Kinetic Study of Post-Combustion CO_2 Absorption by Methyldiethanolamine 30 wt.% and Hexylamine 10 wt.% as New Aqueous Solution

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The main drawback of conventional alkanolamines for post-combustion CO_2 capture is that they cannot combine a low energy consumption for regeneration and a high reactivity. Blends of tertiary and primary amines provide these two advantages at the same time. This study considers a new composition of solvent for carbon capture: methyldiethanolamine (MDEA) 30 wt.% and hexylamine (HA) 10 wt.%. MDEA acts as regeneration promoter and HA as activator. The kinetics of this solvent is assessed through an optimization method based on a genetic algorithm and at different temperatures (25 °C, 40 °C and 60 °C), in order to determine the Arrhenius law. The reaction considered is a first order reaction where each amine reacts with CO_2 in parallel. The composition studied does not give better results than MDEA alone. This is probably due to the addition of a too large amount of hexylamine.

1. Introduction

Carbon emissions Capture, Utilization and Storage (CCUS) is a highly studied technical solution to reduce CO_2 emisions. The first step, separation of CO_2 from flue gas, is the most crucial. Three technologies are in operation, still on a small scale: pre-combustion capture, oxy-combustion and post-combustion capture. In pre-combustion capture, the process is located before the combustion. The reaction of fossil fuel with air forms of CO_2 and H_2O, but the process is complex. In oxy-combustion, the recycled flue gas reacts with high purity O_2 to generate CO_2. However, the energy cost to separate O_2 from air is high. The post-combustion capture is the most mature and used process. It treats flue gas at the output of fossil fuel plants (Ochedi et al., 2020) and consists in a phase of absorption and one of regeneration. The absorption can be physical (the solvent separates the CO_2 from the flue gas thanks to thermodynamic properties, such as Henry's law, and the heating enables the regeneration), or chemical (an intermediate compound is formed from a chemical reaction between the CO_2 and the solvent). Chemical absorption has been the most developed method up to now (Tristano et al., 2018).

Among a great number of processes and solvents studied and used for carbon capture (Ochedi et al., 2020), amine-based absorption is the most common. Amines can be divided into three types. The primary amines such as monoethanolamine (MEA) and hexylamine (HA) are very reactive but have a low absorption capacity. The secondary amines, such as diethanolamine (DEA) and diphenylamine (DPA) are a little less reactive than primary amines. On the contrary, tertiary amines such as N-methyldiethanolamine (MDEA) and dimethylcyclohexylamine (DMCA) have a low reactivity and a high absorption rate. Tertiary amines do not form carbamates and need less energy for regeneration (Mehassouel et al., 2018). The main drawback of the benchmark solvent, monoethanolamine (MEA), is its high energy consumption for regeneration, at temperatures of around 120 - 150 °C. Hexylamine (HA) is an alternative to MEA thanks to its great ability to speed up the reaction and its high absorption rate, but the high cost of regeneration is still an issue.Using tertiary amines consumes less energy but the loading capacity is very low. The solution is to make a mixture of primary or secondary amines with tertiary amines. The first one can be classified as activator and the second one as regeneration promoter (Zhang et al., 2012). This approach is followed in this study, with emphasis on the reaction speed, thanks to the important proportion of hexylamine.

2. Amine selection

Various studies have been carried out on amine blends to determine the most promising solvent (Zhang et al., 2019). The main properties of an ideal solvent for carbon capture are: high CO_2 loading capacity, high absorption kinetics, high regeneration capacity, low volatility and no precipitation phenomenon. El Hadri (2017), characterize the thermodynamics and kinetics of 30 aqueous amine solutions. Ye et al. (2015) based their study on 50 amine-based aqueous solutions, blending activators and regeneration promoters. Mehassouel et al. (2018) experimentally studied the kinetics of aqueous solutions of MDEA and HA at different mass concentrations (MDEA 37 wt.% + HA 3 wt.%, MDEA 35 wt.% + HA 5 wt.% and MDEA 33 wt.% + HA 7 wt.%). MDEA is a benchmark regeneration promoter and HA is an activator, so would speed up the reaction. A mixture of these two amines matches the criteria of an ideal solvent. In their paper, Mehassouel et al. (2018) have only been able to assess the Arrhenius law of MDEA 37 wt.% + HA 3 wt.%, due to insufficient knowledge on the solvent thermo-physical properties. This present work aims to find a new way to evaluate the kinetics of this amine blend's reaction with CO_2, thanks to an optimization method which requires less assumptions on the solvent properties. The chosen solvent, a combine dual chemical with new composition, MDEA 30 wt.% and HA 10 wt.%, highlights also the balance between the speed of the reaction and the regeneration energy cost.

3. Experiment

3.1 Apparatus and procedure

The apparatus used to carrying out experiments is a Lewis Cell reactor type. It is an isothermal cell which allows monitoring the variations of the pressure inside. The apparatus is composed of a double layer of Pyrex glass in which the temperature regulator fluid flows. The maximum pressure allowed in the cell without damaging it, is 3 bar and a temperature of 150 °C. The internal diameter is 63.3 x 10^{-3} m. The effective volume of the cell is 369.5 x 10^{-6} m^2 (Toro Molina and Bouallou, 2014). A Rushton turbine with six blades of 42.5 x 10^{-3} m in diameter stirs the liquid phase, and a four blade impeller of 40 x 10^{-3} m stirs the gas phase. The gas-liquid interfacial area is stabilized by a horizontal ring and equal to 15.34 x 10^{-4} m^2 (Mehassouel et al., 2018).

The experiment begins only when the cell is at the desired temperature and has reached the equilibrium. Then the solvent is added and stirred. When it reaches the selected temperature, the CO_2 is injected via a sluice. The contact between the solvent and the gaseous phase triggers the absorption. Thanks to a pressure sensor DRUCK and a temperature sensor (with platinum probe), data consisting of the values of pressure and temperature inside the cell are collected over a period of time, each 2 s.

3.2 Assessment of thermo-physical properties

The solvent density is determined from the measurements of Mehassouel et al. (2018) during their study of the blends MDEA-HA of different compositions. For each temperature, a linear regression suggests the relation between the density and the weight percentage of MDEA. The results are compared with the correlation elaborated by Al Ghawas et al. (1989) considering the amine blend instead of MDEA alone. This comparison enables one to calculate the uncertainty on the value of density for each temperature.

The same method is used for viscosity: the measurements results of Mehassouel et al. (2018) are exploited. The correlation of Al Ghawas et al. (1989) for viscosity and the one of Rinker et al. (1994) (replacing DEA by HA) are used for comparison. The value experimentally measured by Mehassouel et al. (2018) for MDEA 33 wt.% and HA 7 wt.% is the most coherent value and the one used for this study. The uncertainty is then calculated from the difference between the value chosen and the existing correlations.

The diffusion coefficient is calculated thanks to the correlation of Al Ghawas et al. (1989) for MDEA concentrations under 50 wt.%.The influence of HA is considered negligible and the calculations are made as if MDEA has a weight percentage of 40 %. The lack of physical properties of an aqueous blend of MDEA and HA makes this approximation needed. The formulas are based on the results of diffusivity of N_2O in MDEA solutions, since the molecule is very similar to CO_2.

The liquid side mass transfer coefficient is calculated thanks to the correlation obtained by Amararene and Bouallou (2004) with the analogy of N_2O absorption by aqueous solution of MDEA. The correlation gives a relation between three dimensionless numbers Eq(1): Reynolds (Re), Schmidt (Sc) and Sherwood (Sh). The uncertainty on the liquid side mass transfer coefficient is then calculated.

$$Sh = 0.352 \times Re^{0.618} \times Sc^{0.434} \tag{1}$$

$$Re = \frac{\rho N d_{Ag}^2}{\mu}, \qquad 15 < Re < 5666 \tag{2}$$

$$Sc = \frac{\mu}{\mu D_{CO2}}, \qquad 46 < Sc < 2170 \tag{3}$$

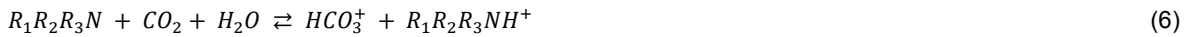$$Sh = \frac{k_L d_{cell}}{D_{CO2}}, \qquad 378 < Sh < 985 \tag{4}$$

All the values of thermo-physical properties mentioned are given in Table 1.

Table 1: Thermo-physics properties of MDEA 30 wt.% and HA 10 wt.%

T(K)	ρ (g×cm^{-3})	μ (mPa×s^{-1})	k_L (×10^{-5} m×s^{-1})
298	1.003 ± 0.033	5.044 ± 1.040	0.7001 ± 0.1672
313	0.9936 ± 0.0334	3.029 ± 0.482	1.122 ± 0.208
333	0.9802 ± 0.0332	1.757 ± 0.242	1.712 ± 0.276

Optimization procedure

The optimization procedure aims to find the optimal values of the kinetic constants in the reaction mechanism, as well as the values of the enhancement factor E and the Henry's constant H_{CO2}. The difficulty of this work is that the reaction mechanism between CO_2 and MDEA-HA has never been characterized before. A simple reaction mechanism is considered where each amine reacts with CO_2 in parallel according to the following reversible reactions, where R is C_6H_{13}, R_1 is CH_3 and R_2 and R_3 are C_2H_4OH:

$$2RNH + CO_2 \rightleftarrows RNHCOO^- + RNH_3^+ \tag{5}$$

$$R_1R_2R_3N + CO_2 + H_2O \rightleftarrows HCO_3^+ + R_1R_2R_3NH^+ \tag{6}$$

Four rates of reaction are associated with this reaction mechanism. The notation adopted afterwards is that the first subscript represents the number of the reaction and the second represents the sense: 1 is the direct verse and 2 the inverse verse. For instance $k_{1,2}$ means "the first reaction constant in the direct sense". The same notation is adopted for the speed R:

$$R_{1,1} = k_{1,1}[CO_2]_l[HA]_l \tag{7}$$

$$R_{1,2} = k_{1,2}[RNHCOO^-]_l[RNH_3^+]_l \tag{8}$$

$$R_{2,1} = k_{2,1}[CO_2]_l[MDEA]_l \tag{9}$$

$$R_{2,2} = k_{2,2}[HCO_3^+]_l[R_1R_2R_3NH^+]_l \tag{10}$$

Since water is present in great abundance in the system, the study is carried out on the eight remaining components. The material balance for each component gives the following system of differential equations:

$$\frac{d[CO_2]_g}{dt} = -k_L Ea(\frac{P_{CO2}}{H_{CO2}} - [CO_2]_l)\frac{V_l}{V_g^2} \tag{11}$$

$$\frac{d[CO_2]_l}{dt} = -k_L Ea(\frac{P_{CO2}}{H_{CO2}} - [CO_2]_l)\frac{1}{V_g} - R_{1,1} + R_{1,2} - R_{2,1} + R_{2,2} \tag{12}$$

$$\frac{d[HA]_l}{dt} = -2R_{1,2} - 2R_{1,1} \tag{13}$$

$$\frac{d[RNHCOO^-]_l}{dt} = R_{1,1} - R_{1,2} \tag{14}$$

$$\frac{d[RNH_3^+]_l}{dt} = R_{1,1} - R_{1,2} \tag{15}$$

$$\frac{d[MDEA]_l}{dt} = R_{2,2} - R_{2,1} \tag{16}$$

$$\frac{d[R_1R_2R_3NH^+]_l}{dt} = R_{2,1} - R_{2,2} \tag{17}$$

$$\frac{d[HCO_3^+]_l}{dt} = R_{2,1} - R_{2,2} \tag{18}$$

Where k_L is the mass transfer coefficient, E is the enhancement factor, V_l is the liquid volume, V_g the gas volume and a the interfacial area. The enhancement factor E assesses the influence of the kinetics of the reaction on the absorption, compared to a purely physic absorption. It is defined as follows, assuming that the concentration of CO_2 in the liquid phase is considered very small compared to the concentration at the interface $C_{CO2,int}$:

$$\Phi_{CO2} = E k_L C_{CO2,int} \tag{19}$$

For the CO_2 both the mass transfer and the chemical reaction are taken into account. The system of differential equations is resolved by *scipy* function *odeiny* in python. Then, the CO_2 pressure is calculated from the concentration:

$$P_{CO2,calc} = [CO_2]_g RT \tag{20}$$

The optimization method involves comparing the pressure calculated $P_{CO2,calc}$ to the experimental value measured in the Lewis cell P_{CO2}. The objective function is defined as the sum of the squared differences between measured and calculated pressures at each recorded time:

$$Objective\ function = \sum_{time} (P_{CO2,cal} - P_{CO2})^2 \tag{21}$$

The aim is to minimize this function. Various methods are available for this type of problem. The genetic algorithm (GA) is one of the heuristic methods, based on random but organised movement. It is one of the ARSMs (Adaptative Random Search Methods). The advantage is the ability to find a global minimum as there is no initial point. However, the computing time is longer than Nelder-Mead minimization. It was used for instance for the kinetics of CO_2 absorption into ammonia aqueous solutions (Toro Molina and Bouallou, 2014) or CO_2 absorption into aqueous blend of DPA and DMCA (Tristano et al., 2018). The GA simulates the natural selection in the evolution process of a population. The set of possible solutions is named population. Each member of the population has a specific genotype. In our case it is the four kinetic constants, the enhancement factor and the Henry's constant ($k_{1,1}$, $k_{1,2}$, $k_{2,1}$, $k_{2,2}$, E, H_{CO2}). The algorithm was implemented in python with the library geneticalgorithm. The population size is set at 300 individuals, the probability of crossover is 0.8 and when reproduction occurs, the probability of mutation is 0.7. The algorithm stops when the maximum number of iterations (500) is passed.

3.3 Results and discussions

The values of the kinetic constants, the enhancement factor and the Henry's constant obtained by the genetic algorithm are reported in Table 2. The error bars for the experimental pressure are set at 8 %, according to the accuracy of the Lewis Cell sensor. The mean absolute error is 4,600 Pa at 298 K, 2,080 Pa at 313 K and 5,150 Pa at 333 K. It is acceptable because under the range of precision of the sensor on average, except small errors at 333 K at the end of the absorption (Figure 2a). The optimization procedure is thus validated. Future work would be necessary to correct the divergence at 333K.

Table 2: Genetic algorithm results for the simple reaction mechanism

T(K)	$k_{1,1}$ (s^{-1})	$k_{1,2}$ (s^{-1})	$k_{2,1}$ (s^{-1})	$k_{2,2}$ (s^{-1})	E	H_{CO2} (Pa.m^3.mol^{-1})
298	0.208	0.310	0.0628	0.347	210	3,400
313	0.405	0.313	0.150	0.764	95.4	4,150
333	0.0724	0.994	0.477	0.802	13.8	6,086

From each kinetic constant calculated by the algorithm, the determination of the apparent kinetic constant k_{app} for CO_2 absorption into the solvent at each temperature is:

$$k_{app} = k_{1,1}[HA]_l + k_{2,1}[MDEA]_l[H_2O]_l \tag{22}$$

The application of Arrhenius law enables one to identify the activation energy (Ea = 47.9 kJ.mol^{-1}) and the pre-exponential factor:

$$k_{CO2,sol} = 1.25 \times 10^{15} \, exp(-\frac{5,758}{T})$$ (23)

$k_{CO2,sol}$ is the kinetic constant of the absorption of CO_2 into the solution of MDEA 30 wt.% and HA 10 wt.%. The high value of the regression's correlation coefficient confirms the validation of the optimization procedure.
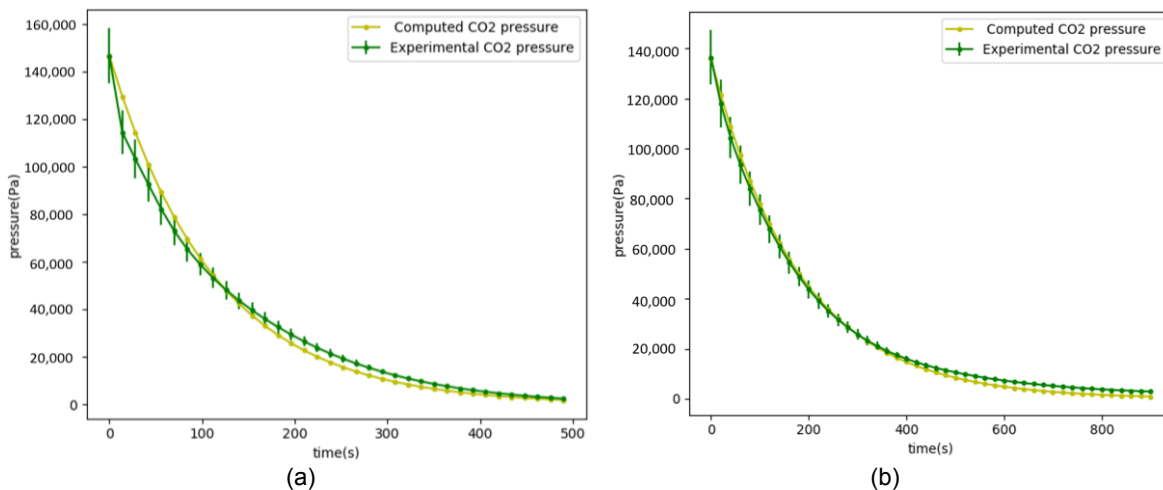

(a)   (b)

Figure 1: (a) Absorption of CO_2 into MDEA 30 wt.% + HA 10 wt.% at 25 °C; (b) Absorption of CO_2 into MDEA 30 wt.% + HA 10 wt.% at 40 °C.

(a)   (b)

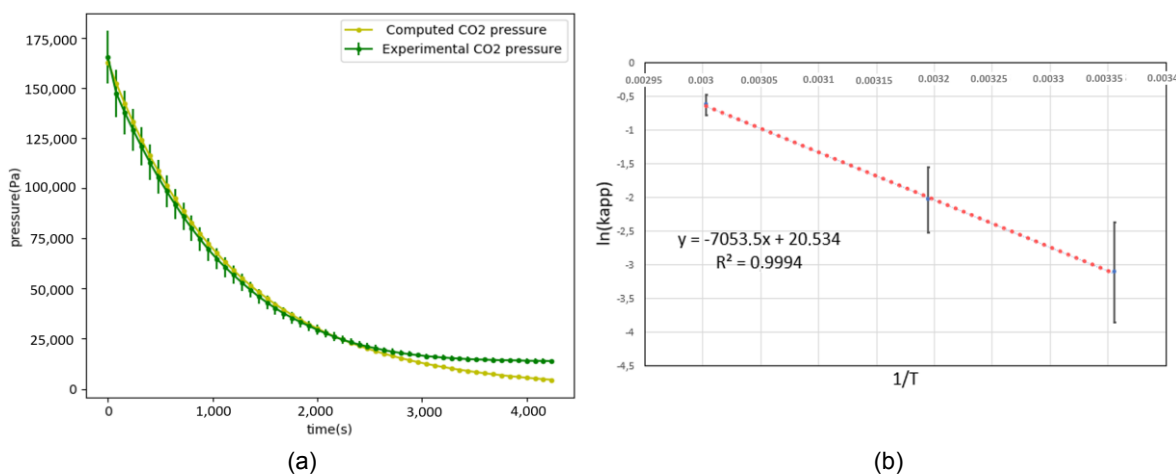Figure 2: (a) Absorption of CO_2 into MDEA 30 wt.% + HA 10 wt.% at 60 °C; (b) Arrhenius law for CO_2 into MDEA 30 wt.% + HA 10 wt.%

Some studies have assessed the Arrhenius law of the reaction between CO_2 and amine based solvents. The benchmark solvent (MEA 30 wt.%) has an activation energy of 44.9 kJ.mol^{-1} and MDEA 40 wt.% has one of 44.3 kJ.mol^{-1}. The value of the activation energy in this study is quite similar to those of the classic solvents which is satisfaying. It can be assumed that the energy demand for regeneration is around 4 GJ/tCO_2, like MEA 30 wt.%. The comparison with the work of Mehassouel et al. (2018) shows that adding a too large amount of hexylamine does not reduce the activation energy, so increases the energy demand for regeneration. Mehassouel suggests that the stability of the hexylamine carbamate is very low or that there is no formation of carbamate for the reaction of CO_2 with MDEA 37 wt.% + HA 3 wt.% (which has an energy cost of 2.9 GJ/tCO_2 for regeneration). This work confirms the hypothesis of Mehassouel: a too large amount of hexylamine does not

reduce the activation energy. However, the influence of hexylamine appears in the speed of absorption and confirms its benefits as activator. At 298 K, the absorption is made in 500 s whereas it takes three more time with only 3 wt.% HA. It must be noticed that the speed of absorption for the solvent studied in this work depends a lot on the temperature: at 333 K the absorption lasts 4,000 s and the best temperature for CO_2 absorption in MDEA 30 wt.% + HA 10 wt.% is 298 K because the reaction is exothermic.

4. Conclusion

The aim of this study was to investigate the kinetics of a new solvent composition for post-combustion carbon capture. The solvent is a blend of primary amine hexylamine as activator and tertiary amine methyldiethanolamine as regeneration promoter. The composition is MDEA 30 wt.% and HA 10 wt.%. The hypothesis of pseudo-order fast reaction is verified in this study. An optimization procedure is carried out to find the kinetic constants for each reaction in a mechanism with two reversible equations. Through this method, the energy activation is 47.9 $kJ.mol^{-1}$ (a little higher than MDEA 40 wt.%), but the presence of HA speeds up the reaction, especially at 298 K which makes the solvent particularly promising. Further work is necessary to assess the total energy cost of absorption with this solvent and to focus more precisely on the reaction mechanism. The use of infrared or NMR analysis can be an option. Finally, the composition suggested by Mehassouel et al. with MDEA 37 wt.% and HA 3 wt.% remains the best to reduce the regeneration energy cost. Adding a too large amount of hexylamine does not provide better results than MDEA alone.

Nomenclature

a – Interface Area (m^2)	k_L – Liquid side masse transfer coefficient (s^{-1})
d_{Ag} – Diameter of the Rushton turbine (m)	N – Stirring speed of the liquid phase (cps)
d_{cell} – Inner diameter of the cell (m)	P_{CO2} – CO_2 pressure (Pa)
D_{CO2} – Diffusivity of CO_2 in the solvent ($m^2.s^{-1}$)	$P_{CO2,calc}$ – CO_2 pressure calculated (Pa)
E – Enhancement Factor	R – Ideal gas constant (8.314 $J.mol^{-1}.K^{-1}$)
H_{CO2} – CO_2 Henry's constant ($Pa.m^3.mol^{-1}$)	T – Temperature (K)
k_{app} – Apparent kinetic constant (s^{-1})	ρ – Density of the solvent ($kg.m^{-3}$)
$k_{CO2,sol}$ – Kinetic constant of the reaction ($s^{-1}.mol^{-1}$)	μ – Dynamic viscosity (Pa.s)
$k_{CO2,sol}$ – Kinetic constant of the reaction ($s^{-1}.mol^{-1}$)	ϕ_{CO2} – CO_2 absorption flux ($mol.s^{-1}.m^{-2}$)

References

Al Ghawas H.A., Hagewiesche D.P., Ruiz-Ibanez G., Sandall O.C., 1989. Physicochemical properties important for carbon dioxide absorption in aqueous methyldiethanolamine. Journal of Chemical & Engineering Data, 34, 385–391.

Amararene F., Bouallou C., 2004. Kinetics of Carbonyl Sulfide (COS) Absorption with Aqueous Solutions Diethanolamine and Methyldiethanolamine. Industrial & Engineering Chemistry Research, 43, 6136-6141.

El Hadri N., 2017. Aqueous amine solution characterization for post-combustion CO_2 capture process. Applied Energy, 185, 1433-1449.

Mehassouel A., Derriche R., Bouallou C., 2018. Kinetics study and simulation of CO_2 absorption into mixed aqueous solutions of methyldiethanolamine and hexylamine. Oil & Gas Science and Technology – Revue d'IFP Energies Nouvelles, 73, 19.

Ochedi F.O., Yu J., Yu H., Liu Y., Hussain A., 2020. Carbon dioxide capture using liquid absorption methods: a review, Environmental Chemistry Letters, 19, 77-109.

Rinker E.B., Oelschlager D.W., Colussi A.T., Henry K.R., Sandall O.C., 1994. Viscosity, Density and surface tension of binary mixtures of water and MDEA and water and DEA and tertiary mixtures of these amines with water over the temperature range 20-100 °C. Jounal of Chemical & Engineering Data, 39, 392-395.

Toro Molina C., Bouallou C., 2014. Comparison of Post-combustion CO_2 Capture by Solutions of Ammonia and Organic Amines: Assessment Using Direct and Indirect Contactors. Energy Procedia, 63, 550-558.

Tristano D.P., Rivera-Tinoco R., Bouallou C., 2018. Experimental study of CO_2 chemical absorption kinetics by a thermomorphic lipophilic biphasic solvent. Chemical Engineering Transactions, 70, 55–60.

Ye Q., Wang X., Lu Y., 2015. Screening and evaluation of novel biphasic solvents for energy-efficient post-combustion CO_2 capture. International Journal of Greenhouse Gas Control, 39, 205–214.

Zhang J., Qiao Y., Agar D.W., 2012. Improvement of Lipophilic-Amine-based Thermomorphic Biphasic Solvent for Energy Efficient Carbon Capture. Energy Procedia, 23, 92–101.

Zhang S., Shen Y., Wang L., Chen J., Lu Y., 2019. Phase change solvents for post-combustion CO_2 capture: Principle, advances, and challenges. Applied Energy, 239, 876–897.