

Comparison of Different Amine Solvents for the Absorption of CO₂

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For the capture of CO₂ the most promising method is chemical absorption in aqueous amine solutions. The most common solvent recycled in the absorber-stripper system is aqueous monoethanolamine (MEA). However other amines such as diethanolamine (DEA) and methyldiethanolamine (MDEA) are also considered as potential suitable solvents. The reduction by 85 % of the CO₂ emission of a coal fired power plant is studied by simulation with a professional flow-sheet simulator. The simulation is done in two steps: first in open loop without recycling the lean solvent and wash water, then in closed loop. The influence of the most important operational parameters is studied. The optimal values where the desorption energy is minimal are determined for the temperature, flow rate and composition (CO₂ and amine content) of the cold lean solvent, for the stripper: top pressure, location of the feed stage(s). The heat duties of all heat exchangers are also compared for the three different solvents.

1. Introduction

From all the greenhouse effect gases, the atmospheric concentration of CO₂ shows the most significant increase. For the capture of CO₂ from flue gases several methods exist, such as water or amine scrubbing, or membrane separation. These methods are presented among others in the book of Stolten and Scherer (2011) and the review papers of Wang et al. (2011) and Leung et al. (2014). The most promising method is the chemical absorption in aqueous amine solutions. This process was studied by several authors. The most common solvent recycled in the absorber-stripper system is aqueous solution of monoethanolamine (MEA) studied experimentally among others by Mangalapally and Hasse (2011), Chavez and Guadarrama (2015), and Gao et al. (2016). In all the three articles the effect of operational parameters were studied and different structured packing types were compared: Sulzer BX500 and Sulzer Mellapak 250Y by Mangalapally and Hasse (2011), ININ 18, Sulzer BX500, and Mellapak 250Y by Chavez and Guadarrama (2015), and Sulzer BX500, Mellapak Y500, and Pall rings 16 x 16 by Gao et al. (2016). Though the absorption process is efficient but the energy demand of desorption is very high and this considerably decreases the efficiency of power plants. The other solvents must be also taken into consideration in order to decrease the energy demand of the process and to eliminate the other disadvantages of the MEA (e.g. danger of corrosion). From among the other potential solvents the aqueous solution of diethanolamine (DEA) and that of methyldiethanolamine (MDEA) were also frequently studied. Kothandaraman (2010) developed a consistent framework for the comparison of the performance of different solvents, which was tested for three materials. Rodriguez et al. (2011) modelled and optimized the post-combustion CO₂ capture. In this study MDEA, DEA and their mixture were applied. Erfani et al. (2015) analyzed three different thermodynamic models capable for the description of the amine scrubbing for six different amines and for their mixtures. Borhani et al. (2016) studied the rate-based model of a packed column for simultaneous absorption of CO₂ and H₂S into the aqueous solution of MDEA. The maximal concentration of MEA in the lean solvent is 30 mass%, whilst for the DEA (approx. 40 %) and MDEA (50 %) higher concentration is permitted. The criteria for selecting a solvent are described among others by Zarogiannis et al. (2015). The design and operational parameters of the columns are determined by the following parameters:

reaction rate with CO₂, absorption ability of CO₂ (the (theoretical) loading capacity for MDEA is 1, for DEA and MEA: 0.5 mol CO₂/mol amine, respectively), heat of reaction, thermal and chemical stability, environmental effect, corrosivity. The following physical parameters also must be taken into consideration, e.g. Lang et al. (2016): volatility (boiling points: MEA: 171 °C, DEA: 268 °C, MDEA: 247 °C), freezing point (MEA: 10 °C, DEA: 28 °C, MDEA: -21 °C), molecular weight (MEA: 61.1 g/mol, DEA: 105.1 g/mol, MDEA: 119.2 g/mol), liquid density (MEA: 993 kg/m³, DEA:1017, MDEA:1010), viscosity and surface tension.

The goals of this paper are as follows: to study the operation of the absorber-stripper system by simulation with the professional flow-sheet simulator ChemCad, to study the influence of the main operational parameters, to select the optimal values of these parameters providing the minimal heat duty of the reboiler of the stripper for each amine solvent, and to compare the heat duties of all heat exchangers for these parameter values.

For the vapour-liquid equilibrium and enthalpy calculations the "AMINE" model of the simulator was applied.

2. Simulation method

2.1 The process

Before entering the absorber, the flue gas must be purified (desulphurisation, denitrification, removal of fly ash), saturated with water (in order to decrease the loss of solvent), cooled down and slightly compressed (the pressure drop of the absorber has to be covered).

The removal of CO₂ from the flue gas is performed in an absorber-stripper system. The CO₂ is absorbed from the flue gas by the (cold) solvent lean in CO₂ in the absorber, operating at nearly atmospheric pressure. In the case of MEA, the gas leaving the column is washed with water in a washing section, in order to reduce solvent loss. For the DEA and MDEA there is no need for washing sections. With the water make-up mixed to either the wash water or the lean solvent (LS) the water loss of the system can be compensated. The (cold) solvent rich in CO₂ leaves the bottom of the absorber and after being preheated by the (warm) lean solvent in the cross (rich/lean) heat exchanger, enters the stripper, which is operated under pressure. The vapour generated in the reboiler strips the CO₂ out of the solvent. The (warm) lean solvent leaving the bottom of the stripper is cooled down by the (cold) rich solvent and then in an aftercooler, and it is recycled to the absorber. The stripped gas can be washed in a washing section, after which its water content is condensed in a partial condenser. The condensate can serve as the washing liquid and one part of it can be withdrawn, if necessary.

2.2 Simulation method

For the rigorous simulation of the system, the professional flow-sheet separator ChemCad 6.5.6 (2014) is used. The two columns are simulated with the module SCDS. For the vapour-liquid equilibrium and enthalpy calculations, the model AMINE is applied. Before simulating the columns, the authors made equilibrium calculations for the measurement data published for the system CO₂-MEA-water by Aronu et al. (2011) and for CO₂-MDEA-water by Park and Sandall (2001).

By applying MEA, DEA and MDEA as absorbent from the flue gas of a lignite fuelled subcritical power plant of 400 MW 85 % of CO₂ is removed and produced in a purity of 95 mol%. This specification permits to practically know the flow rates of all components (excepted water) in the two products (flue gas purified and CO₂) and in the solvent recovered, which is recycled. With dew point calculation, the temperature of the CO₂ product can be accurately estimated. The temperature of the purified gas where the material balance of water is satisfied and hence neither make-up nor withdrawal of water would be necessary can be also well estimated with dew point calculation.

After the simulation of the absorber the amount of water make-up or that of water to be withdrawn (from the condensate of the stripper) can be determined. With bubble point calculation, the temperature of the (warm) lean solvent can be calculated. By specifying the minimal temperature difference of the cross-heat exchanger (ΔT_{min}) the heat duty can be well estimated. ΔT is minimal on the cold side of the exchanger since the lean solvent is partially vaporised in the exchanger otherwise the maximal capacity of the exchanger is not exploited. The heat transferred in the cross-heat exchanger decreases the heat duty of the reboiler and the after-cooler. First the authors studied the operation of the absorber, cross-heat exchanger and stripper separately in open loop. Open loop means that recycling of the cold lean solvent and of wash water is cut off. The amine and CO₂ content of the lean solvent and the recovery of CO₂ can be specified. In the absorber, the flow rate of the lean solvent (F_{LS}) is varied by a (feed backward) controller which ensures absorption of 85 % of CO₂ arrived in the flue gas.

In the second stage closed-loop simulation is performed, that is, the controller manipulating the flow rate of lean solvent is omitted (or switched off), the cold lean solvent is recycled to the absorber, the washing water (cooled back) is also recycled to the top of the absorber, the solvent loss is compensated with a make-up if necessary (in our case there is no need for this).

The closed-loop ChemCad model suitable for simulating all the three cases is shown in Figure 1.

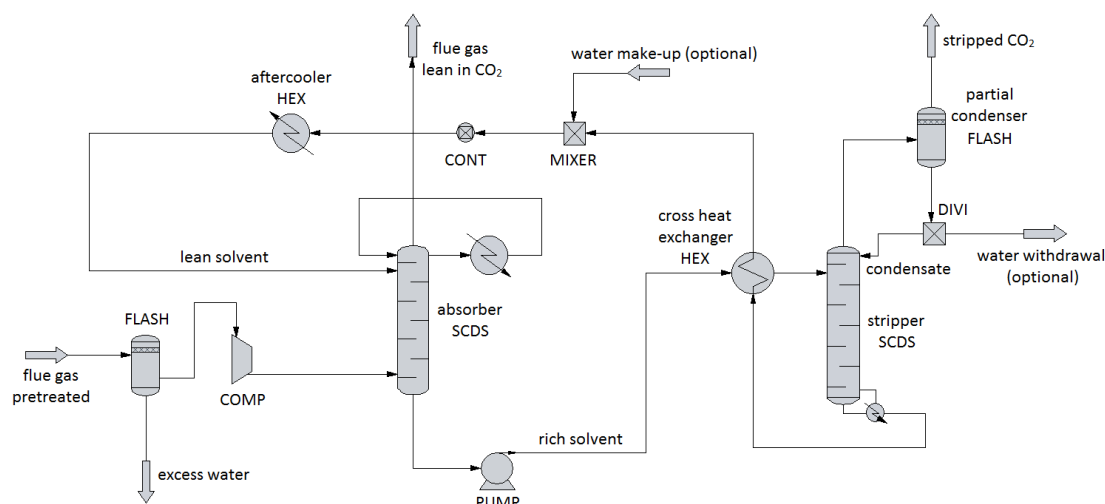


Figure 1: The general closed loop ChemCad model of the system.

3. Results

The simulation is begun with the cooling of the flue gas onto 40 (or 30) °C. The excess water is separated, and the flue gas leaving is saturated with water vapour. In the compressor, the pressure of the gas is increased onto the bottom pressure of the absorber, and its temperature also increases onto 47.9 (37.7) °C. The flow rate of the components in the gas entering the absorber (kmol/s): CO₂: 1.9927, water: 0.9471 (0.5271), amine: 0, nitrogen: 9.7119, oxygen: 0.2353, argon: 0.1149.

First the influence of the operational parameters is studied for the two columns in open loop.

3.1 Parametric study for the two columns

First for the absorber (Column I) the effects of the following parameters are studied: number of (theoretical) stages (N^I), temperature (T_F^I) and composition of the cold lean solvent (mass% of amine ($x_{A,LS}$) and molar ratio CO₂/amine (r_{LS})). The bottom pressure is 1.1 bar. For MEA the washing section is always the 1-st and the 2nd stage of the column, the flow rate of wash water is 70 kg/s, its inlet temperature is equal to that of the cold lean solvent and its total mass flow rate is withdrawn from stage 2. The basic values of the parameters and the most important results are shown in Tables 1 and 2a.

Table 1: Basic values of the parametric study for the absorber and for the stripper

Absorber		Stripper	
Parameter	Basic value	Parameter	Basic value
N^I	9	N^{II}	8
$T_{F,1}^I$, °C	30	f^{II}	3.0
$x_{A,LS}$, mass%	30	P^{II}_1 , bar	2.0
r_{LS} , mol/mol	0.2	-	-

The most important conclusions are as follows. The increase of CO₂ load in the absorber (Δr) had the expected value for the MEA and DEA whilst it remained much below it for the MDEA. The CO₂ load of the rich solvent (r_{RS}) leaving the absorber was slightly above 0.5 for MEA and DEA, whilst it remained much below the theoretical maximal value for MDEA. The increase of N^I caused only a slight decrease in the flow rate of lean solvent (F_{LS}) in all cases. The diminution of T_F^I had favourable effect for DEA and MEA whilst it had only very slight effect for MEA. On the increase of $x_{A,LS}$ F_{LS} considerably decreased as it was expected. As it was already mentioned the make-up/withdrawal of water depends on the top temperature (T_1^I). For MEA always make-up was needed, for DEA make-up or withdrawal depending on its value, whilst for MDEA in each case studied withdrawal was necessary. On the increase of the load of CO₂ in the lean solvent F_{LS} considerably increased because of the diminution of Δr . The performance of the absorber-stripper system can be improved by better exploiting the cross-heat exchanger (diminution of ΔT_{min}) therefore a low ΔT_{min} (5 °C) is chosen.

For the stripper, the following parameters are studied: number of plates (N^{II}), feed plate location (f^{II}), top pressure (P^{II}). The basic parameter values and the most important results are shown in Tables 1 and 2b.

On the increase of P^{II} the heat duty of the reboiler (Q_{II}^{N}) decreased mainly due to the better exploitation of the cross-heat exchanger. The further increase of N^{II} from the basic value had significant positive effect only for MEA. The feed plate can be located near to the top of the column.

Table 2a: Results of the parametric study for the absorber

Solvent	F_{LS}^{I} , kmol/s		Δr , mol/mol		T_1^{I} , °C		T_N^{I} , °C		$\Delta m_{\text{H}_2\text{O}}$, kg/s				
	basic		44.8466		0.3256		54.64		46.89		18.2		
M E A	Parameter	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.
	N^{I}	6	15	45.50	44.39	0.3210	0.3290	53.0	55.8	48.8	45.5	15.2	20.4
	T_{LS}^{I} , °C	20	50	44.37	45.35	0.3292	0.3219	46.6	65.5	45.6	47.9	5.9	47.5
	$x_{\text{A,LS}}$, mass%	20	30	69.82	44.85	0.3463	0.3256	47.1	54.6	47.1	46.9	6.6	18.2
	r_{LS} , mol/mol	0.0	0.3	28.31	64.36	0.5330	0.2231	59.7	47.2	44.1	47.7	29.5	6.6
D E A	basic		82.66		0.2936		41.8		46.1		0.8		
	Parameter	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.
	N^{I}	6	15	82.71	82.63	0.2934	0.2938	41.8	41.8	46.1	46.1	0.8	0.8
	T_{LS}^{I} , °C	20	50	73.92	110.02	0.3283	0.2206	34.0	56.9	40.6	56.1	-5.1	22.8
	$x_{\text{A,LS}}$, mass%	20	40	115.92	62.00	0.3515	0.2586	38.6	45.0	43.0	48.3	-1.9	4.0
	r_{LS} , mol/mol	0.0	0.3	51.46	112.79	0.4811	0.2130	52.4	36.9	48.1	42.9	14.1	-3.2
M D E A	basic		165.21		0.1655		30.8		39.4		-6.9		
	Parameter	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.
	N^{I}	6	15	170.37	164.48	0.1605	0.1663	30.8	30.9	39.1	39.5	-6.9	-6.9
	T_{LS}^{I} , °C	20	33	120.61	192.52	0.2268	0.1421	23.5	33.0	33.9	40.9	-10.0	-5.7
	$x_{\text{A,LS}}$, mass%	20	35	194.28	156.86	0.2369	0.1403	31.7	30.3	38.5	39.6	-6.4	-7.2
	r_{LS} , mol/mol	0.0	0.219	89.56	192.37	0.3108	0.1419	39.6	30.0	45.3	38.2	-1.1	-7.3

Table 2b: Results of the parametric study for the stripper

Solvent	Q_{N}^{II} , MW		R^{II}		T_1^{II} , °C		T_N^{II} , °C		Q_{CHX} , MW				
	basic		260.7		1.078		45.74		120.0		258.0		
M E A	Parameter	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.
	N^{II}	4	12	523.4	242.1	4.327	0.850	45.7		120.0		258.0	
	f^{II}	2	4	255.2	274.9	1.008	1.252	45.7		120.0		258.0	
	P_1^{II} , bar	1.8	2.2	273.4	251.9	1.235	0.969	43.7	47.6	117.1	122.7	246.9	268.3
D E A	basic		219.7		0.673		45.7		113.4		465.1		
	Parameter	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.
	N^{II}	4	12	237.7	219.9	0.894	0.676	45.7		113.4		465.1	
	f^{II}	2	4	223.8	219.1	0.723	0.666	45.7		113.4		465.1	
	P_1^{II} , bar	1.8	2.2	221.5	218.0	0.697	0.651	43.6	47.6	111.0	115.7	446.3	482.2
M D E A	basic		222.5		0.134		45.5		96.6		785.0		
	Parameter	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.
	N^{II}	4	12	222.8	222.6	0.137	0.135	45.5		96.6		785.0	
	f^{II}	2	4	223.5	222.2	0.146	0.131	45.5		96.6		785.0	
	P_1^{II} , bar	1.8	2.2	223.2	221.8	0.145	0.124	43.5	47.4	94.4	98.5	751.6	815.5

3.2 Simulation results for the whole system

On the basis of the results of the parametric study the values of the operational parameters are so chosen to minimise the heat demand of desorption (Q_{II}^{N}). The numbers of stages (N^{I} , N^{II}) are 15 for all solvents and for the two columns. For MEA the minimal value of TCLS (40 °C) is specified within the optimal temperature range (40-60 °C, Aronowilas et al. (2001)). For DEA and MDEA the minimal temperature (30 °C) is chosen where cooling of the lean solvent in the aftercooler is performed with normal cooling water. (The pre-treated flue gas is always cooled onto the temperature of the cold lean solvent. The energy demand of further cooling of flue gas from 40 to 30 °C is 22.66 MW.) The amine concentration in the lean solvent ($x_{\text{A,LS}}$) is the maximum permitted (MEA: 30 mass%, DEA: 40 %, MDEA: 50 %). The location of the feed plate is 3 for all solvents. For the top pressure of the stripper (P^{II}) the highest value studied is chosen (2.2 bar). The molar ratio CO_2/amine (r_{LS}) in the lean solvent is varied in order to find the minimum of the heat duty of the reboiler (Figure 2).

The optimal CO₂ load (r_{LS}) is the highest for DEA (0.28), the lowest for MDEA (0.13) and it has a medium value (0.20) for MEA. The results obtained for open loop provided good starting values for the simulation of the closed loop system and the calculations converged rapidly. The detailed results are shown in Table 3.

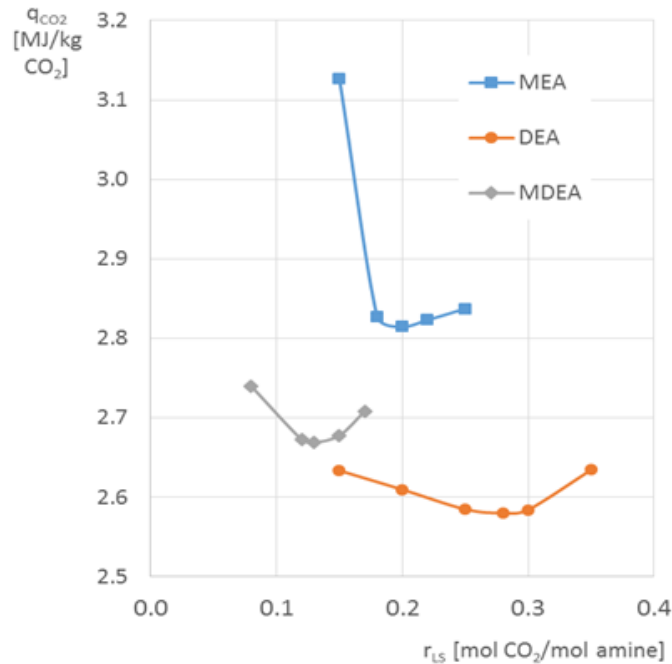


Figure 2: Specific heat demand of the desorption in the function of the CO₂ load of the lean solvent

Table 3: The most important results of simulation

	MEA	DEA	MDEA
r_{LS} , mol CO ₂ /mol amine	0.20	0.28	0.13
Q_N^I , MW	209.8	192.3	199.0
q_N^I , MJ/kg CO ₂	2.82	2.58	2.67
r_{RS} , mol CO ₂ /mol amine	0.529	0.484	0.271
F_{LS}^I , kmol/s	44.43	77.62	89.08
T_1^I , °C	62.4	39.6	33.3
T_N^I , °C	45.9	43.6	41.9
T_1^{II} , °C	47.6	47.6	47.5
T_N^{II} , °C	122.7	106.9	103.4
Q_1^{II} , MW	-73.6	-37.0	-33.2
Q_{CHX} , MW	273.8	442.1	554.3
Q_{AC} , MW	-41.1	-138.7	-162.1
Δm_{H_2O} , kg/s	37.1	6.46	2.04

The heat demand of desorption (Q_N^I) is the lowest for DEA. For MDEA it is close to that of DEA (+3.5 %) and for MEA it is higher by 9.1 % than for DEA. For MEA and DEA the CO₂ load of the rich solvent (r_{RS}) is close to the value expected whilst for MDEA it is much less than the theoretical maximum. The flow rate of the lean solvent (F_{LS}^I) is much lower for MEA than for the other two solvents. The top temperature of the absorber (T_1^I) is the highest for MEA, partially due to the higher temperature of the lean solvent fed. The difference in the bottom temperatures (T_N^I) is much smaller. The top temperatures of the stripper (T_1^{II}) are practically equal since the product CO₂ has the same composition for all solvents. The bottom temperature (T_N^{II}) is the highest for MEA and the lowest for MDEA. (The lower T_N^{II} , the lower the pressure of the heating steam. If in the reboiler $\Delta T = 10$ °C, for MEA steam of 3 bar whilst for MDEA only that of 1.6 bar is needed.)

The heat duty of the partial condenser (Q_1^{II}) is the lowest for MDEA and the highest for MEA. The heat duty of the cross-heat exchanger (Q_{CHX}) is much higher for MDEA and DEA than for MEA. The heat duty of the

aftercooler is the lowest for MEA and the highest for MDEA. The absorber-stripper system needs much greater water make-up for MEA than for the other solvents. After studying the molar flow rate profiles of CO₂ of the column the number of stages of the absorber could be reduced to 12 and that of the stripper to 6 for DEA and MDEA without significant change of the results. For MEA considerable reduction was not possible.

4. Conclusions

The post combustion capture of CO₂ from the pretreated flue gas of a lignite fuelled subcritical power plant of 400 MW by absorption in aqueous solution of different amines (MEA, DEA and MDEA) was studied by simulation with the ChemCad flow-sheet simulator. 85 % of CO₂ is removed and produced in a purity of 95 mol%. First the influence of the most important operational parameters of the absorber and stripper columns was studied in open loop (without recycling the lean solvent and wash water), then the whole system was simulated in closed loop. In the absorber, the decrease of temperature of the lean solvent had considerably favourable effect only for DEA and MDEA. For MEA the mass flow rate of solvent is less than half of that of the other two amines. The CO₂ load of the rich solvent was close to the theoretical maximum for MEA and DEA whilst it remained much below the maximum for MDEA. The (slight) increase of the pressure of the stripper made possible the reduction of the heat duty of its reboiler by better exploitation of the cross-heat exchanger. The lowest specific heat demands of desorption (MW/kg CO₂): MEA: 2.82, DEA: 2.58, MDEA: 2.67. However, the heat duty of the cross-heat exchanger and the total cooling energy demand are much lower for MEA than for the other solvents.

Acknowledgments

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References

- Aronu U.E., Hessen E.T., Haug-Warberg T., Hoff K.A., Svendsen H.F., 2011. Equilibrium in the H₂O-MEA-CO₂ system: new data and modeling, 1st Post Combustion Capture Conference, Abu Dhabi, Paper number: 40.
- Aroonwilas A., Tontiwachwuthikul P., Chakma A., 2001. Effects of operating and design parameters on CO₂ absorption in columns with structured packings, *Separation and Purification Technology*, 24, 403–411.
- Borhani T.N.G., Afkhamipour M., Azarpour A., Akbari V., Emadi, S.H., Manan, Z.A., 2016. Modeling study on CO₂ and H₂S simultaneous removal using MDEA solution, *Journal of Industrial and Engineering Chemistry*, 34, 344–355.
- Chavez R.H., Guadarrama J.J., 2015. Numerical Evaluation of CO₂ Capture on Post-combustion Processes, *Chemical Engineering Transactions*, 45, 271–276.
- ChemCad 6.5.6, 2014. Chemstations Inc., Houston, TX.
- Erfani A., Boroojerdi S., Dehghani A., 2015. Simulation of an operational amine based CO₂ capture at coal-fired power plants, *Petroleum & Coal*, 57(1), 85–92.
- Gao J., Yin J., Zhu F., Chen X., Tong M., Kang W., Zhou Y., Lu J., 2016. Experimental study of a hybrid solvent MEA-Methanol for post-combustion CO₂ absorption, *Separation and Purification Technology*, 163, 23–29.
- Kothandaraman A., 2010. Carbon Dioxide Capture by Chemical Absorption: A Solvent Comparison Study, Ph.D. Dissertation, Massachusetts Institute of Technology, Cambridge, MA, USA.
- Leung D.Y.C., Caramanna G., Maroto-Valer M.M., 2014. An overview of current status of carbon dioxide capture and storage technologies, *Renewable and Sustainable Energy Reviews*, 39, 426–443.
- Mangalapally H.P., Hasse H., 2011. Pilot plant study of post-combustion carbon dioxide capture by reactive absorption: Methodology, comparison of different structured packings, and comprehensive results for monoethanolamine, *Chemical Engineering Research and Design*, 89, 1216–1228.
- Park M.K., Sandall O.C., 2001. Solubility of Carbon Dioxide and Nitrous Oxide in 50 mass% Methyl-diethanolamine, *Journal of Chemical and Engineering Data*, 46, 166–168.
- Rodríguez N., Mussati S., Scenna N., 2011. Optimization of post-combustion CO₂ process using DEA–MDEA mixtures, *Chemical Engineering Research and Design*, 89, 1763–1773.
- Stolten D., Scherer V., 2011. *Efficient Carbon Capture for Coal Power Plants*, WILEY-VCH Verlag GMBh & Co KGaA, Weinheim, Germany, ISBN: 978-3-527-33002-7.
- Wang M., Lawal A., Stephenson P., Sidders J., Ramshaw C., 2011. Post-combustion CO₂ capture with chemical absorption: A state-of-the-art review, *Chemical Engineering Research & Design*, 89, 1609–1624.
- Zarogiannis T., Papadopoulos A.I., Seferlis P., 2015. Systematic Selection of Mixtures as Post-Combustion CO₂ Capture Solvent Candidates, *Chemical Engineering Transactions*, 45, 805–810.