U.P.B. Sci. Bull., Series C, Vol. 79, Iss. 1, 2017 ISSN 2286-3540

EVALUATION OF THE PHYSICAL SOLVENTS USED IN CO_2 POST-COMBUSTION PROCESSES

Adrian PASCU[1], Nela SLAVU[2], Adrian BADEA[3], Cristian DINCA[4]

The aim of this article consists in comparing the physical adsorption process using various physical solvents with the chemical absorption process which uses the monoethanolamine (MEA) chemical solvents. We noted that the CO_2 capture efficiency increased with increasing the L/G ratio respectively with decreasing temperature of the solvent (in the case of physical solvents) when entering the absorption column. The L/G ratio value obtained for a 90% efficiency varied depending on the physical solvent used. Thus, when using the methanol (MeOH) the L/G ratio was of 61.22 $mol_{solvent}/mol_{flue\ gas}$ (considering the input temperature of the solvent 20 °C), when using the propylene carbonate (PC) the L/G ratio was of 6.12 $mol_{solvent}/mol_{flue\ gas}$ (considering the input temperature of the solvent -50 °C) and when using the N-Methyl-2-pyrrolidone (NMP) the L/G ratio was of 4 $mol_{solvent}/mol_{flue\ gas}$ (considering the input temperature of the solvent -50 °C).

Keywords: physical absorption process, Aspen Plus, physical absorption process integration, CO_2 capture

1. Introduction

The main method used today to capture the carbon dioxide from flue gases resulted from fossil fuel power plants is based on chemical absorption which uses chemical solvents [1]. The most common chemical solvent in the process of retaining through chemical absorption is monoethanolamine due to its physico-chemical properties and high capacity to absorb carbon dioxide [2 – 6].

The physical absorption process takes place at high pressures and low temperatures (in the case of methanol the process is conducted at a pressure of 28 bar and a temperature of 30°C). The carbon dioxide separation from the physical solvent takes place by expanding it in expanders or turbines when we want to recover a share of the mechanical energy used by the compressors. The separation

[1] PhD eng., Power Plant Department, University POLITEHNICA of Bucharest, Romania, e-mail: adryan_pascu@yahoo.com

[2] PhD eng., Power Plant Department, University POLITEHNICA of Bucharest, Romania, e-mail: slavunela@yahoo.com

[3] Prof., Power Plant Department, University POLITEHNICA of Bucharest, Academy of Romanian Scientists, Romania, e-mail: badea46@yahoo.fr

[4] Assoc. Prof., Power Plant Department, University POLITEHNICA of Bucharest, Romania, e-mail: crisflor75@yahoo.com

process can take place by using expanders / turbines connected in series when the pressure is high [7].

Solubility measures the dissolved gas in a homogeneous liquid in which the atoms and molecules distribution is uniform. In general, in order to increase the solubility of a gas in a liquid we have to increase the gas partial pressure and decrease temperature of the solvent.The physical solvents analysed in this study (its physical properties are presented in Table 1) are non-corrosive and non-toxic. Propylene Carbonate solvent (PC) works at lower temperatures without becoming too viscous, in which case the mass transfer coefficient is better. N-methyl-2-pyrrolidone (NMP) and methanol (MeOH) solvents show a higher degree of selectivity than the PC to remove the H_2S from gases containing CO_2 [8]. The physical solvents capacity to absorb gases resulted from fossil fuel combustion increases as temperature decreases.

Table 1

Properties of physical solvents [7, 9, 10]

Solvent/ Parameter	**PC**	**NMP**	**MeOH**
Process Name	Fluor Solvent	Purisol	Rectisol
Viscosity at 25 °C (cP)	3.0	1.65	0.6
Specific Gravity at 25 °C (kg/m^3)	1195	1027	785
Molecular Weight	102	99	32
Vapor Pressure at 25 °C (mmHg)	0.085	0.40	125
Freezing Point (°C)	-48	-24	-92
Boiling Point at 760 mmHg (°C)	240	202	65
Maximum Operating Temperature (°C)	65	-	-
Specific Heat 25°C	0.339	0.40	0.566
CO_2 solubility at 25 °C (m^3/l)	0.003402	0.003567	0.003178

In 2015, at UN Climate Change Conference (COP21) in Paris, was approved the framework for action on Climate and Energy policies for period 2020 – 2030 [11]. For the European Union was established a GHG emission reduction by 20% until 2020 compared whit year 1990 [11]. For the European Union was established a GHG emission reduction by 30% until 2020 compared whit year 1990 [11]. The target for Romania is to reduce the GHG emissions by 19% until 2030 [12].

The end of pipe technologies that are used for capturing the CO_2 from flue gases is mainly based on physical and chemical absorption processes. The drawbacks of the chemical absorption processes consist of a high thermal energy consumption for the solvents regeneration and of a high rate of corrosion of metallic surface [13, 14]. The CO_2 capture by physical absorption processes depends both on the partial pressure of the physical solvent and on the flue gases temperature. As the partial pressure increases and the temperature decreases, the CO_2 solubility in the solvent increases [15]. The physical and chemical processes could be both integrated in the new or existing coal power plants.

The aim of this study was to establish the physical solvents advantages compared to the chemical ones knowing that the latter have two major drawbacks: a) their corrosive nature greatly affect the metal surfaces of the equipment in the CO_2 capture power plant; and b) in the regeneration of chemical solvents we need a significant amount of heat for their regeneration.

2. Description of the physical absorption process in Aspen PLUS

The scheme of the analyzed process was built in the ASPEN Plus work environment and in which we defined the parameters for all the equipment used [18]. Table 2 shows the parameters defined for each equipment used in the physical absorption process shown in Figure 1.

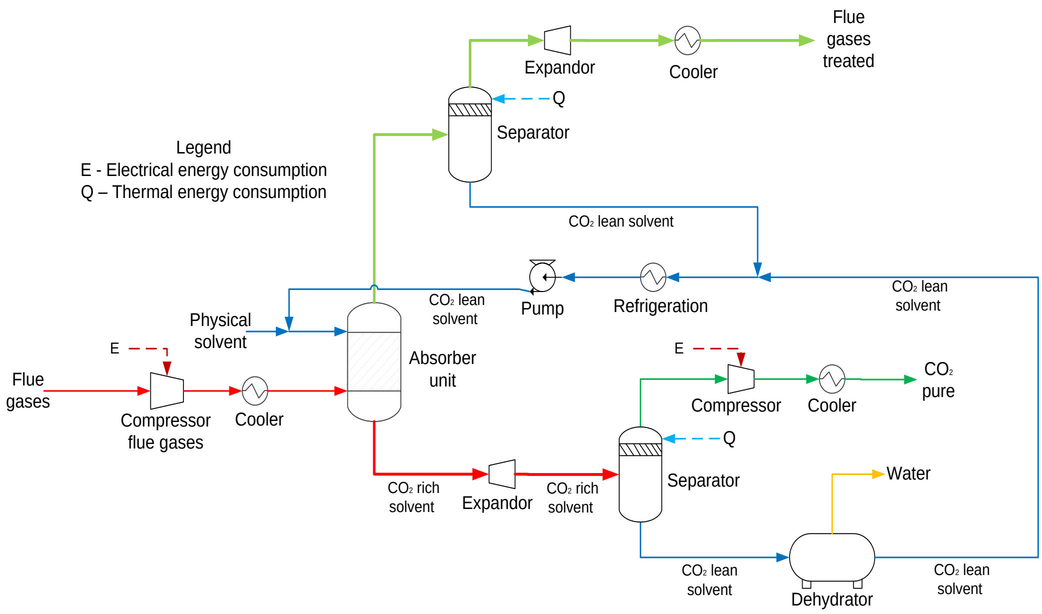

Fig. 1. The CO_2 physical absorption process [16]

The flue gases are introduced into the absorption unit at the bottom, but not before being compressed and cooled so as to maintain in the absorption column a cold temperature. The gases introduced in the absorption unit circulate in countercurrent with the physical solvent introduced at the top of the absorption column.

For a high value of CO_2 capture efficiency, the process is performed at high pressure (between 20 bar and 30 bar) [17] and low temperatures (between -50°C and 20°C) [18]. In this context, we have chosen the values for each equipment in the absorption process in order to reduce the energy consumption and to increase the CO_2 capture efficiency. After the absorption, the CO_2-rich solvent exits at the bottom of the absorption column and enters an expander (depending on the pressure of the solvent we can use more expanders / turbines connected in series). The expander's aim is to reduce solvent's pressure (from 28 bar to about 6 bar) [19]. Subsequently, the CO_2 rich solvent is introduced into a separator where the CO_2 is separated from the physical solvent. The CO_2 flow with a purity of over 95% is cooled and compressed to 70 bar for shipment to the storage area. The lean CO_2 physical solvent comes out at the bottom of the separator and enters a moisture separator where the water will be eliminated from the solvent. The lean CO_2 physical solvent is transported through a heat exchanger to be cooled to the operating temperature (the parameter values are presented in Table 2) and reintroduced into the absorption column.

Table 2

Installation parameters

No. Crt.	Equipment	Parameters
1.	Compressor flue gases	T = 80°C / P_{in} = 1 bar / P_{out} = 28 bar
2.	Cooler flue gases	T_{in} = 80°C / T_{out} = 30°C / P = 28 bar
3.	Absorber unit	Stage no. : 10 / P = 28 bar
4.	Expander CO_2 rich solvent	T = -15.4°C / P_{in} = 28 bar / P_{out} = 6 bar
5.	Separator CO_2 rich solvent	T = 40°C / P_{in} = 6 bar / P_{out} = 1 bar
6.	Dehydrator	T = 30°C / P_{in} = 1 bar / P_{out} = 1 bar
7.	Refrigeration	T_{in} = 18°C / T_{out} = 0°C / P_{in} = 1 bar / P_{out} = 1 bar
8.	Separator flue gases treated	T = 7°C / P_{in} = 28 bar / P_{out} = 28 bar
9.	Expander flue geses treated	T = 26°C / P_{in} = 28 bar / P_{out} = 1 bar

Table 3 shows the parameters defined for each stream:

a) physical solvents: temperature, pressure, weight concentration, lean / rich loading solvent; b) combustion gases: composition, temperature, pressure.

The physical solvents and flue gases parameters were chosen to have a high CO_2 capture efficiency. Thus, in the absorption unit, the solvent temperature was established at 40°C and the pressure of the CO_2 capture process was maintained at 1.4 bar. The weight concentration of the physical solvent was chosen of 100% due to the non – corrosive its properties [20].

Table 3

Stream parameters

No. Crt.	Stream	Parameters
1.	Physical solvent	T = - 20°C / P = 28 bar MeOH = 100 wt. % / NMP = 100 wt. % / PC = 100 wt. %
2.	Flue gases	T = 12°C / P = 28 bar CO_2 = 10.081 %; N_2 = 70.629 %; H_2O = 12.048 %; O_2 = 7.041 %
3.	Rich loading solvent	T = - 15.4°C / P = 28 bar γ_{rich} = 0.005 mol CO_2/ mol solvent

The elementary analysis of the flue gases analyzed in this study is presented in Table 4.

Table 4

Analysis of the lignite used in the combustion process [2, 6]

Elementary composition of lignite

C^i, [%]	H^i, [%]	S^i, [%]	O^i, [%]	N^i, [%]	W^i, [%]	A^i, [%]	LHV*, [kJ/kg]
24.27	1.4	1.3	1.8	0.86	31	39.37	8935.54

Flue gases composition

	Dry condition	**Wet condition**
CO_2, [%]	11.461	10.081
SO_2, [%]	0.23	0.202
N_2, [%]	80.304	70.629
O_2, [%]	8.005	7.041
H_2O, [%]	-	12.048

* LHV – low heating value of lignite

3. Results and discussions

In this study we performed a comparative analysis of the CO_2 capture efficiency from the flue gases for the (MEA) chemical solvent and, respectively, for the physical solvents: MeOH, PC, NMP, for different values of the L/G ratio and for different temperatures of the solvent .

Table 5 presents the results obtained from the analysis carried out on chemical solvents. The simulations were made for different chemical solvents in order to see which solvent has the highest absorption capacity. In these simulations, there were varied the followings parameters: the L/G ratio, the solvent temperature, and weight concentration, in order to identify their influence on the CO_2 capture efficiency. So, we determined the values of each parameter considering the carbon dioxide capture efficiency of 90% and the lean loading solvent of 0.21 $mol_{CO2}/mol_{solvent}$.

Table 5

The chemical absorption simultion

Nr.	Chemical solvent	Weight concentration (%)	L/G ratio (mol_liquid/ mol_flue_gas)	Thermal energy consumption (GJ/tCO_2)
1	MEA	20	1.86	2.27
2		30	1.13	2.37
3		40	0.8	2.49
4	DEA	20	2.86	2.37
5		30	2.46	2.12
6		40	1.6	1.78
7	MDEA	20	3.25	1.38
8		30	2.33	0.91
9	TEA	20	6.25	5.72
10		30	4.79	3.61
11		40	3.91	2.25
12	MEA + MDEA	20 – 10	1.18	3.23
13		20 – 20	0.85	2.88
14		20 – 30	0.65	2.65
15	MEA + TEA	20 – 10	1.16	3.22
16		20 – 20	0,93	2.99
17		20 – 30	0.77	3.42
18	DEA + MDEA	20 – 10	2.0	5.37
19		20 – 20	1.67	4.37
20		20 – 30	1.55	3.77

When sizing the CO_2 capture plants by chemical absorption it is preferable that the ratio L/G to be as low as possile because of the high degree of the amines corrosion and high thermal energy consumption necessary for the regeneration. In the case of 30 wt. %, MEA, the thermal energy consumption obtained was of 2.37 GJ/tCO_2 for a L/G ratio of 1.13 $mol_{MEA}/mol_{flue\ gases}$.

3.1. The influence of the L/G ratio on the CO_2 capture efficiency when using the monoethanolamine (MEA)

Fig. 2 shows the influence of the L/G ratio on the CO_2 capture efficiency and respectively on the rich loading solvent at the bottom of the absorption column. We can see that the higher the L/G ratio, the greater the CO_2 capture efficiency. Thus, when using the MEA with a weight concentration of 30% we obtained a capture efficiency of 90% for an L/G ratio of 1.2 $mol_{MEA}/mole_{flue\ gas}$. To obtain a higher CO_2 capture efficiency we increased the L/G ratio, but with increasing the L/G ratio there also increased the energy consumption for the solvent regeneration. However, given that the rich loading solvent decreases with increasing the L/G ratio, the consumption of energy showed a maximum [5].

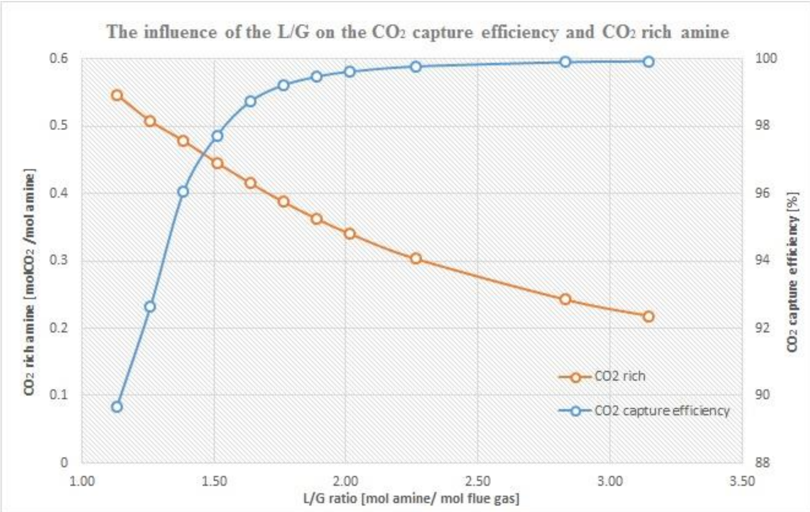

Fig. 2. The influence of the L/G ratio on the CO_2 capture efficiency and on the absorption capacity of the solvent using the MEA of 30%

3.2. The influence of the L/G ratio on the CO_2 capture efficiency when using the methanol (MeOH)

In Fig. 3 we present the results obtained when using the methanol (MeOH) physical solvent for capturing CO_2 from the flue gases. In the case of using the methanol, the simulations were carried out varying both the L/G ratio and the temperature of the solvent (the temperatures used were of 20°C, -20°C, -37°C, -50°C). When using the MeOH, we can see that the highest CO_2 capture efficiency (70%) was obtained for the solvent temperature of -20°C and respectively for an L/G ratio of 14.29 $mol_{MeOH}/mol_{flue\ gas}$. However, we do not recommend using a high flow rate of the physical solvent which even if it is not corrosive it requires a high energy pumping consumption.

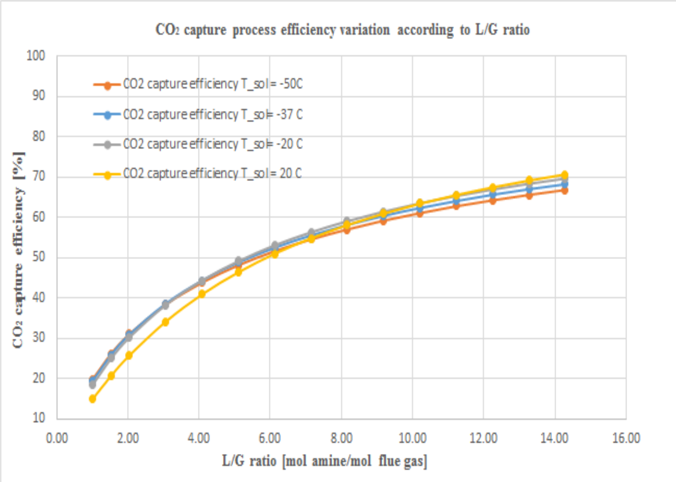

Fig. 3. The influence of the L/G ratio on the CO_2 capture efficiency using the MeOH for different temperatures

3.3. The influence of the L/G ratio on the CO_2 capture efficiency when using the Propylene - Carbonate (PC)

When using the PC (Propylene - Carbonate) solvent (Fig. 4), we observed that the CO_2 capture efficiency from the flue gases has increased with the L/G ratio. The amount of the CO_2 capture efficiency of 90% was obtained for the L/G ratio of 6 $mol_{PC}/mol_{flue\ gas}$, and for the temperature of the solvent of -50°C. From the simulations performed at different temperatures and different L/G ratios we observed that with decreasing the solvent temperature, the CO_2 capture efficiency increased. Moreover, the physical properties of the PC solvent indicate that its capture efficiency is better in the case of reducing the temperature from 0°C to - 60°C.

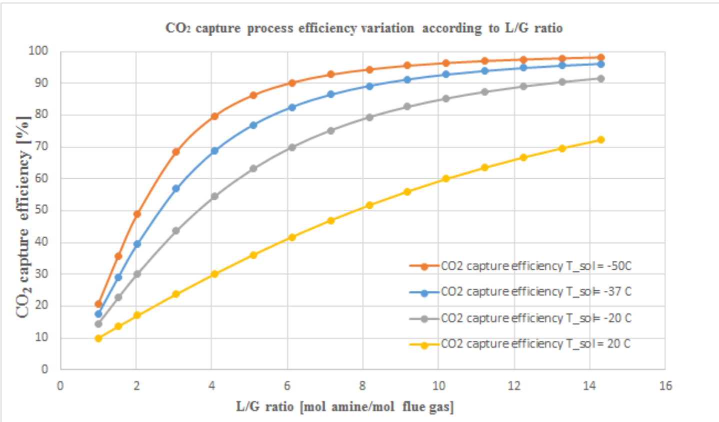

Fig. 4. The influence of the L/G ratio on the CO_2 capture efficiency using the PC

3.4. The influence of the L/G ratio on the CO_2 capture efficiency when using the N-Methyl-2-pyrrolidone (NMP)

In the case of using the NMP (N-Methyl-2-pyrrolidone) solvent for an L/G ratio of 4 $mol_{NMP}/mol_{flue\ gas}$ we had 90% efficiency at a solvent temperature of -50°C. As with using the PC solvents we observed that the lower the temperature is, the higher the capture efficiency is.

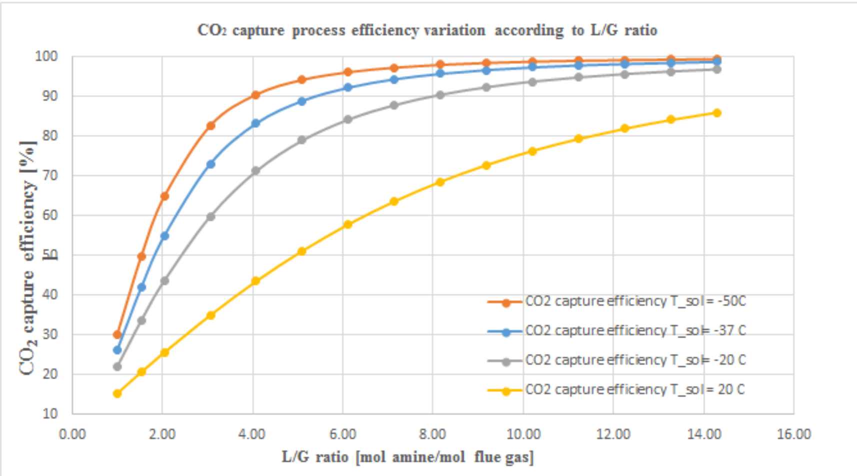

Fig. 5. The influence of the L/G ratio on the CO_2 capture efficiency using the NMP

The results of simulations using the physical solvents are summarized in Table 6. We considered that the CO_2 capture efficiency is of 90%; the only exception was noticed in the case of the MeOH solvent where the CO_2 capture maximum efficiency from the flue gases was of 70%.

Table 6

Comparative assessment of the physical – chemical solvents used according to the CO_2 capture efficiency

Nr. Crt.	Solvent	Concentration [%]	T_solvent [°C]	L/G ratio [mol solvent/mol flue gas]	CO_2 capture efficiency [%]
1.	MEA	30	50	1.2	90
2.	MeOH	100	20	61.22	90
3.		100	-20	91.84	90
4.		100	-37	122.45	90
5.		100	-50	163.27	90
6.	PC	100	20	28.57	90
7.		100	-20	13.27	90
8.		100	-37	8.16	90
9.		100	-50	6.12	90
10.	NMP	100	20	17.35	90
11.		100	-20	8.16	90
12.		100	-37	5.10	90
13.		100	-50	4	90

Fig. 6 presents a comparison between the chemical solvent (MEA 30%) and the physical solvents (MeOH, PC, NMP), in the case of a CO_2 capture efficiency of 90% (except for the MeOH where the maximum CO_2 capture efficiency was of 70 %) for different L/G ratios. If we maintain a CO_2 capture efficiency of 90%, the L/G ratio varied with the inlet temperature of the solvent in the absorption column. It is interesting the fact that in the case of the MeOH solvent, decreasing the L/G ratio was possible by raising the temperature at the entrance into the absorption column unlike the PC and NMP solvents in whose case the reduction of ratio L/G the was obtained by lowering the temperature.

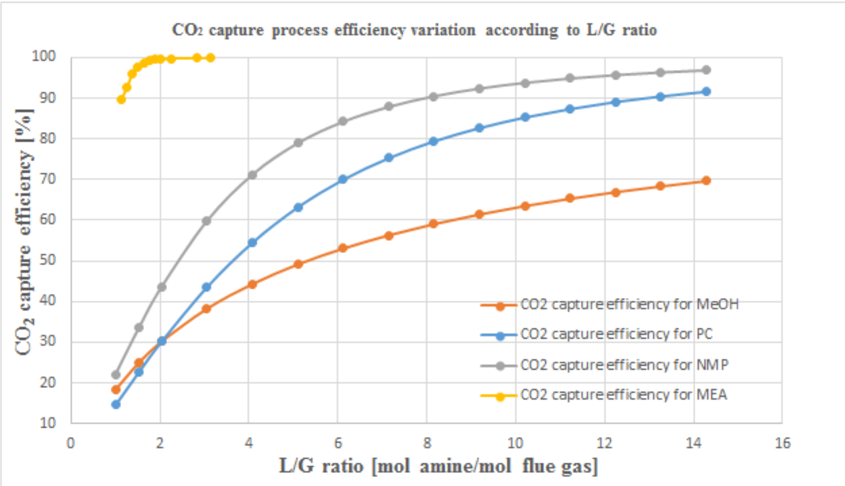

Fig. 6. Comparative analysis between chemical and physical solvents

4. Conclusions

The simulation of CO_2 post-combustion capture by chemical and physical absorption processes have been developed based in the simulation program ASPEN Plus.

Following the simulations carried out we observed that with decreasing temperature of the solvent, there increased the CO_2 absorption capacity of physical solvents. In the case of the MeOH solvent, the CO_2 capture efficiency of 70% was obtained for an L/G ratio of 14.29 $mol_{MeOH}/mol_{flue\ gas}$. For the NMP solvent, the capture efficiency of 90% was obtained for an L/G ratio of 4 $mol_{NMP}/mol_{flue\ gas}$. In the latter case analysed (the PC solvent) we saw that the CO_2 capture efficiency of 90% was obtained for an L/G ratio of 6 $mol_{PC}/mol_{flue\ gas}$.

From the point of view of the solvent amount used, considering the same CO_2 capture efficiency, it is preferred to use the NMP solvent for which the L/G ratio was 4 at the inlet temperature of - 50°C.

Acknowledgement

The study has been funded by the UEFISCDI within the National Project number 38/2012 with the title: "Technical-economic and environmental optimization of CCS technologies integration in power plants based on solid fossil fuel and renewable energy sources (biomass)" – CARBOTECH. The work has also been funded by the Sectorial Operational Program Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/134398 and of the national project P 95/2014.

R E F E R E N C E S

[1]. *http://www.iea.org/topics/climatechange/, accessed 07 December 2015*;
[2]. *A. Pascu, A. Badea, C. Dincă, and L. Stoica,* "Simulation of polymeric membrane in Aspen Plus for CO_2 post-combustion capture", in Engineering Optimization, Vol. IV, 2015, pp. 303-307;
[3]. *M. Norisor, A. Badea, and C. Dincă,* "Economical and technical analysis of CO_2 transort ways", in U.P.B Sci. Bull., Series C, Vol. 74, Iss. 1, 2012, pp. 127-138;
[4]. *A.M. Cormos, C. Dincă, and C.C. Cormos,* "Multi-fuel multi-product operation of IGCC powerplants with carbon capture and storage (CCS)", in Applied Thermal Engineering, Vol. 74, 2015, pp. 20-27;
[5]. *A. Badea, and C. Dincă,* "CO_2 capture from post-combustion gas by employing MEA absorption process - experimental investigations for pilot studies", in U.P.B Sci. Bull., Series D, Vol. 74, Iss. 1, 2012, pp. 21-32;
[6]. *C. Dincă, A. Badea, L. Stoica, and A. Pascu,* "Absorber design for the improvement of the efficiency of post-combustion CO_2 capture", in Journal of the Energy Institute, Vol. 88, 2015, pp. 304-313;
[7]. *R.W. Bucklin, and R.L. Schendel,* "Comparison of physical solvent used for gas processing", in Energy Progress, Octomber, 1948;
[8]. *R.W. Rousseau, J.N. Matange, and J.K. Ferrell,* "Solubilities of carbon dioxide, hydrogen sulfide, and nitrogen mixtures in methanol", in AIChE Journal, Vol. 27, No. 4, July, 1981, pp 605-613;
[9]. *S.H. Park, S.J. Lee, J.W. Lee, J.Wook. Lee, S.N. Chun, and J.B. Lee* , "The quantitative evaluation of two-stage pre-combustion CO_2 capture processes using the physical solvents with various design parameters", in Energy, Vol. 81, 2015, pp. 47 - 55;
[10]. *M. Sharifzadeh, and N. Shah,* "Comparative studies of CO_2 capture solvents for gas – fired power plants: Integrated modelling and pilot plant assessments", in International Journal of Greenhouse Gas Control, Vol. 43, 2015, pp. 124 - 132;
[11]. *Institute for Climate Economics* „Key figures on climate – France and worldwide" COP21 – CMP11, PARIS 2015, 2016 Edition;
[12]. *European Environmental Agency* „Greenhouse gase emission trends and projections in Europe 2011 – Tracking progress towards Kyoto and 2020 targets " EEA Report, No 4, 2011;
[13]. *S. Zhao, P.H.M. Feron, L. Deng, E. Favre, E. Chabanon, S. Yan, J. Hou, V. Chen, and H. Qi,* "Status and progress of membrane contactors in post – combustion carbon capture: Astate-of-the-art review of new development", in Journal of Membrane Science, Vol. 511, 2016, pp. 180 - 206;

[14]. *X. Wu, Y. Yu, Z. Qin, Z. Zhang,* “The advances of post – combustion CO_2 capture with chemical solvents: review and quidelines”, in Energy Procedia, Vol. 63, 2014, pp. 1339 - 1346;
[15]. *E. Ali, M.K. Hadj-Kali, S. Mulyono, and I. Alnashef,* “Analysis of operating conditions for CO_2 capturing process using deep eutectic solvents”, in International Journal of Greenhouse Gas Control, Vol. 47, 2016, pp 342 - 350;
[16]. *W. Guo, F. Feng, G. Song, J. Xion, L. Shen,* “Simulation and energy performance assessment of CO2 removal from crude synthetic natural gas via physical absorption process”, in Journal of Natural Gas Chemistry, Vol. 21, 2012, pp. 633 - 638;
[17]. *W. Guo, F. Feng, G. Song, J. Xiao and L. Shen,* “Simulation and energy performance assessment of CO_2 removal from crude synthetic natural gas via physical absorption process”, in Journal of Natural Gas Chemistry, Vol. 21, 2012, pp. 633-638;
[18]. *Y. J. Heintz, L. Sehabiague, B.I. Morsi, K. L. Jones, and H.W. Pennline,* “Novel physical solvents for selective CO2 capture from fuel gas streams at elevated pressures and temperatures”, in Energy Fuels, Vol. 22, 2008, pp. 3824 – 3837;
[19]. *C. A. Scholes, C. J. Andreson, G. W. Stevens, S. E. Kentish,* “Membrane gas separation – physical solvent absorption combined plant simulation for pre – combustion capture”, in Energy Procedia, Vol. 37, 2013, pp. 1039 - 1049;
[20]. *D. Berstad, R. Anantharaman, P. Neksa,* “Low – temperature CCs from an IGCC power plant and comparison with physical solvents”, in Energy Procedia, Vol. 37, 2013, pp. 2204 - 2211;