J. M. Plaza, G. T. Rochelle, *Modeling pilot plant results for CO<sub>2</sub> capture by aqueous piperazine*, ENERG. PROCEDIA 4 (2011) 1593–1600, doi: 10.1016/j.egypro.2011.02.029.
- [57] V. Feyzi, M. Beheshti, A. Gharibi Kharaji, *Exergy analysis: A CO<sub>2</sub> removal plant using a-MDEA as the solvent*, ENERG. 118 (2017) 77–84, doi: 10.1016/j.energy.2016.12.020.
- [58] S. S. Warudkar, K. R. Cox, M. S. Wong, G. J. Hirasaki, *Influence of stripper operating parameters on the performance of amine absorption systems for post-combustion carbon capture: Part I. High pressure strippers*, INT. J. GREENH. GAS CON. 16 (2013) 342–350, doi: 10.1016/j.ijggc.2013.01.050.
- [59] A. Aboudheir, W. Elmoudir, *Optimization of an Existing 130 Tonne Per Day CO<sub>2</sub> Capture Plant from a Flue Gas Slipstream of a Coal Power Plant*, ENERG. PROCEDIA 37 (2013) 1509–1516, doi: 10.1016/j.egypro.2013.06.026.
- [60] S. A. Freeman, R. Dugas, D. H. Van Wagener, T. Nguyen, G. T. Rochelle, *Carbon dioxide capture with concentrated, aqueous piperazine*, INT. J. GREENH. GAS CON. 4(2) (2010) 119–124, doi: 10.1016/j.ijggc.2009.10.008.
- [61] C. Nwaoha, K. Odoh, E. Ikpatt, R. Orji, R. Idem, *Process simulation, parametric sensitivity analysis and ANFIS modeling of CO<sub>2</sub> capture from natural gas using aqueous MDEA-PZ blend solution*, J. ENVIRON. CHEM. ENG. 5(6) (2017) 5588–5598, doi: 10.1016/j.jece.2017.10.038.
- [62] H. M. Kvamsdal, G. T. Rochelle, *Effects of the Temperature Bulge in CO<sub>2</sub>Absorption from Flue Gas by Aqueous Monoethanolamine*, IND. ENG. CHEM. 47(3) (2008) 867–875, doi:10.1021/ie061651s.
- [63] S. Moioli, L. A. Pellegrini, B. Picutti, P. Vergani, *Improved Rate-Based Modeling of H<sub>2</sub>S and CO<sub>2</sub> Removal by Methyldiethanolamine Scrubbing*, IND. ENG. CHEM. 52(5) (2013) 2056–2065, doi:10.1021/ie301967t.

- [64] T. N. G. Borhani, M. Afkhamipour, A. Azarpour, V. Akbari, S. H. Emadi, Z. A. Manan, *Modeling study on CO<sub>2</sub> and H<sub>2</sub>S simultaneous removal using MDEA solution*, IND. ENG. CHEM. 34 (2016) 344–355, doi: 10.1016/j.jiec.2015.12.003.
- [65] A. Shahsavand, A. Garmroodi, *Simulation of Khangiran gas treating units for various cooling scenarios*, J. NAT. GAS SCI. ENG. 2(6) (2010) 277–283.doi: 10.1016/j.jngse.2010.08.006.
- [66] J. P. Gutierrez, L. A. Benitez, E.L. Ale Ruiz, E. Erdmann, *A sensitivity analysis and a comparison of two simulators performance for the process of natural gas sweetening*, J. NAT. GAS SCI. ENG. 31 (2016) 800–807, doi: 10.1016/j.jngse.2016.04.015.
- [67] S. Mudhasakul, H. Ku, P. L. Douglas, *A simulation model of a CO<sub>2</sub> absorption process with methyldiethanolamine solvent and piperazine as an activator*, INT. J. GREENH. GAS CON. 15 (2013) 134–141.doi: 10.1016/j.ijggc.2013.01.023.
- [68] J. Oexmann, C. Hensel, A. Kather, *Post-combustion CO<sub>2</sub>-capture from coal-fired power plants: Preliminary evaluation of an integrated chemical absorption process with piperazine-promoted potassium carbonate*, INT. J. GREENH. GAS CON. 2(4) (2018) 539–552, doi: 10.1016/j.ijggc.2008.04.002.
- [69] A. Raksajati, M. T. Ho, D. E. Wiley, *Reducing the Cost of CO<sub>2</sub> Capture from Flue Gases Using Aqueous Chemical Absorption*, IND. ENG. CHEM. 52(47) (2013) 16887–16901, doi:10.1021/ie402185h.
- [70] L. Ghalib, B. S. Ali, W. M. Ashri, S. Mazari, L. M. Saeed, Modeling the effect of piperazine on CO<sub>2</sub> loading in MDEA/PZ mixture. FLUID PHASE EQUILIBR. 434 (2017) 233–243, doi: 10.1016/j.fluid.2016.10.022.
- [71] A. Dashti, M Raji, A. Razmi, N. Rezaei, S. Zendehboudi, M. Asghari, *Efficient Hybrid Modeling of CO<sub>2</sub> Absorption in Aqueous Solution of Piperazine: Applications to Energy and Environment*, CHEM. ENG. RES. DES. (2019), doi: 10.1016/j.cherd.2019.01.019.
- [72] L. Addington, C. Ness, *An evaluation of general “Rules of Thumb” in amine sweetening unit design and operation*. In: 89th Annual Convention of the Gas Processors Association, Austin, Texas, USA, Vol. 1, (2010) pp. 119–135.

- [73] J. Jung, Y. S. Jeong, U. Lee, Y. Lim, C. Han, *New Configuration of the CO<sub>2</sub> Capture Process Using Aqueous Monoethanolamine for Coal-Fired Power Plants*, IND. ENG. CHEM. 54(15) (2015) 3865–3878, doi:10.1021/ie504784p.
- [74] O. Younas, F. Banat, *Parametric sensitivity analysis on a GASCO's acid gas removal plant using ProMax simulator*, J. NAT. GAS SCI. ENG. 18 (2014) 247–253, doi: 10.1016/j.jngse.2014.03.007.
- [75] M. F. De Figueiredo, K. D. Brito, W. B. Ramos, L. G. Sales Vasconcelos, R. P. Brito, *Effect of Solvent Content on the Separation and the Energy Consumption of Extractive Distillation Columns*, CHEM ENG COMMUN 202(9) (2014) 1191–1199, doi:10.1080/00986445.2014.900053.
- [76] W. A. Fouad, A. S. Berrouk, *Using mixed tertiary amines for gas sweetening energy requirement reduction*, J. NAT. GAS SCI. ENG. 11 (2013) 12–17, doi: 10.1016/j.jngse.2012.07.003.
- [77] A. Haghtalab, A. Izadi, *Simultaneous measurement solubility of carbon dioxide + hydrogen sulfide into aqueous blends of alkanolamines at high pressure*, FLUID PHASE EQUILIBR 375 (2014) 181–190, doi: 10.1016/j.fluid.2014.05.017.

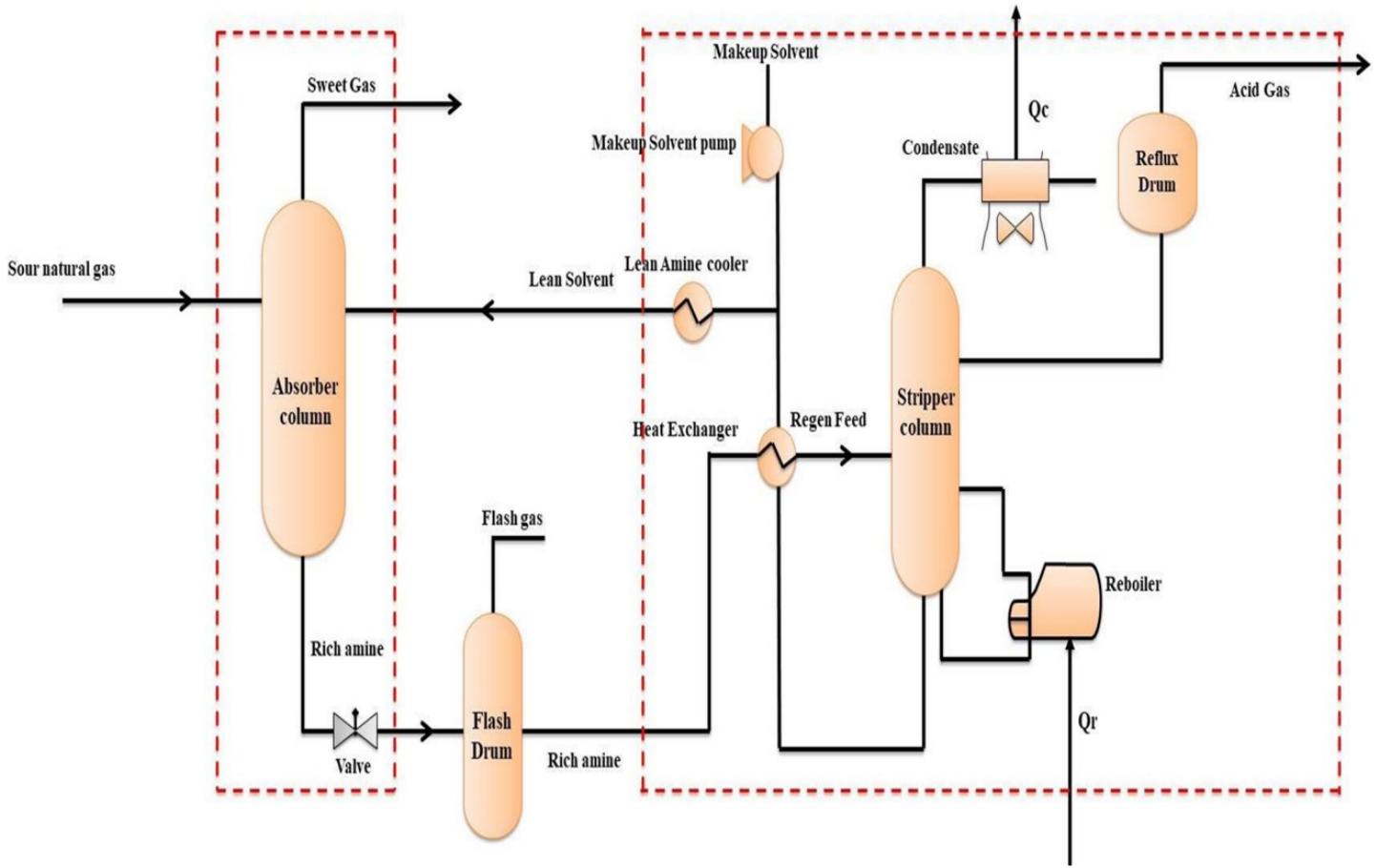


Figure 1

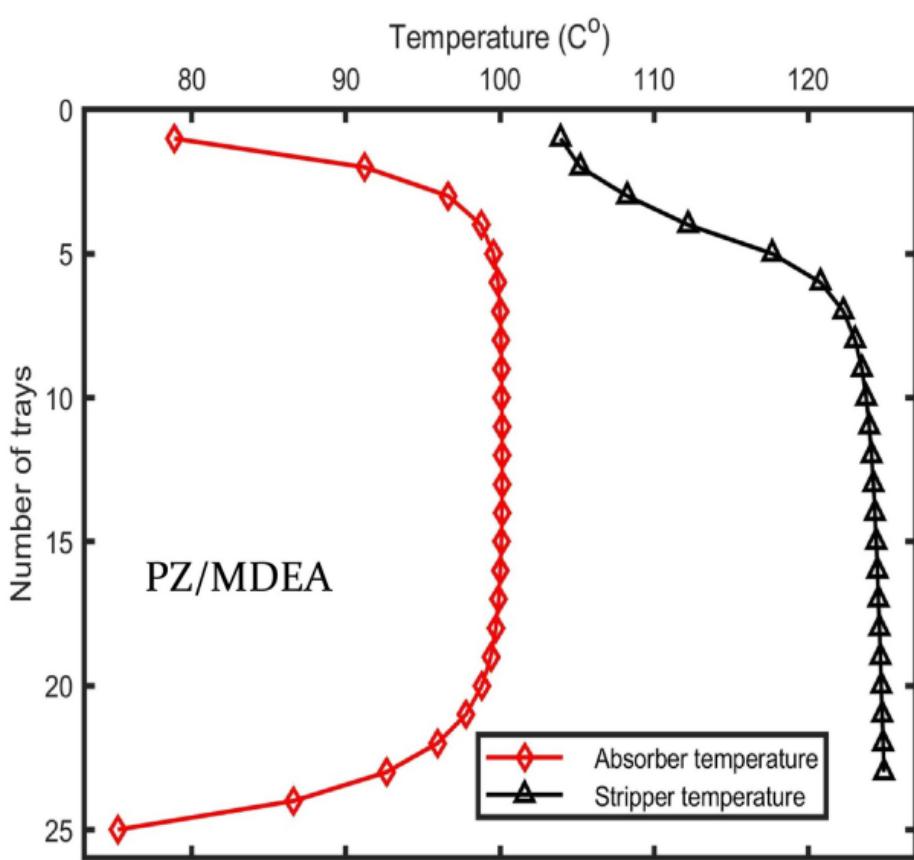
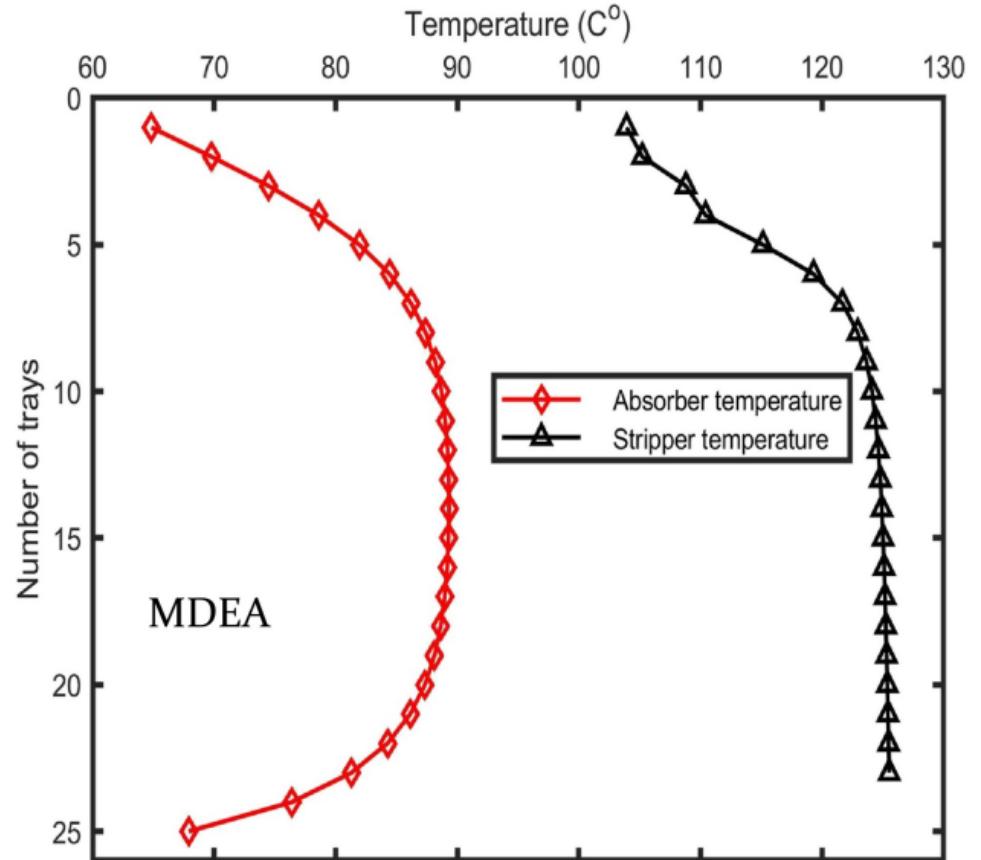
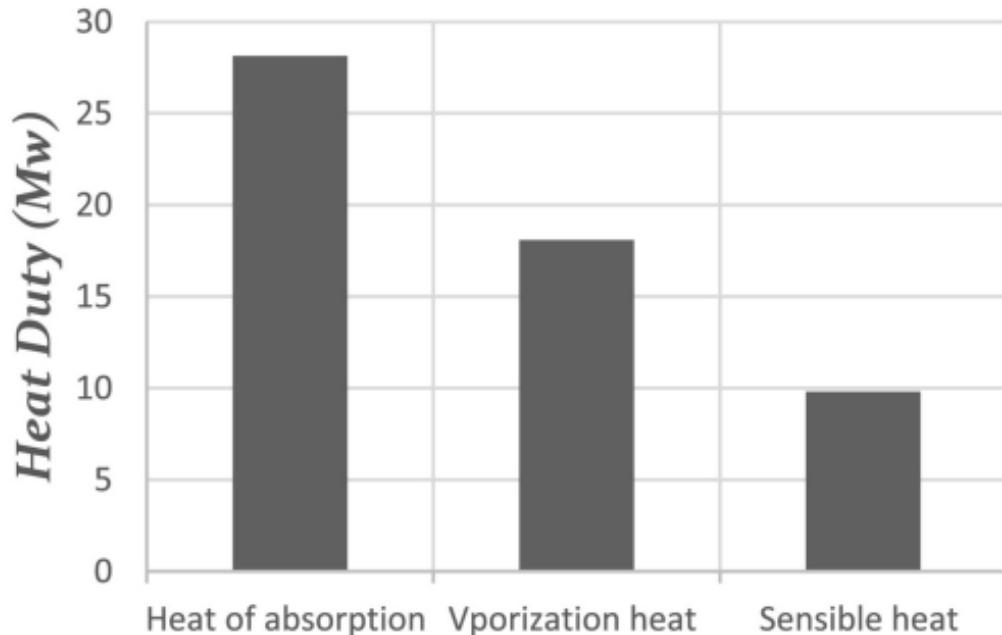


Figure 2

*PZ/MDEA solvent*



*MDEA solvent*

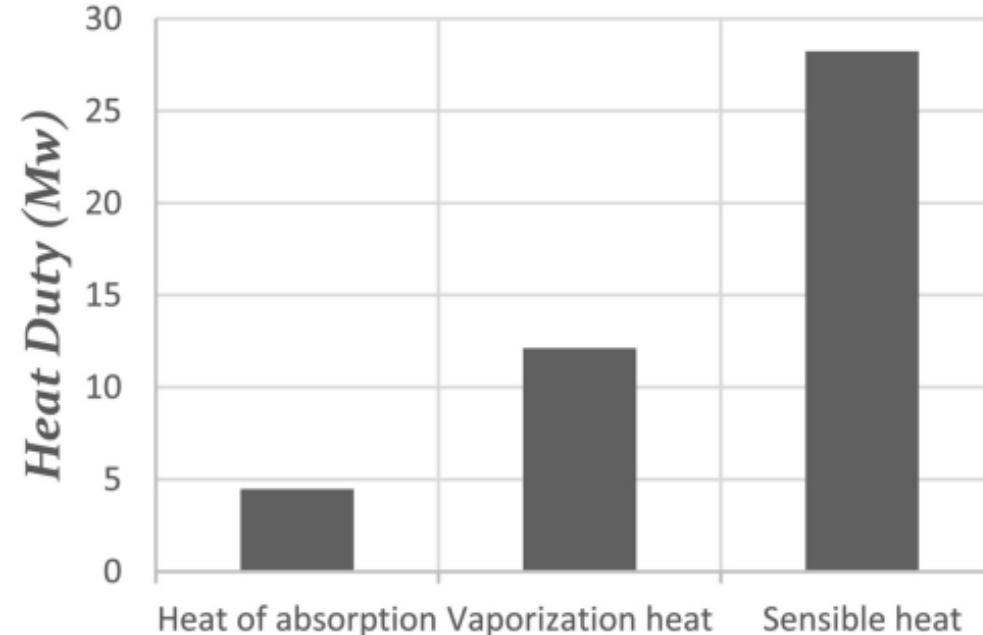


Figure 3

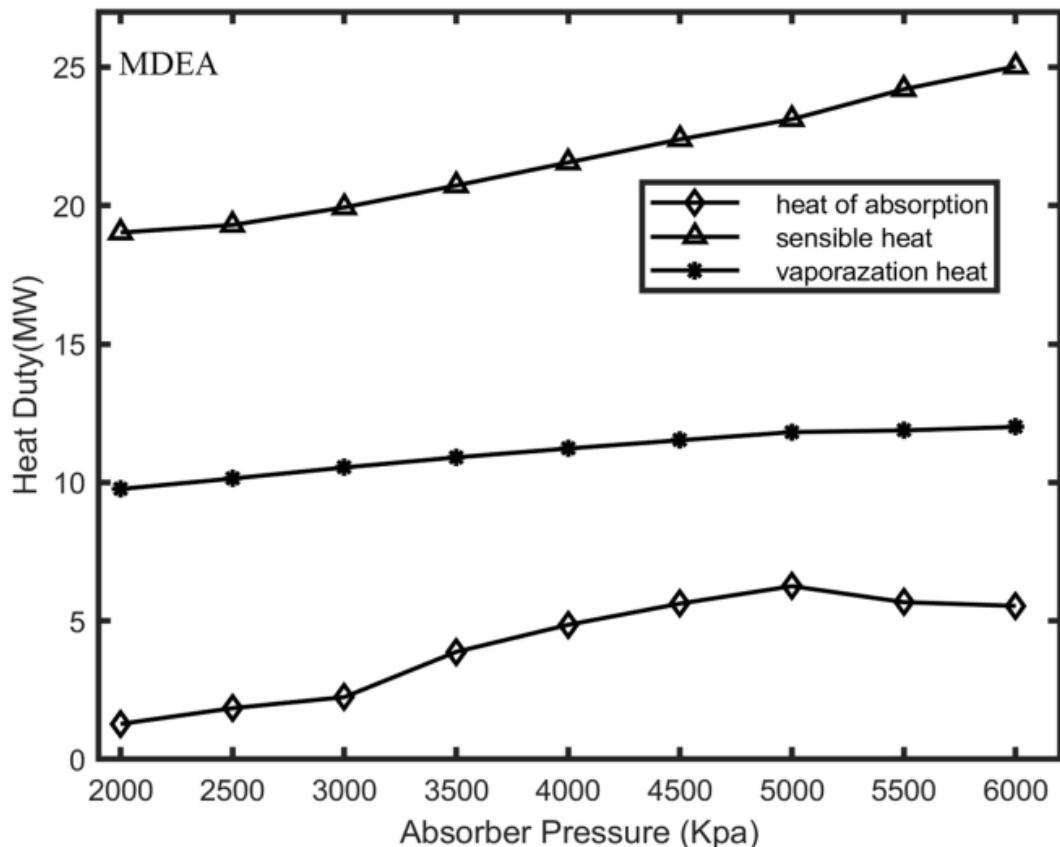
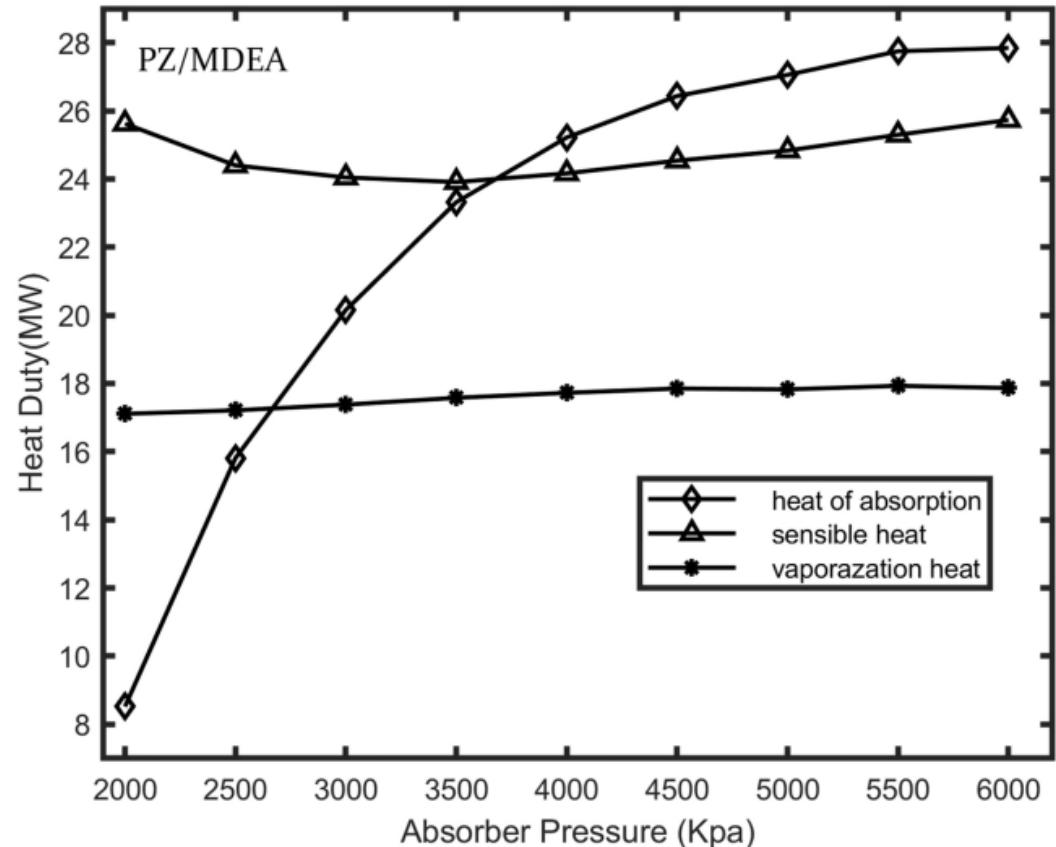


Figure 4

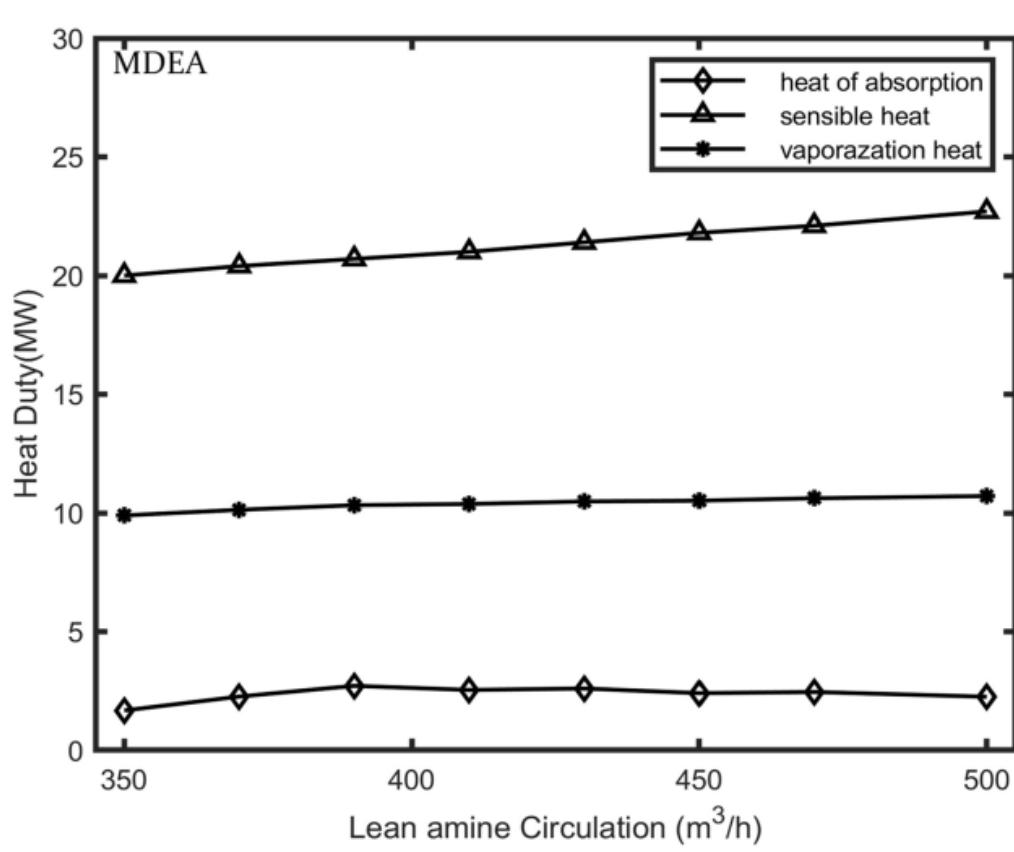
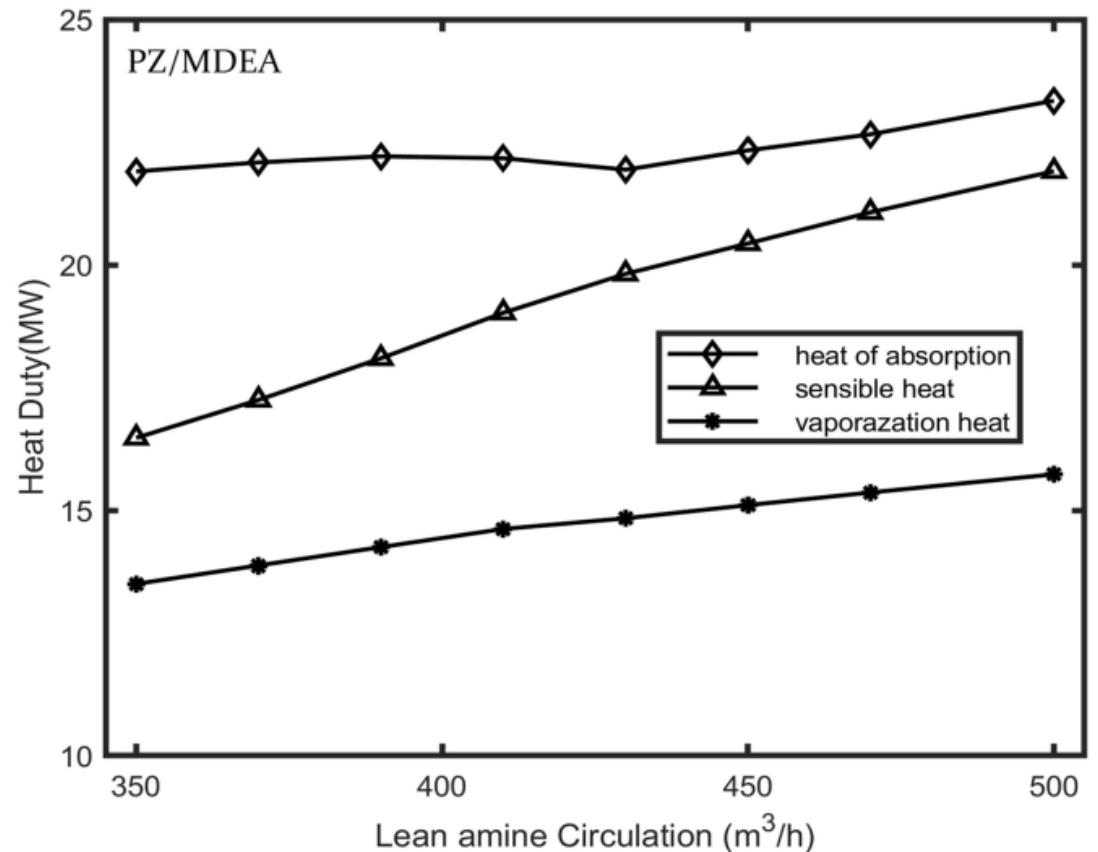


Figure 5

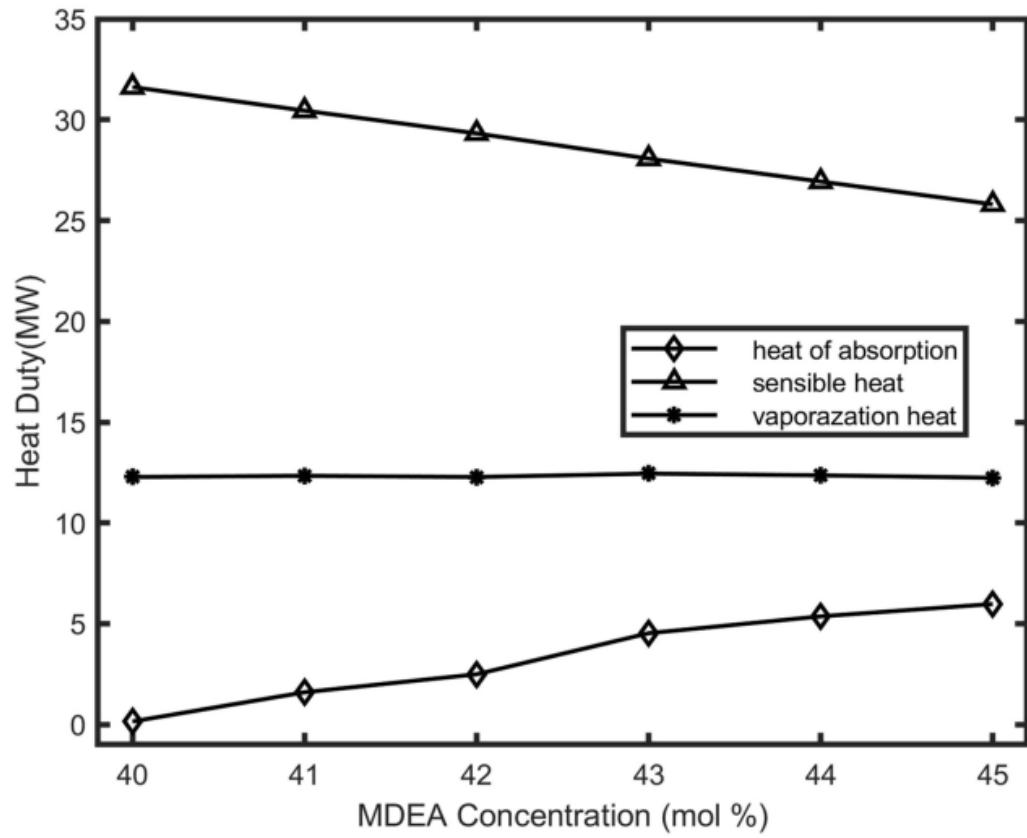
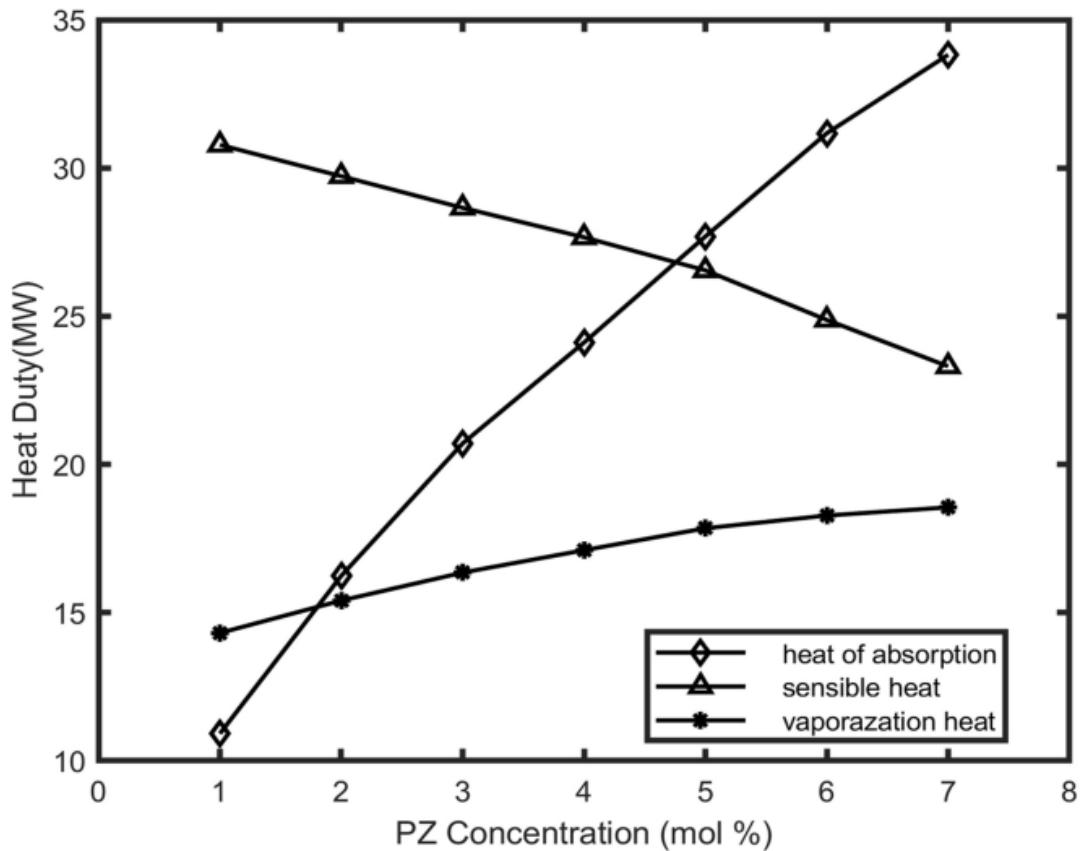


Figure 6

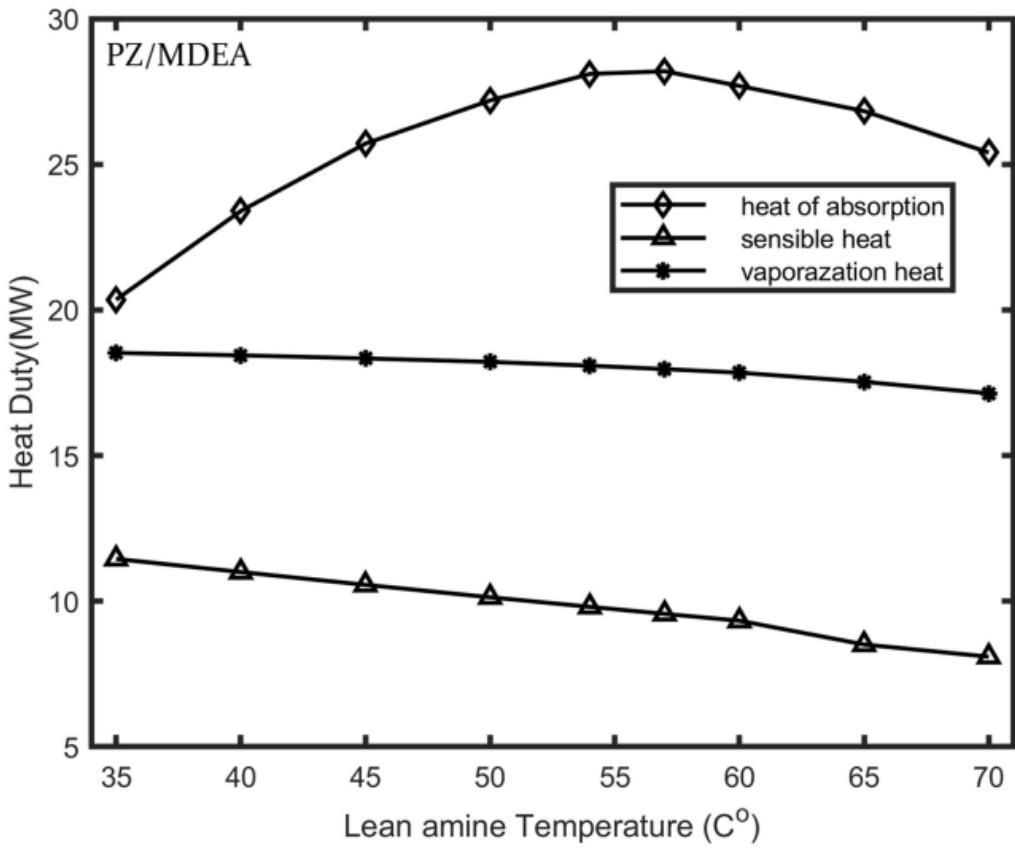
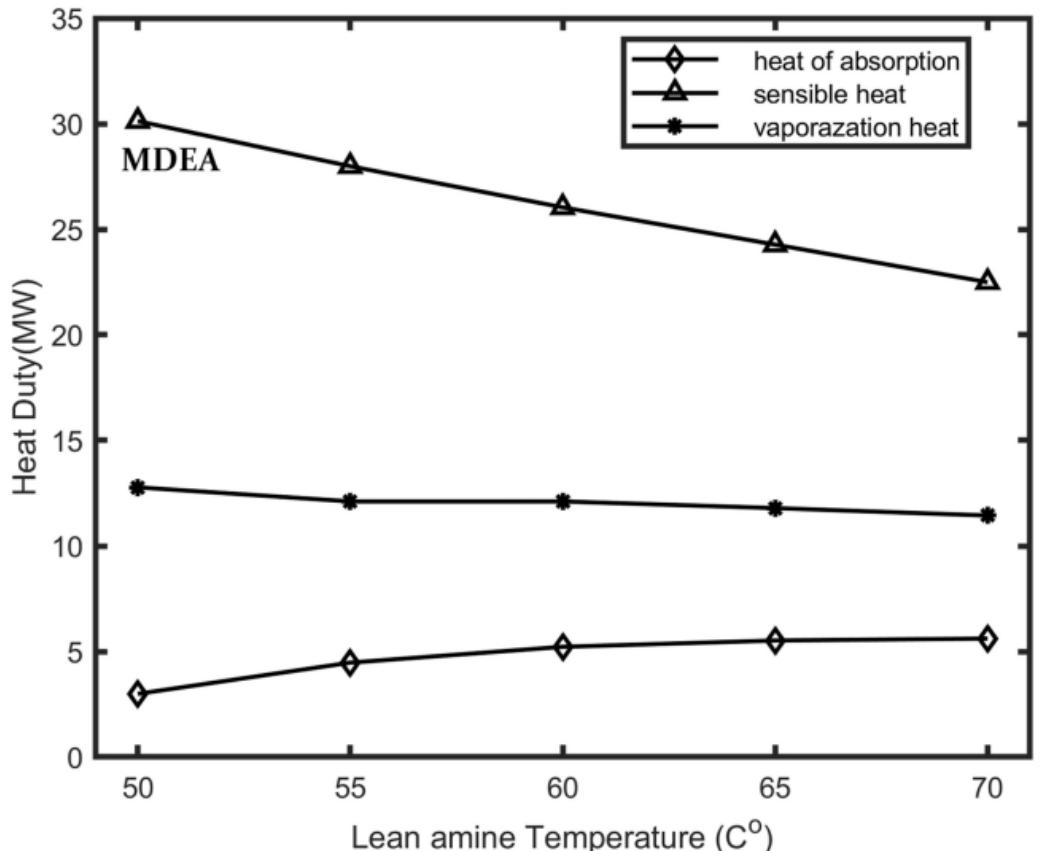


Figure 7

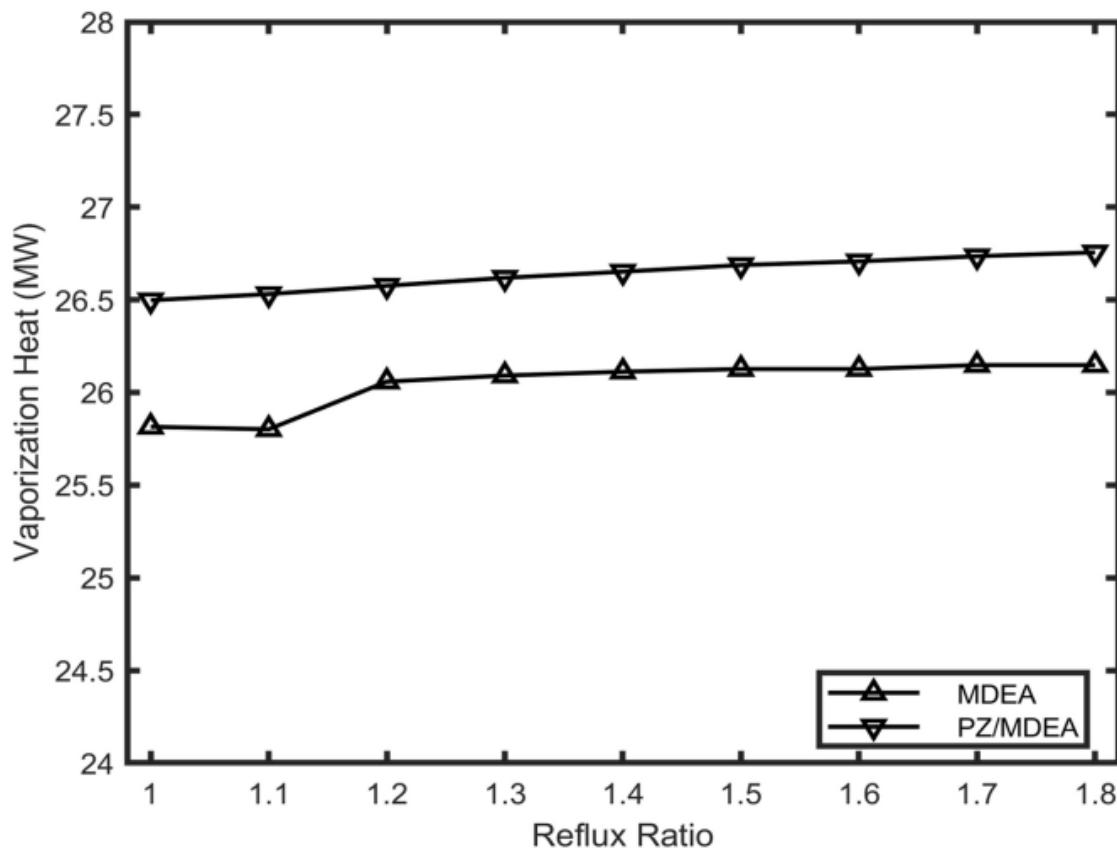


Figure 8

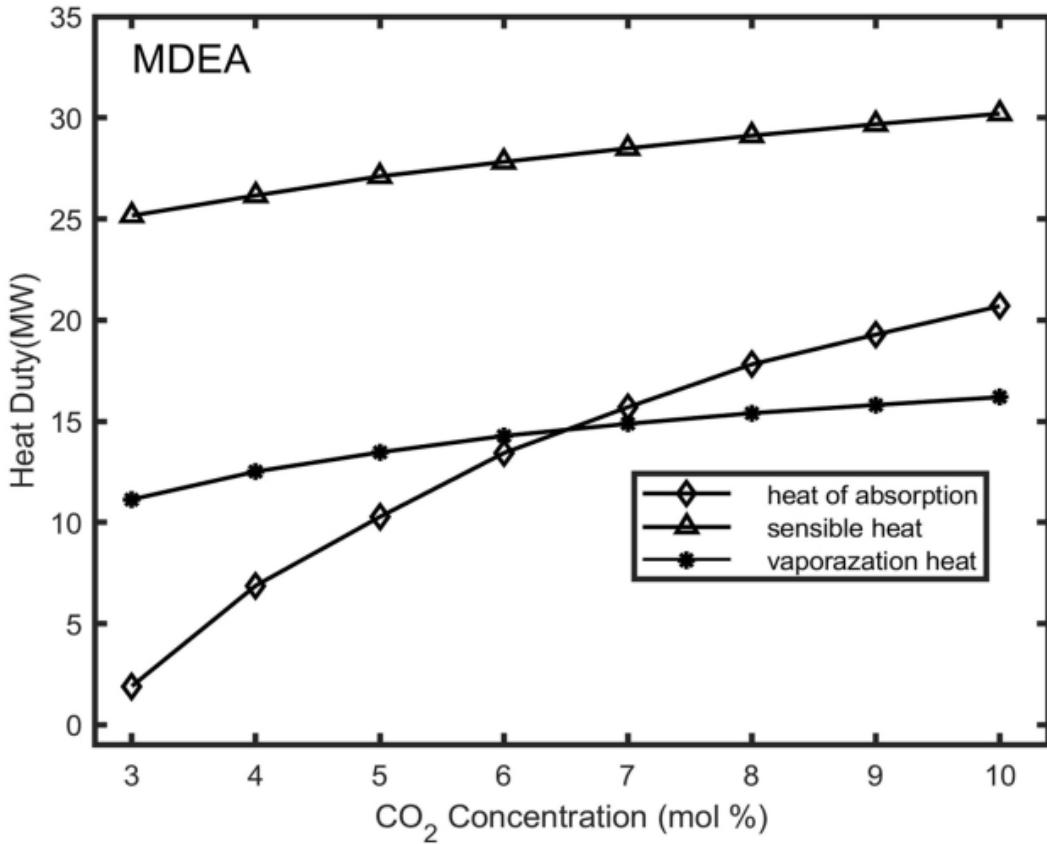
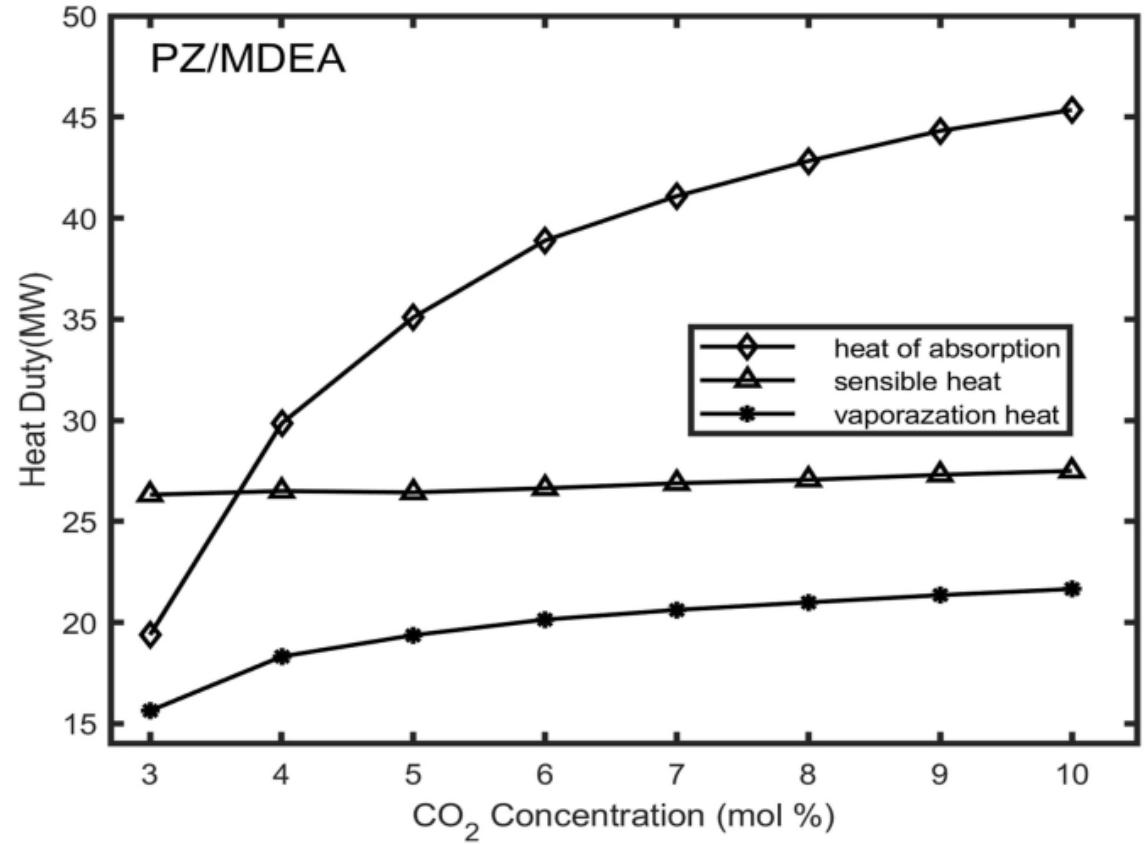


Figure 9

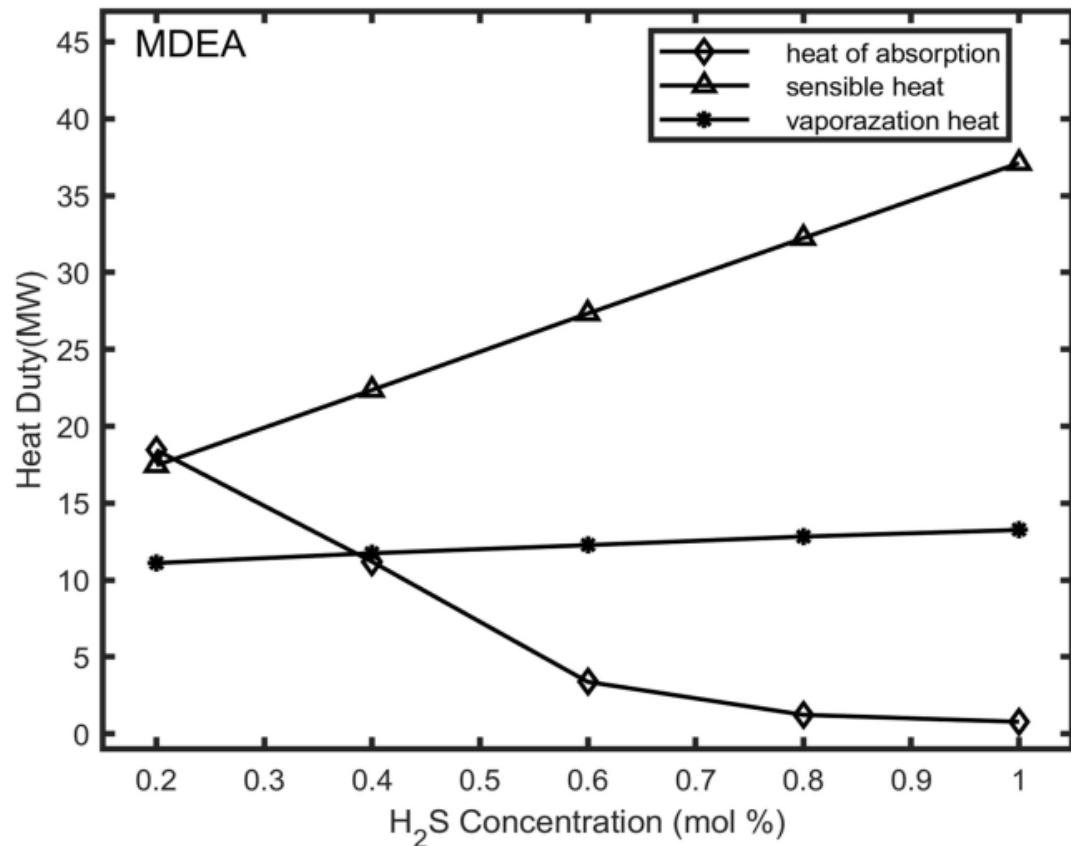
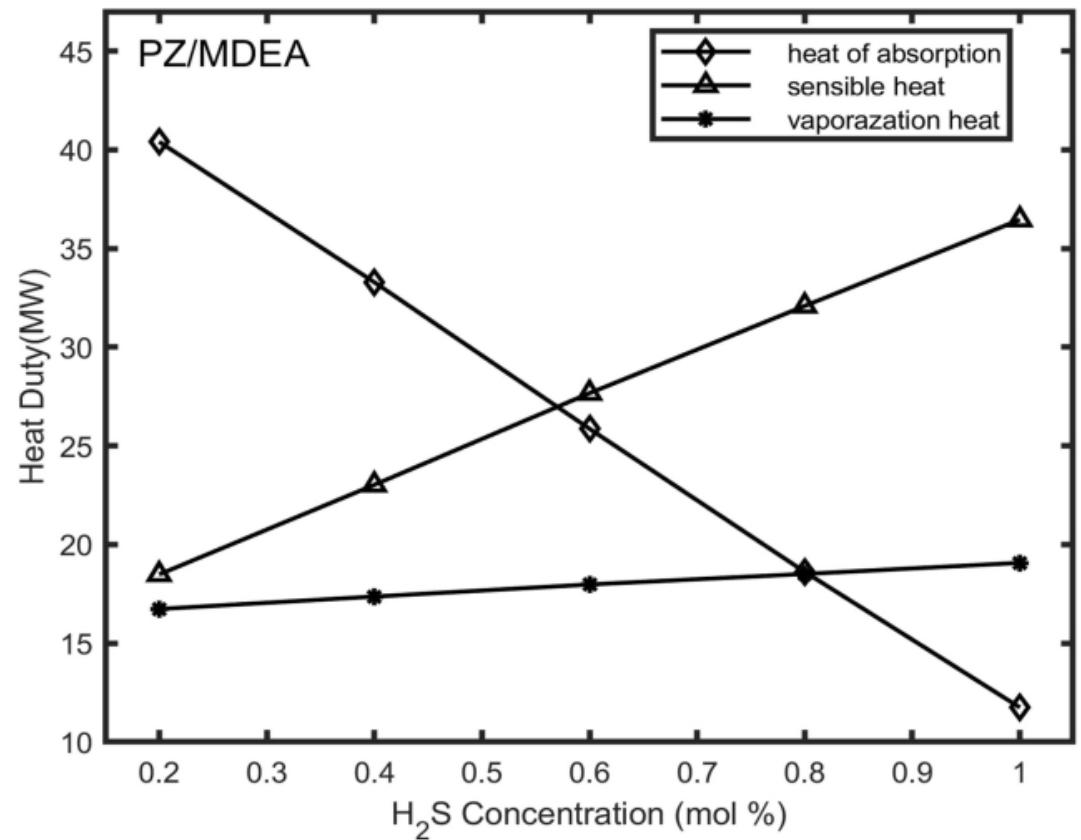


Figure 10