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PARAMETRIC STUDY OF THE ETHANOLAMINE DEGRADATION IN THE ABSORPTION PROCESS

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The purpose of the article consists in determining the effect of the chemical absorption process parameters on the thermal degradation of the ethanolamine. The study was conducted for ethanolamine using with the following concentrations (three cases): 20 wt. %; 30 wt. %, and 40 wt. %. For simplifying analyze, the CO_2 capture efficiency was kept constant of 90 %. The pressure in the absorption column was kept constant to 140 kPa irrespective the solvent concentration, while the process temperature varied in the range 53-58 °C according to the MEA concentration. The amine lost in the whole chemical absorption process was, for each case considered 20%, 30%, and 40%: 6 246.9 tons/year; 11 382.9 tons/year; and 18 481.3 tons/year.

Keywords: CO_2 capture, post – combustion process, CFBC, MEA degradation, Aspen Plus.

1. Introduction

In a time where the economy tends to globalize and the energy consumption to increase, the reduction of the greenhouse gases emissions (GHG) generates by the energy sector became a priority [1-3]. The concentration of greenhouse gases from the atmosphere increased from 284 ppm, in the preindustrial period, at 402.26 ppm in present [4,5]. In Fig. 1 there is presented the tendency of the CO_2 concentration in the atmosphere.

The CO_2 capture technologies are divided in three categories according to the integration position into a power plant: post-combustion, pre-combustion and oxy-combustion [6,7]. Unfortunately, only a few technologies for capturing the carbon dioxide are available at industrial scale [8-10]. One of them is the CO_2 capture post-combustion by chemical absorption process [11-13]. At present, the chemical absorption using alkanolamines is the most developed process to separate the carbon dioxide after the fuel combustion [14,15].

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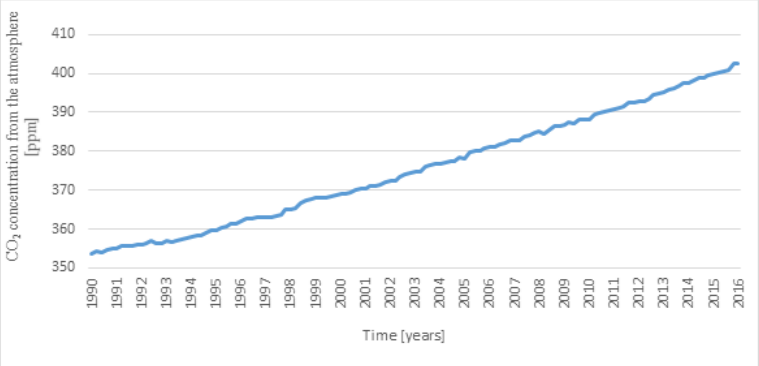

Fig. 1. CO_2 concentration in atmosphere in the period 1990-2016 [4]

The main advantage of the chemical absorption process is that it can be applied to a new or existent power plant [10]. On the other hand, the main drawback of the process is represented by the high energy consumption required for the chemical solvent regeneration [16]. In most cases, the thermal energy for solvent regeneration is taken from the low-pressure steam turbine leading to decrease in the global efficiency of power plant [11,13]. In scientific literature, varies value for the thermal energy was reported (3-6 GJ/ton_{CO2}) according to the CO_2 capture efficiency considered, the solvent used and the process parameters (the amine mass concentration in the solvent, the solvent flow, the process temperature, and pressure, etc.) [12,17].

Another drawback of the chemical absorption process is represented by the losses of the chemical solvent in the absorption/desorption column. Currently, many studies are concentrated on the degradation process of the chemical solvent [18-20]. The amine losses have a negative economic and environmental impact. The largest amount of the lost amine is due to the temperature at which the absorption/desorption process is performed [21]. Several researchers have studied the thermal degradation of the chemical solvent in the absorption/desorption unit for different solvents (ethanolamine, diethanolamine, methyldiethanolamine etc.) [22,25]. In addition to thermal degradation, an oxidative degradation of the chemical solvent is performed in the absorption unit due to the oxygen in the flue gases [26-28].

In order to evaluate the performance of the CO_2 capture process (from the technical and economical point of view), it is necessary to consider the solvent losses during the absorption/desorption process. The solvent losses can occur by thermal solvent degradation [22]. In this study, we performed an analysis of the ethanolamine (MEA) losses due to the thermal degradation. The purpose of the article consists in determining the effects of the chemical absorption parameters on the ethanolamine thermal degradation.

2. Method

The experimental study was conducted on the Circulated Fluidized Bed Combustion (CFBC) pilot installation with CO_2 capture by chemical absorption. The pilot installation is placed in the Renewable Energy Laboratory from University Politehnica of Bucharest. The simulation results were performed in the Aspen Plus software and it was compared and validated with the results obtained experimentally. The scheme of the chemical absorption process using MEA is presented in Fig. 2.

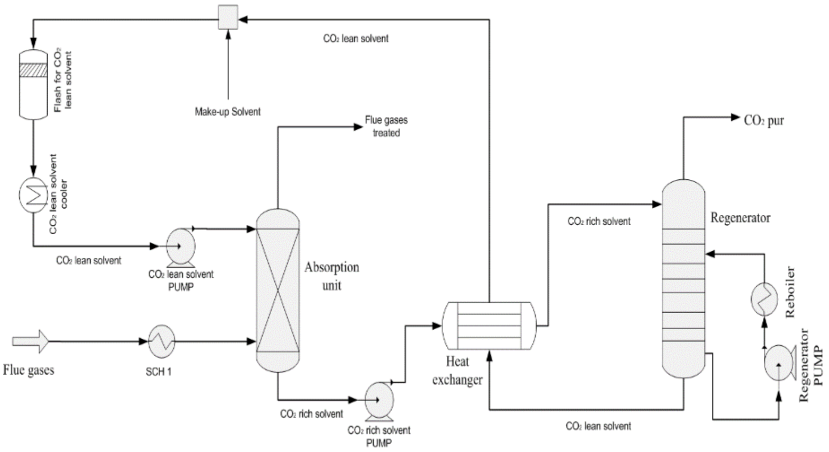

Fig. 2. Chemical absorption pilot installation [11]

The chemical absorption process has an absorption unit and a desorption one. The flue gasses enter the absorption unit at the bottom, but not before being cooled to about 40°C. In this case, the acid gases such as SO_x or NO_x have to be removed before cooling in order to avoid the corrosion of the metallic surfaces. The MEA solution enters the upper side of the absorption unit thus the two flows circulate in counter-current for improving the global coefficient of the mass transfer. At the exit from the absorption unit, the MEA solution is characterized by a high value of the CO_2 loading ($\gamma_{rich} = 0.47\text{-}0.6\ mol_{CO2}/mol_{solvent}$) [11]. In Fig. 3 there are shown the flows entering (chemical solvent flow 1, flue gasses flow 2) and exiting the absorber unit. The flue gases treated (flow 3) are evacuated at the top of the column and the CO_2 rich chemical solvent (flow 4) at the bottom. Also, the value for each parameter taken into account in our analysis is presented.

In our analysis, the mass concentration of MEA in the chemical solvent was varied between 20-40 wt. %. The mass concentration was limited at 40 % due to its corrosiveness. On the other hand, we intend to examine the effects of the amine concentration variation on the amine losses in the stripper unit.

In Table 1 there are presented the results obtained for the ratio between chemical solvent and flue gases (L/G) and the heat duty for solvent regeneration. All results are obtained considering the following assumptions: the CO_2 capture efficiency is of 90 %, the chemical solvent temperature is of 50 ^{o}C and the pressure absorption process is of 140 kPa. In this study, we do not take into account the electricity consumption required for the absorption process.

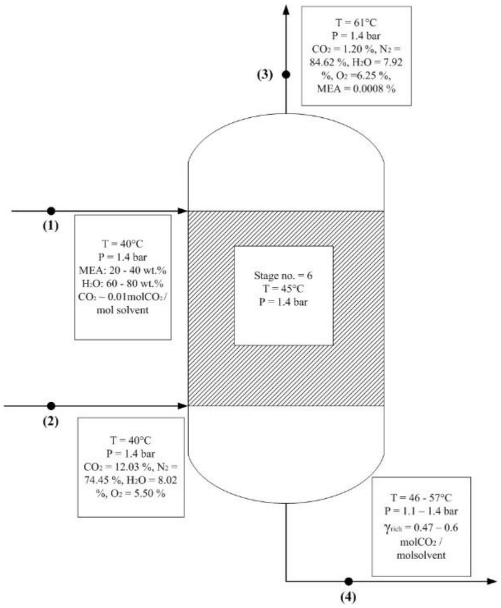

Fig. 3. Absorption unit parameters

Table 1

L/G ratio and heat duty according to weight concentration of MEA

MEA wt. [%]	L/G ratio [kg_{sol}/kg_{flue_gas}]	Heat duty [GJ/t_{CO2}]
20	1.85	2.49
30	1.13	3.07
40	0.8	3.11

The CO_2 chemical absorption process takes place at a temperature of 45 °C and at a pressure of 1.4 bar. For a higher efficiency of the absorption process, it was necessary to have a number of 6 stages into the absorption unit. The flue gases treated leaves the absorption unit at a temperature of 61 °C and at a pressure of 150 kPa. At the bottom, the CO_2 rich solvent leaves the absorption unit. The temperature in the absorption unit varied between 46-57 °C at a pressure of 1.4 bar. The rich loading solvent varied between 0.47-0.6 mol_{CO2}/ mol_{MEA}.

The rich solvent is introduced into the desorption unit, but not before going through a heat exchanger for heating. The optimization of the pinch point in the heat exchanger is essential for reducing the heat duty required for the solvent regeneration. In the Fig. 4 there is shown the scheme of the heat exchanger and the flows which enter and leave, respectively. Thus, in the heat exchanger, the rich solvent is heated from a temperature of 57 °C up to 83 °C, using a part of the heat of the lean solvent. The measurements for the flows which circulate through the heat exchanger were made in the points (5-8). Afterward, the rich solvent is introduced into the absorption unit at the top side of it.

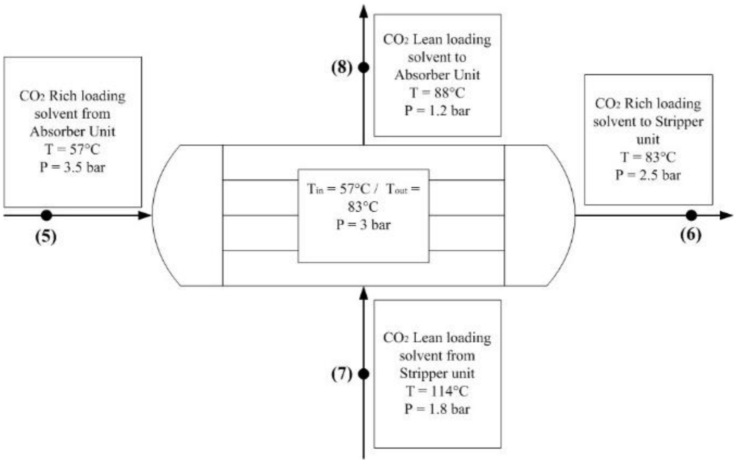

Fig. 4. Heat exchanger parameters

In the desorption process (Fig. 5) the rich solvent is heated to 120 °C. The CO_2 loading solvent was maintained constant of 0.21 mol_{CO2}/mol_{MEA}. The rich solvent at the entrance in the stripper unit has a temperature of 83 °C and a pressure of 250 kPa. In order to increase the temperature fixed in the desorption process, the solvent flow is heated in the re-boiler. Prior to the desorption process, the separated CO_2 flow is transported to the compression stage and the lean solvent is transported to the absorption process.

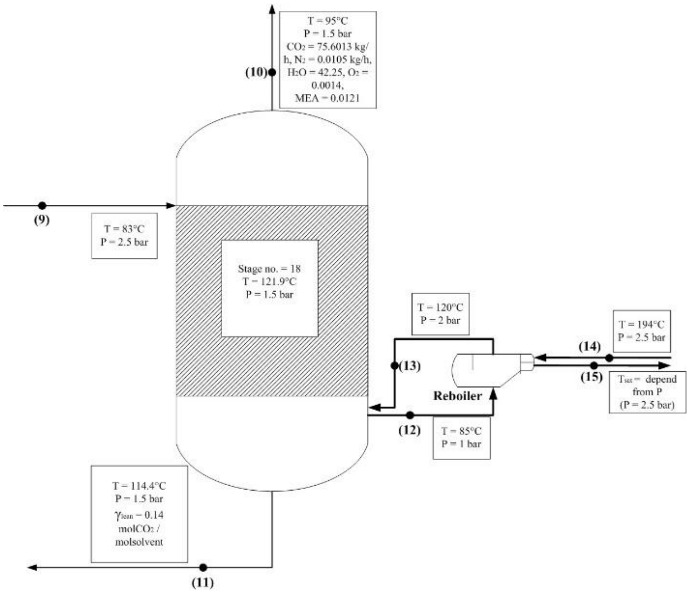

Fig.5. Desorption unit parameters

3. Results and discussion

In this section, the amount of the MEA lost was studied according to the temperature and pressure of the absorption process. The analyses were performed for an MEA concentration in the solvent of 20 wt. %, 30 wt. %, and 40 wt. %. The MEA temperature at the inlet in the absorption unit was varied between 30..50 °C. Also, the pressure of the absorption process influences the amount of the MEA lost and the CO_2 capture efficiency. The pressure was varied between 140..350 kPa. In this study we centralized and analyzed the results obtained for the thermal power required for the solvent regeneration, taking into account the conditions from the absorption column.

3.1. The influence of the chemical solvent temperature on the chemical absorption process performances

In this section, there was followed the influence of the temperature variation on the MEA losses. The pressure of the absorption process was of 140 kPa. In Table 2 there are summarized the results obtained.

Table 2

Parameters of chemical absorption process according to the temperature of the chemical solvent

MEA wt. [%]	T_{MEA} [°C]	L/G ratio [mol_{MEA}/mol_{fg}]	Heat duty [GJ/t_{CO2}]	MEA lost in absorber unit [kg/h]
20	30	1.85	3.03	335.66
	35	1.85	3.01	456.51
	40	1.85	3.00	590.02
	45	1.85	3.00	735.54
	50	1.85	2.98	892.28
30	30	1.13	2.71	942.79
	35	1.13	2.71	1098.4
	40	1.13	2.70	1263.9
	45	1.13	2.72	1438.7
	50	1.13	2.75	1623.7
40	30	0.79	2.65	1827.7
	35	0.79	2.63	2024.5
	40	0.79	2.65	2230.3
	45	0.79	2.65	2448.6
	50	0.79	2.64	2675

The CO_2 capture efficiency was maintained at approximately 90 % and the L/G ratio was calculated for all cases studied. For a higher concentration of amine in the solvent, the L/G ratio is smaller. The temperature of the chemical solvent at the inlet in the absorber unit influences the amount of the MEA lost. The thermal degradation of the solvent can be observed on the MEA losses at a different temperature. At a temperature of 50 °C the amount of amine lost is higher than at a temperature of 30 °C. In Fig. 6-11 there are represented the MEA lost and the heat duty according to the temperature of the chemical solvent. The heat duty for solvent regeneration did not suffer a major change in the case of the weight concentration of MEA in the chemical solvent is constant and it is varied the temperature at inlet absorption unit. If we analyze the heat duty for the three cases studied, we observe that the heat duty decreases with increasing the weight concentration of MEA.

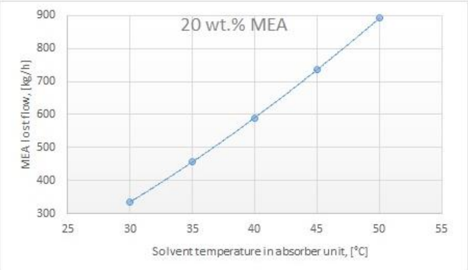

Fig. 6. MEA lost according to the chemical solvent temperature in absorber unit for 20 wt. % MEA

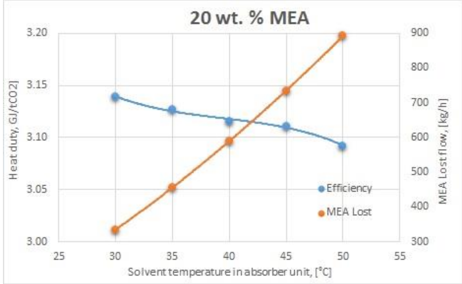

Fig. 7. Heat duty according to the chemical solvent temperature in absorber unit 20 wt. % MEA

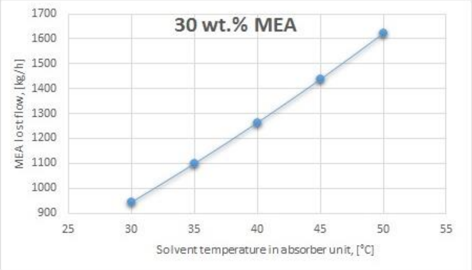

Fig. 8. MEA lost according to the chemical solvent temperature in absorber unit 30 wt. % MEA

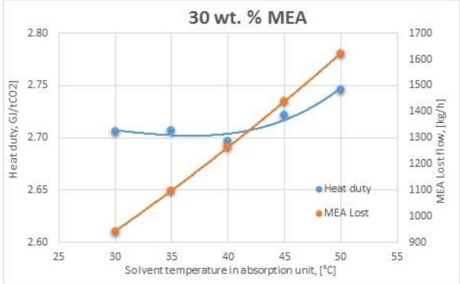

Fig. 9. Heat duty according to the chemical solvent temperature in absorber unit 30 wt. % MEA

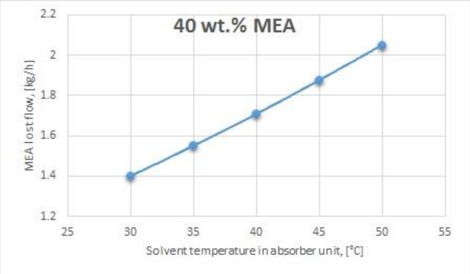

Fig. 10. MEA lost according to the chemical solvent temperature in absorber unit 40 wt. % MEA

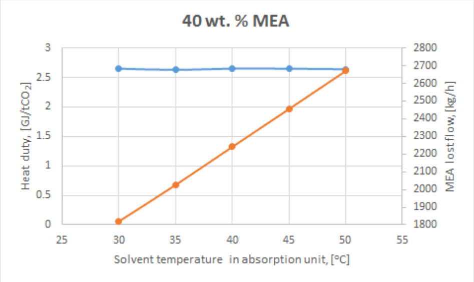

Fig. 11. Heat duty according to the chemical solvent temperature in absorber unit 40 wt. % MEA

Comparing the results obtained for cases analyzed, the amount of MEA lost is higher for a higher weight concentration of MEA in the chemical solvent. Also, taking into account and the value of the L/G ratio, the losses have a greater impact on the case the weight concentration is higher. It is observed (Fig. 11) that the MEA lost flow depends on the absorption column temperature and not on the heat duty which is related to the process from the stripper column.

3.2. The pressure influence on the chemical absorption process performances

In this section, we analyzed the effects of pressure variation on the amount of the MEA lost during the chemical absorption process. The studied cases were the same as the previous point (20, 30, 40 wt. % MEA). The pressure was varied between 140 and 350 kPa for different temperatures of the process (30 - 50 °C). The results obtained are represented graphically in Fig. 12-16.

The amount of the chemical solvent lost decreases with the process pressure increases and the MEA losses are higher when the temperature of the process is higher. The optimal case is for a temperature of the chemical solvent of 30 °C and a pressure of 350 kPa.

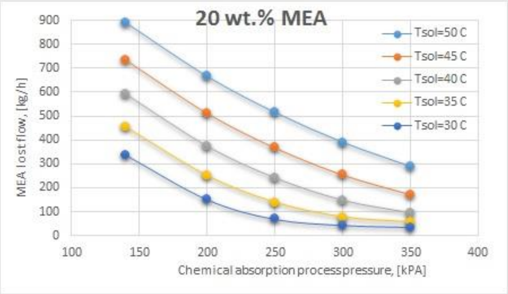

Fig. 12. MEA lost according to pressure and temperature of absorption process pressure for 20 wt. % MEA

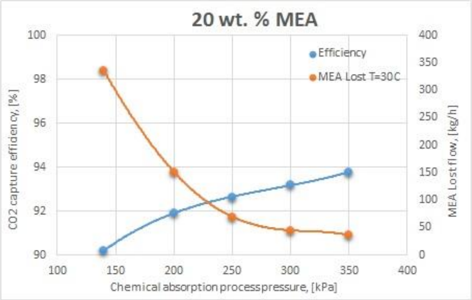

Fig. 13. CO_2 capture efficiency and MEA lost according to absorption process pressure for 20 wt. % MEA

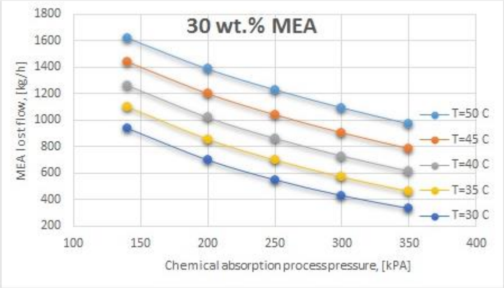

Fig. 14. MEA lost according to pressure and temperature of absorption process pressure for

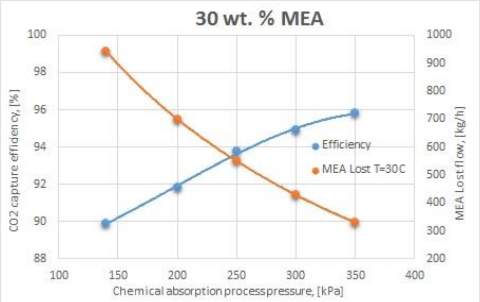

Fig. 15. CO_2 capture efficiency and MEA lost according to absorption process pressure

30 wt. % MEA

for 30 wt. % MEA

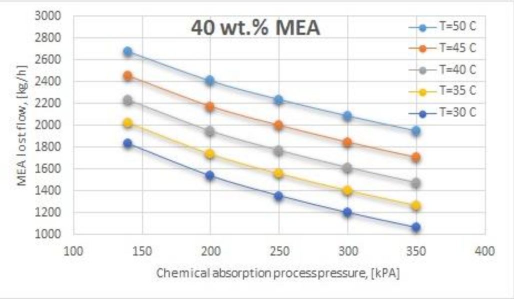

Fig. 16. MEA lost according to pressure and temperature of absorption process pressure for 40 wt. % MEA

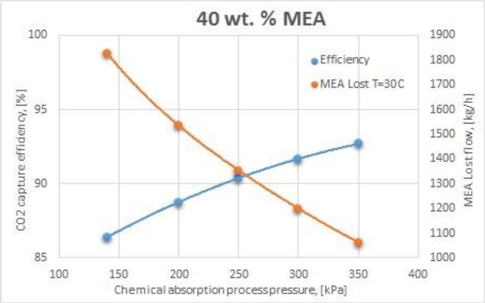

Fig. 17. CO_2 capture efficiency and MEA lost according to absorption process pressure for 40 wt. % MEA

In the case of the chemical solvent temperature variation no significant variations of CO_2 capture efficiency were observed. Instead, when the absorption process pressure increases the CO_2 capture efficiency increases due to the higher efficiency of CO_2 separation in the stripper column. For example, the CO_2 capture efficiency increased from 90 % to 94 % when the pressure in the stripper column varied between 140 kPa to 350 kPa (Fig. 13).

3.3. The comparative analysis of the three cases studied

In this section, three cases previously analyzed (MEA wt. 20%, MEA wt. 30%, and MEA wt. 40%) for the chemical solvent temperature variation were compared. From this analyze it can be noted that the solution whit MEA wt. 40% generated the high losses of solvent (Fig. 18), and with increasing the solvent temperature is increase the solvent losses in all cases.

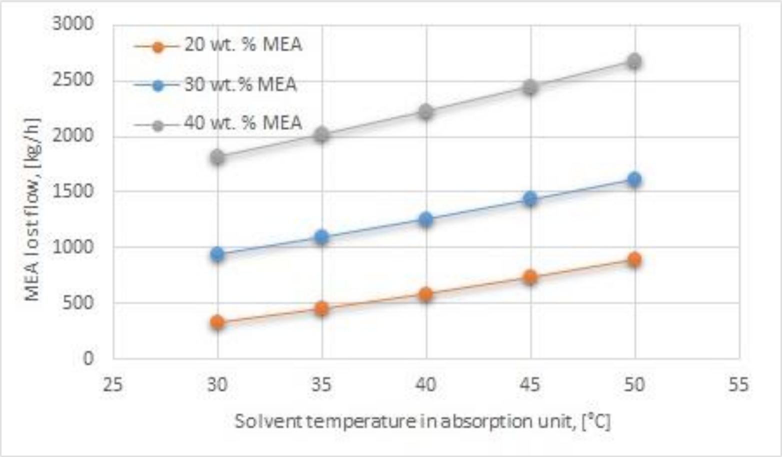

Fig. 18. MEA lost according to the chemical solvent temperature in absorber unit

In the case of variation of the chemical absorption process pressure, the influence of the MEA concentration on the chemical solvent lost in the absorption process was analyzed. The temperature of the absorption process varies between 30-50 ^{o}C. For reducing the chemical solvent lost in the absorption column, the temperature of the process was established to 30 ^{o}C (Fig. 19).

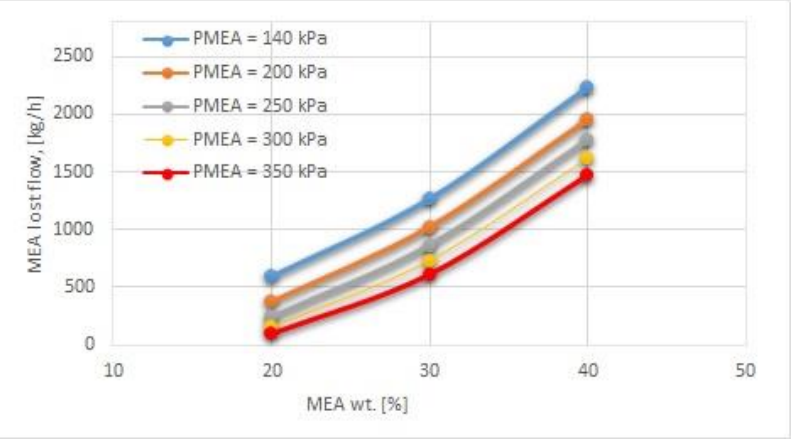

Fig. 19. MEA lost according to absorption process pressure

In this case, at a higher pressure of the absorption process, the MEA losses in the absorption unit are reduced. When MEA concentration is higher, the MEA lost increases.

4. Conclusions

In this paper, for minimizing the MEA amount lost during the chemical absorption process, a parametrical study for determining the optimal value according to the temperature and pressure in the absorption column was performed. The assessment was conducted for different MEA weight concentration in the solvent (three cases): 20 wt. %, 30 wt. %, 40 wt. %.

The major conclusions of the current study are:

- The solvent temperature varied between 30 and 50 °C and the amount of MEA lost in the absorber unit were between 335.66 kg/h (for an MEA wt. 20%) and 2675.03 kg/h (for an MEA wt. 40%);
- The process pressure varied between 140..350 kPa for different value of solvent temperature (30..50 °C) and the amount of MEA lost in the absorber unit were between 36.02 kg/h (for MEA wt. 20%, solvent temperature of 30°C and pressure at 350 kPa) and 2675.03 kg/h (for MEA wt. 40%, solvent temperature of 50°C and pressure at 140 kPa);

- The minimal amount of thermal energy required was of 2.55 GJ/t_{CO2} obtained for a temperature of 30 °C and an absorption pressure of 350 kPa;
- The minimal MEA losses (36.02 kg/h) in absorber unit was obtained when a solvent temperature in the absorber was 30 °C and a process pressure of 350 kPa.

In the future study, we are interested to determine the influence of the energy consumption for the solvent desorption process in order to assure the optimal parameters obtained in this study.

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