Comparative Analyses of Primary and Secondary Amines for CO_2 Chemical Process Capture in a CFBC Pilot Installation

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***Abstract*—The aim of this paper is to optimize the integration of post-combustion CO_2 capture by chemical absorption in the technology of circulating fluidized bed combustion of coal, by comparing the effects of the usage of primary amines (MEA) and of secondary amines (DEA). The validation of the results obtained after the HYSYS 3.2 modeling of the CFBC technology with post-combustion CO_2 capture by chemical absorption was based on experimental results. The minimum quantity of required energy (2.65 GJ/tCO_2) was obtained in the case when DEA (40 wt.%) was used, for the following values of process parameters: the CO_2 capture process efficiency of 85%; the ratio L/G = 1, lean loading solvent was of 0.22 mol_CO_2/mol_DEA, the rich solvent loading was of 0.45 mol_CO_2/mol_DEA; the stripper inlet solvent temperature was of approximately 85 ^oC, while the optimal number of stages in the absorber was 8.**

***Index Terms*—CO_2 capture, CFBC, MEA, DEA.**

I. Introduction

The CO_2 emissions generated by burning coal (lignite) are between 800 and 1000 g/kWh, according to the combustion technology type. Taking into account the existing coal reserves and the current coal production, the estimated lifespan of coal is of 220 years [1]. In this article it have analyzed the effects that the integration in CFBC technolgy of chemical absorption processes using primary, and secondary amines has on flue gas CO_2 capture.

The studies in the specialized literature [2]-[4] do not deal with the optimization of all parameters within the chemical absorption processes; they focus only on certain local parameters specific to the absorption and desorption units (temperature, pressure, flow). For example, in the study carried out in HYSYS 3.2 on the simulation of the chemical absorption process using equal blends of MDEA and DEA (20% MDEA, 20 % DEA and 60 % H_2O), obtained an energy consumption of 2.3 GJ/ton CO_2 for a CO_2 capture efficiency of 80%; a quantity of required energy of 2.4 GJ/ton CO_2 for a CO_2 capture efficiency of 85%; a quantity of required energy of 2.7 GJ/ton CO_2 for a CO_2 capture efficiency of 90%; and of 2.95 GJ/ton CO_2 for a CO_2 capture efficiency of 95%. In the study [3] the authors used the ASPEN Plus simulation program in order to study the integration of CO_2 chemical absorption process using MEA in a thermo-electrical unit of 600 MW fueled by bituminous coal. For different MEA solvent concentrations (20, 30 and 40%) and for different efficiencies of the CO_2 capture process (80, 90, 95 and 99%), the author highlighted the decrease of the quantity of the required energy to a value considered to be minimal (3.45 GJ/ton CO_2 for an efficiency of 90% and a concentration of 30% solvent MEA) as a result of the increase of the lean solvent loading of approximately 0.30 mol CO_2/mol MEA [5].

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II. Setup of the Experimental Process

A. Description of the Experimental Installation with CO_2 Capture

The experimental study was performed on the existing pilot installation designed and commissioned in the Environmental Analysis Laboratory within the Power Plant Department – University POLITEHNICA of Bucharest. The technical particularities of the pilot installation are described below:

- Thermal load 75 kWt;
- Feed-in flow: up to 20 kg/h (depending of fuel type and particles size);
- Combustion air: up to 175 m^3/h;
- Temperature flue gas in the combustor: 850°C-1000°C;

Fig. 1 shows the process of CFBC equipped with post-combustion CO_2 capture using chemical absorption. The installation of CFBC is equipped with the capture of SO_2 emissions using the NaOH-based solution. In this article we have not studied the influence of SO_2 on the amine-based solution because, after the desulphurization process, the SO_2 concentration in flue gases was less than 2ppm. Moreover, the recirculation of flue gases allowed the NO_x concentration to be maintained under 50 ppm. Mention must be made of the fact that the CFBC installation is to be found in the laboratory of Renewable Energy Sources and Environmental Analyses within the Power Engineering department of Politehnica University of Bucharest.

In this article, the objective consists in reducing the quantity of energy required for solvent regeneration by using primary, secondary or blended amines, by recuperating the flue gas heat.

Consequently, before being evacuated in the environment, flue gases passed through the surface heat exchanger and lent their heat to the solvent which circulates counter-currently, and which thus is heated in a first stage. Afterwards, the

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solvent is introduced in a re-boiler which is heated electrically using electric resistances with a total electrical power of 4 kW.

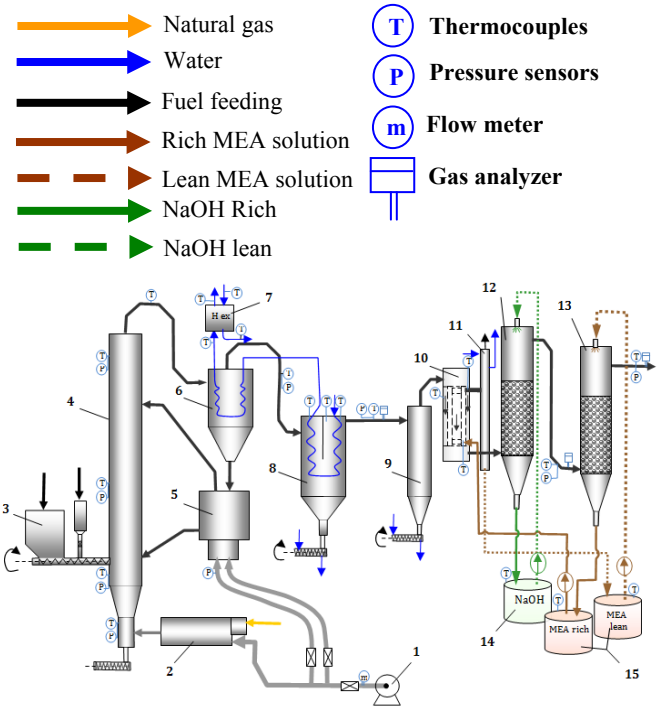

Fig. 1. The main components of the CFBC pilot installation.

Both the heat exchange surface and the electric resistances were dimensioned so that the temperature of the solution in the re-boiler should be of approximately 95 °C. After the desorption process, the solution was introduced in a heat exchanger with plates and gaskets, in view of reducing the temperature corresponding to the absorption process (40 – 45 °C). The solution was cooled by using the cold water from the laboratory water system. In order to maintain the temperature of the absorption process constant, the cooling water flow was varied between 5-7 l/min. Before evacuating the flue gases in the environment, they passed through the desulphurization unit, the CO_2 absorber, respectively, so that the evacuation unit should be less than 50 °C. In the case of the study of the flue gas influence on the absorption process, the flue gases were cooled for a cooling water flow of 12 l/min, and the installation outlet flue gas temperature was of approximately 25 °C.

TESTO gas analyzer was used in order to monitor the pollutant emissions on the flue gases evacuation track. Thus, the CO_2 emissions, dust, NO, NO_2, SO_x, CO were recorded in a special software connected to the monitoring unit. The pollutant emissions were recorded before and after the CO_2 unit absorption. TOC analyzer (Total Organic Compounds) was used in order to determine the CO_2 content in the amine solution (lean and rich loading solvent).

B. Procedure for the Experimental Study

In this paper it was study the effects of using primary amines (MEA) and secondary (DEA) amine on the energy consumption, and on the CO_2 capture efficiency, respectively. Monoethalomine (MEA) and diethanolamine (DEA) were chosen as being the most representative for the class they belong to.

The experimental study was carried out under the following conditions of the chemical absorption –desorption process: a) the fuel flow was of 10 kg/h; b) the excess of air was maintained around 1.5, a value which corresponds to the reference value of oxygen content specific to the type of installation used; c) the cooling water temperature was considered constant, approximately 15 °C; d) the cooling water flow was maintained constant at 5 l/min; d) the composition of the lignite used: 1.25%; C: 21.55%; N: 0.65%; O_2: 2.55%; S: 1%; W: 36%; A: 37%; the calculated calorific power it was 7 543 kJ/kg.

In order to decrease the quantity of energy required for solvent regeneration, in this article it was studied the effects of the solvent regeneration in two stages using the heat recovered from flue gases, on the one hand, and on the other hand, the heat generated by two electric resistances, so that the required quantity of energy corresponding to a certain CO_2 capture process efficiency should be ensured. Consequently, the energy required for solvent regeneration was considered to be only the electric energy consumed in the second regeneration stage, namely the heat generated by the two electric resistances.

In view of determining the effects on the energy consumption, and respectively, on the CO_2 capture efficiency of the regeneration in stages of various types of amines, it was analyzed 6 cases (A1-A6) according to the amine solvent concentration (MEA, DEA), as it follows: A) A1-A3: MEA concentration in the water solution: 20 %, 30 respectively 40 %; the maximum MEA solvent concentration was limited to 40 % due to the corrosive effects on pilot plant installation; B) A4-A6: DEA concentration in the water solution: 25 %, 30 % respectively 40 %.

For each case (A1-A6), the following parameters were analyzed: a) ratio L/G in [kg_liquid/kg_gas]; b) temperature of the inlet amine in the stripper/absorber unit; d) liquid flow rate; e) the operation conditions of the stripper unit (pressure and number of stages).

III. Results and Discussion

A. The effect of the Variation of the Number of Stages on the Energy Consumption

In this paragraph it was analyzed the influence that the variation of the number of stages in the desorption unit has on the energy consumption. During the experimental study we obtained results related to the energy consumption when the desorption unit was made of 20 stages. Consequently, the energy consumption obtained for variants A1-A6 was of 4 GJ/tCO_2 in the case of a concentration of 20% MEA in the solution; 3.7 GJ/tCO_2 in the case of a concentration of 30 % MEA in the solution and of 4.2 GJ/tCO_2 respectively, in the case of a concentration of 40% MEA in the solution. When the solution of DEA was used, the minimum energy consumption was: 3 GJ/tCO_2 for a concentration of 25% DEA in the solution; 2.5 GJ/tCO_2 for a concentration of 30% DEA in the solution and 2.8 GJ/tCO_2 in the case of a concentration of 40% DEA in the solution.

Fig. 2 and Fig. 3 show the influence that the number of stages in the desorption unit has on the quantity of energy needed to regenerate the solvent for different MEA

concentrations in the solution (20, 30 and 40% respectively); and DEA in the solution (25, 30 and 40%, respectively). One can notice that, for a constant value of the CO_2 capture process efficiency, the energy consumption decreases while of the number of stages increases up to an optimal value according to the type of amine used and to the value of the concentration in the solution.

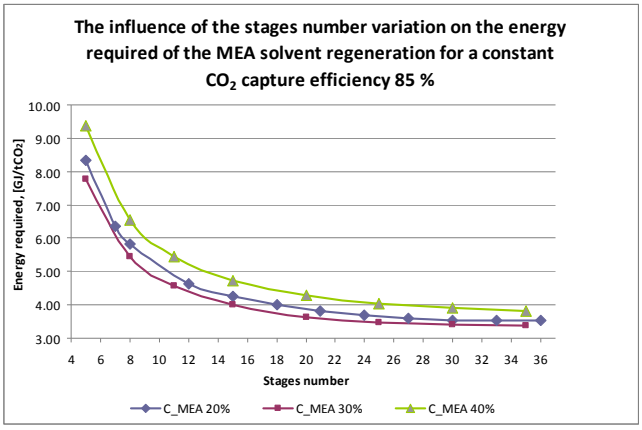

Fig. 2. The stages number variation influence on the energy required of the MEA solvent regeneration for a constant CO_2 capture efficiency 85 %.

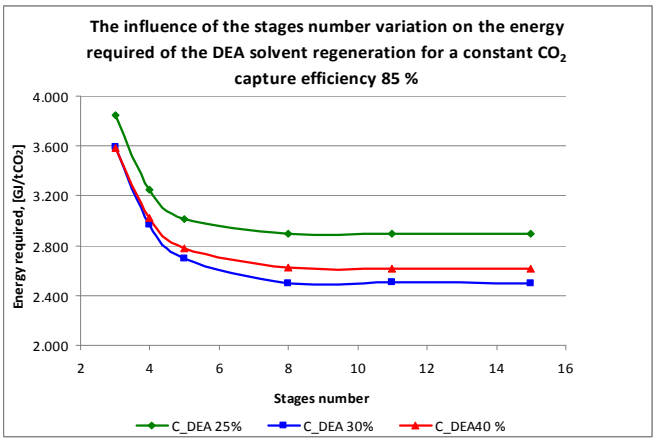

Fig. 3. The stages number variation influence on the energy required of the DEA solvent regeneration for a constant CO_2 capture efficiency 85 %.

In the case when MEA is used, the minimum energy consumption was of 3.4 GJ/tCO_2 obtained for a concentration in the solution of 30%, and for a number of 22 stages in the stripper, respectively. One can notice that for the same CO_2 capture process efficiency of 85%, and, for 22 stages in the desorption unit, respectively, the minimum energy consumption obtained for a concentration of MEA in the solution of 20%, and of 40%, respectively, was approximately of 3.8 GJ/tCO_2, and of 4.1 GJ/tCO_2, respectively.

When the DEA solution was used, the minimum energy consumption was of approximately 2.5 GJ/tCO_2, obtained for a number of 8 stages in the desorption unit and for a concentration of 30%. It was noticed that after increasing or decreasing the DEA concentration in the solution (40% and 25%, respectively), the energy consumption was higher, 2.65 GJ/tCO_2 and 2.9 GJ/tCO_2, respectively. As compared to MEA, when DEA was used, it was noticed that there was a decrease of the energy consumption for the same CO_2 capture process efficiency, and for a smaller number of stages in the desorption unit, which reduces the investment considerably.

B. The Influence of the Stripper Inlet Solvent Temperature

In this paragraph it were analyzed the influence that the stripper unit inlet solvent temperature has on the required regeneration energy. The solvent temperature was increased by reducing the solvent flow for the same flue gas flow of 58 kg/h. The solvent flow varied between 0.8 and 1.8 l/min. When MEA was used, it was noticed that there was a decrease of approximately 20 % (Fig. 4) of the energy required for solvent regeneration when the solvent temperature increased from 87.7 to 92 °C, indifferent of the CO_2 capture process efficiency. For the constant value of the CO_2 capture process efficiency, the minimum required energy was obtained for the inlet solvent temperature of approximately 92 °C; this energy varied according to the CO_2 capture process efficiency from 3.1 GJ/tCO_2 for the efficiency of 85% to 5.5 GJ/tCO_2 corresponding to a CO_2 capture process efficiency of 92%. Analyzing and comparing the experimental and simulation results it is notice that the difference between them is maxim 10 %.

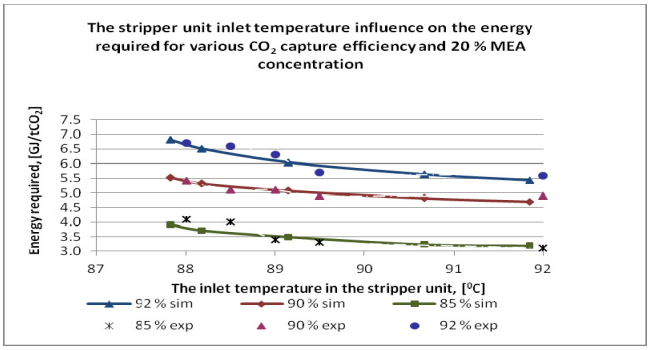

Fig. 4. The stripper inlet temperature influence on the energy required of the 20% MEA solvent regeneration for a various CO_2 capture efficiency.

When a 30 % MEA concentration solution is used (Fig. 5), one can notice another trend of the variation of the required regeneration energy as compared with the case discussed above. Moreover, one can notice that the increase of the solvent temperature from 87 to approximately 91 °C led to the decrease of the required regeneration energy by approximately 27% to 3.1 GJ/tCO_2, according to the CO_2 capture process efficiency of 85%.

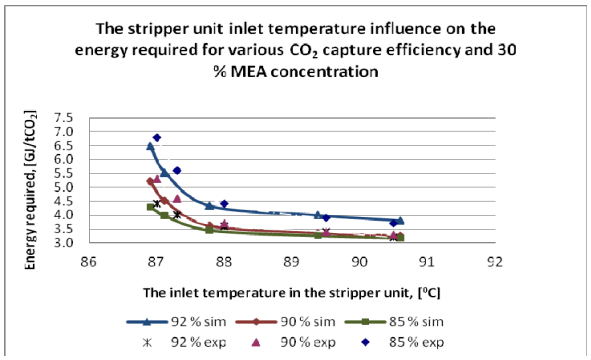

Fig. 5. The stripper inlet temperature influence on the energy required of the 30% MEA solvent regeneration for a various CO_2 capture efficiency.

Fig. 6 shows the variation of the required energy according to the stripper inlet temperature for a 40% MEA concentration. In this case, one can notice that the increase of the temperature from 86 to 88 °C led to a decrease of the required energy by 46% up to 3 GJ/tCO_2 for a CO_2 capture process efficiency of 85%.

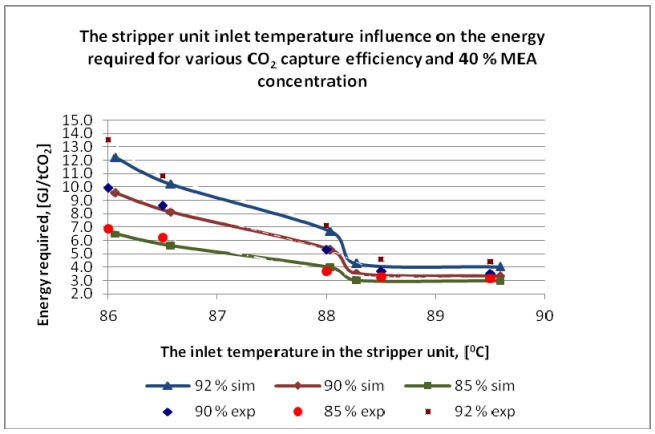

Fig. 6. The stripper inlet temperature influence on the energy required of the 40% MEA solvent regeneration for a various CO_2 capture efficiency.

Therefore, it is not efficient to use solution temperatures which are higher than 88 °C, since the required energy remains constant, according to the CO_2 capture process efficiency.

When a 25 % DEA concentration is used (Fig. 7), one can notice an increase of the energy required for the solution regeneration process by approximately 20% when the solution temperature increases from 84.5 to 89 °C, for a constant efficiency of the CO_2 capture process of 85%, of 3.1 GJ/tCO_2 respectively, for an efficiency of 90 and 92%, respectively.

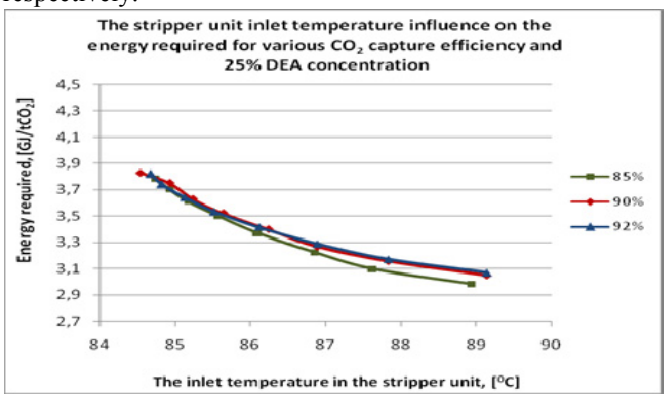

Fig. 7. The stripper inlet temperature influence on the energy required of the 25% DEA solvent regeneration for a constant CO_2 capture efficiency 85%.

Fig. 8 shows the variation of solvent regeneration required energy according to the stripper inlet temperature for a 30 % DEA concentration for various values of the capture process efficiency. One can notice that when the solution temperature increased from 84.7 to 88.9 °C for a capture efficiency of 85 %, the energy required for regeneration decreased by 27%, and reached the value of 2.7 GJ/tCO_2, the decrease of the energy required being slightly smaller in the case of the capture efficiency of 90 and 92%. When the DEA concentration is modified in the solution one can notice a decrease of the energy required for solvent regeneration by approximately 10% in the case of a 30% concentration, as compared to a concentration of 25% for a stripper inlet temperature of 89 °C and an efficiency of the capture process of 85%.

When a 40% DEA concentration is used (Fig. 9), one can notice a decrease of the required energy by 34%, down to 2.5 GJ/tCO_2, in the case when the solvent temperature increases from 83.5 to 88 °C , for a CO_2 capture process efficiency of 85%. For values of the capture process efficiency which are higher than 90, and than 92%, respectively, and for the same interval of the inlet stripper temperature, one can notice a decrease of the required energy by 31%.

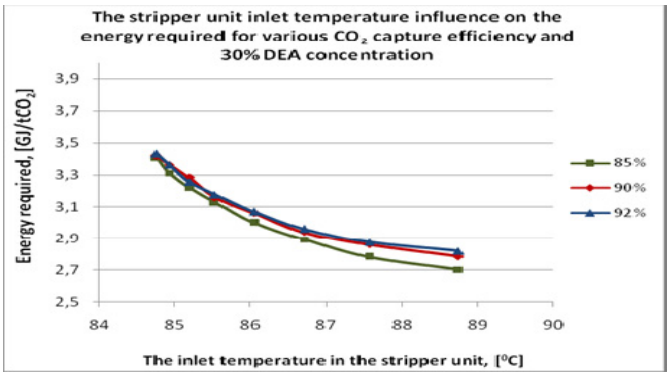

Fig. 8. The stripper inlet temperature influence on the energy required of the 30% DEA solvent regeneration for a constant CO_2 capture efficiency 85%.

The increase of the DEA concentration from 25 to 40% led to the decrease of the energy required for the solvent regeneration from 3 to 2.45 GJ/tCO_2 for the same stripper inlet temperature (88 °C), and for the same CO_2 capture efficiency.

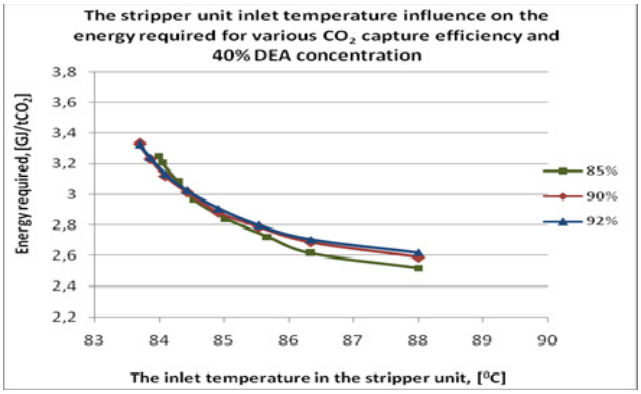

Fig. 9. The stripper inlet temperature influence on the energy required of the 40% DEA solvent regeneration for a constant CO_2 capture efficiency 85%.

C. The influence of the L/G Ratio on the Quantity of Required Energy

The study of the influence of the ratio L/G on the energy required for the solvent regeneration process aimed at identifying the optimum L/G ratio for primary and secondary amines, and for primary and secondary amine blends, respectively. The variation of the L/G ratio was obtained by maintaining the flue gas flow constant (58 kg/h) and by varying the solution flow between 40 and 110 kg/h.

Fig. 10 shows the variation of the energy required for solvent regeneration, according to the ratio L/G for a MEA concentration between 20 and 40%. It was noticed that as the MEA solvent concentration increased, the optimal value of L/G ratio decreased, while the minimum required energy is of 3.1 GJ/tCO_2 for an optimal ratio L/G=1. When the MEA solvent concentration was of 30%, and 20% respectively, the minimal required energy (3.2 GJ/tCO_2, and 3.4 GJ/tCO_2, respectively) was obtained for the optimal ratio L/G=0,7, and L/G=1, respectively. On the other hand, one can notice that for a value of the L/G ratio which is higher than 1.3, the

energy required for solvent regeneration increases as the MEA concentration increases.

When DEA was used, it was noticed that, irrespective of the concentration used, the optimal L/G ratio was obtained around value 1, and that the required energy decreased as the DEA concentration increased. In comparison with the time when MEA was used, in the case of DEA the minimum required energy was of 2.7 GJ/tCO_2 obtained for a 40% DEA concentration. When the value of the L/G ratio was higher than 1.3, the energy required for solvent regeneration increased very much, irrespective of the DEA solvent concentration (Fig. 11).

The comparative analysis between the variants presented above was carried out for a CO_2 capture process efficiency of 85% in order to compare the values obtained experimentally (the CO_2 capture process efficiency obtained as a result of the experimental study was of 85%) with those obtained during the simulation study. However, when the CO_2capture process efficiency increased from 85% to 90% there was a relatively small increase of the energy in comparison with the variation of other parameters. The results are comparable to those from scientific literature [6]-[8].

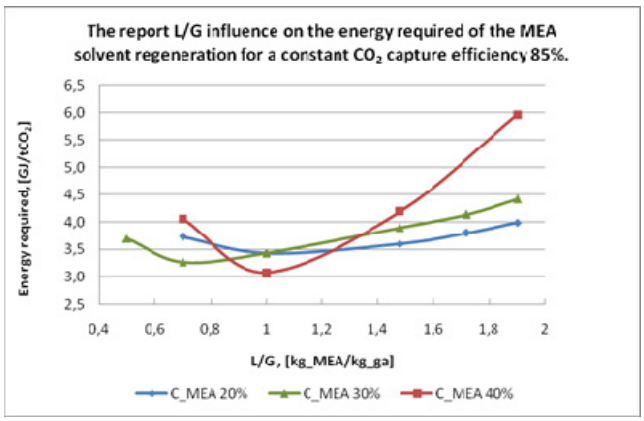

Fig. 10. The L/G index influence on the energy required of the various MEA concentration solvent for a constant CO_2 capture efficiency 85%.

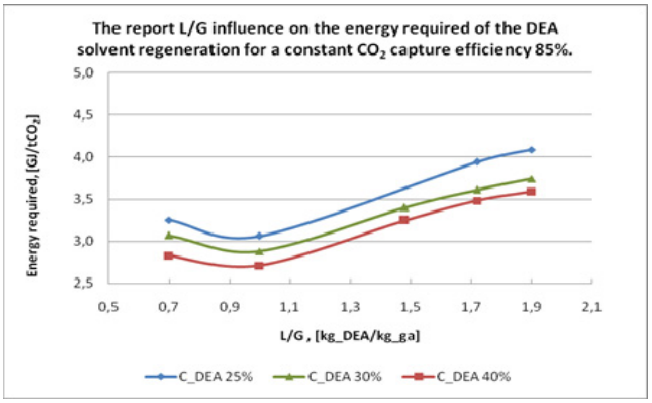

Fig. 11. The L/G index influence on the energy required of the various DEA solvent regeneration for a constant CO_2 capture efficiency 85%.

To highlight the importance of the solvent type in the capture process, the Table I presents the comparative analysis of different cases defined in section II B. Comparative analysis was performed maintaining constant the CO2 capture process efficiency (85 %) and the flow gases (58 kg/h). It was found that the minimum energy requirement, 2.65 GJ/tCO2, was obtained for a concentration of 40% DEA in solution.

TABLE I: THE RESULTS OF THE PROCESS PARAMETERS FOR VARIOUS ANALYZED CASES

Parameter	Cases studied					
	Var A1	Var A2	Var A3	Var A4	Var A5	Var A6
CO_2 capture process efficiency %	85	85	85	85	85	85
Energy process required, GJ/tCO_2	3.4	3.34	3.12	3.1	2.9	2.65
Gas flow rate, kg/h	58	58	58	58	58	58
Ratio L/G, kg_l/kg_gas	1.05	0.72	1	1	1	0.95
Absorber/Stripper inlet temperature, °C	35/91	38/91	37/92	41/92	42/93	41/92
Stripper pressure process, kPa	310	310	290	125	155	118
Lean CO_2 loading solvent, in mol CO_2/mol amine	0.37	0.31	0.3	0.26	0.24	0.22
Rich CO_2 loading solvent, in mol CO_2/mol amine	0.55	0.5	0.49	0.49	0.46	0.45
Gas temperature, °C	47	47	46	52	52	52

IV. CONCLUSION

The aim of this paper was to optimize the parameters of the post-combustion CO_2 capture from the flue gases resulted from brown coal combustion in the CFBC installation, by using primary amines (MEA), and secondary amines (DEA). For the optimal number of stages (20 stages when MEA was used, and 8 stages when DEA was used) in the desorption unit, the quantity of energy required varied according to the amine solvent concentration, and the minimal value was obtained both in the case of MEA (3,5 GJ/tCO_2), and in the case of DEA (2.5 GJ/tCO_2) for 30% solvent concentration.

When stripper solvent temperature was varied between 86 and 92 °C the minimum quantity of required energy was relatively the same in the case of MEA, approximately 3.1 GJ/tCO_2, obtained at solvent temperatures of de 92 °C (20 % MEA), 90.5 °C (30 % MEA), and 88.5 °C (40 % MEA), respectively. In the case of DEA the minimum quantity of required energy, 2.5 GJ/tCO_2, was obtained for a concentration of 40% and at a temperature of 88 °C. It was noticed that once the MEA concentration increased in the solvent, the optimal value of the L/G ratio decreased, and the minimum quantity of required energy is of 3.1 GJ/tCO_2 for an optimal ratio of L/G=1. When a 30% and a 20% MEA concentrations were used, the minimum required energy (3.2 GJ/tCO_2, and 3.4 GJ/tCO_2, respectively) was obtained for the optimal ratio L/G=0.7, and L/G=1, respectively. On the other hand, it was noticed that for a value of the L/G ratio which is bigger than 1.3, the quantity of the energy required for solvent regeneration increases once the MEA solvent concentration increases.

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His scientific research activities focus on optimized the CO_2 capture process using different type of solvents. In this way, he is the responsible of the two projects concerning the CO_2 capture process integration in the power plants based on coal. His research interests are in: environmental impact of energy systems, power engineering process, chemical reaction engineering, mathematical modeling, simulation and optimization of chemical and thermo-chemical processes, process synthesis and design, technical and economical assessments, process integration, carbon capture technologies. Hi is also teaching courses for the following academic disciplines: Life Cycle Assessment of fossil fuel, Energy and Environment, Environmental evaluation of energy process; Renewable energy sources, and monitoring of energy systems pollutants.

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