



# Investigating best available technique for CO<sub>2</sub> chemical absorption: solvent selection based on empirical surrogate model and exergy loss

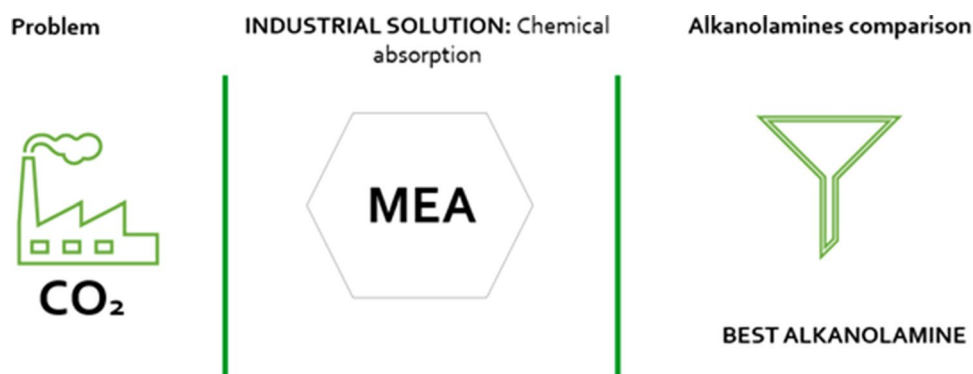
Alexandra Elena Plesu Popescu<sup>1</sup> · Àgata González<sup>1</sup> · Joan Llorens<sup>1</sup> · Jordi Bonet<sup>1</sup>

Received: 30 January 2021 / Accepted: 13 June 2021  
© The Author(s) 2021, corrected publication 2021

## Abstract

The carbon dioxide concentration in the atmosphere has reached extremely high levels, generating environmental concerns. Unfortunately, despite the climate change, CO<sub>2</sub> is not included nowadays as a key environmental issue in Best Available Technique (BAT) reference documents (BREF). Industrially, the widespread industrial technology to capture CO<sub>2</sub> is the chemical absorption using aqueous monoethanolamine (MEA) at 30%wt, which is the basis of comparison for novel alternative techniques in the literature and seems a suitable candidate to be proposed as Best Available Technique. Nevertheless, there is an intense research to find alternative solvents that decrease the energy consumption for carbon capture and many solvents are claimed in the literature to outperform MEA. A novel empirical surrogate model and exergy balances are used to confirm that MEA is still the best candidate to be proposed as Best Available Technique. The surrogate model proposed in this study properly regresses the CO<sub>2</sub> gas liquid equilibrium data. The regressed parameters of the model are tabulated in this study for many aqueous alkanolamines and their mixtures, being the basis for computationally inexpensive chemical absorption column design. The surrogate model parameter considering the temperature is related with the chemical absorption energy and the consumed energy for solvent recovery. The obtained results show that none of the considered alkanolamine outperforms MEA in all the considered aspects, i.e. energy and solvent flowrate. MEA minimum flowrate is 15.62 mol solvent/mol gas and its heat of absorption regression parameter is  $-27,745$  J/mol. The proposed mathematical method is useful as a fast assessment for other novel alternatives that will be proposed in the future, providing energetically more efficient and cleaner technologies for CO<sub>2</sub> capture.

## Graphic abstract



**Keywords** Minimum solvent flow rate · Energy parameter · Surrogate model · Aqueous alkanolamines · Post-combustion capture

✉ Alexandra Elena Plesu Popescu  
a\_plesu@ub.edu

Extended author information available on the last page of the article

## Abbreviations

MEA	Monoethanolamine
AMP	2-Amino-2-methyl-1-propanol
DEA	Diethanolamine

AEEA	2-(2-Aminoethylamine) etanol
DAP	1–3-Diaminopropane
DGA	Diglycolamine
DPTA	Dipropylenetriamine
DIPA	Diisopropanolamine
MDEA	Methyldietanolamine
TEA	Triethanolamine
PZ	Piperazine
1DMA2P	1-Dimethylamino-2-propanol
DA2MP	1,5-Diamino-2-methylpentane
DMCA	<i>N,N</i> -Dimethylcyclohexylamine
MCA	Methylcyclohexylamine
MAPA	3-(Methylamino)propylamine
DEEA	Diethylmonoethanolamine
DMEA	Dimethylmonoethanolamine
SIN	N1-cyclohexylpropane-1,3-diamine
$\alpha$	Relationship between the composition of CO <sub>2</sub> in a determined stream and total alkanolamine
$w$	Flow rate
Mw	Molar weight

## Introduction

### Techniques for CO<sub>2</sub> capture

At present, greenhouse effect is a big environmental problem. The CO<sub>2</sub> concentration in atmosphere has increased exponentially to global warming. This includes several forecasted changes such as sea level rise, physical and health impacts, changes in seasons. (European commission 2020). Currently, the concentration of CO<sub>2</sub> in the atmosphere is at its highest level according to available records in the past 800,000 years: before the industrial revolution, the CO<sub>2</sub> atmospheric concentration did not exceed 300 ppm, but at present exceeds 400 ppm (Ritchie and Roser 2020). Yadav et al (2020) claim that carbon should not be used as a source of fuel or energy but be valorised to other products. As currently a large proportion of the energy produced comes from combustion, some other authors propose the biofixation of CO<sub>2</sub> from the exhaust gases, e.g. Hashemi et al (2020), or electricity production by reactive gas electro-sorption (Alaba et al. 2020). Coal-fired power plants are the largest source of carbon dioxide (CO<sub>2</sub>) emissions into the atmosphere and net CO<sub>2</sub> emissions achieve negative values when carbon is captured from the biomass co-firing plants (Cebucean et al. 2020) and stored in safe geological sites (Aviso et al. 2019) or saline aquifers (Mahmoodpour et al. 2018). Carbon emission Pinch Analysis is a useful tool for planning the electricity generation mix (Salman et al. 2019). Besides of burning biomass to produce energy, negative values are also achievable by biomass pyrolysis to produce biochar as a stable form of carbon storable under the soil, improving

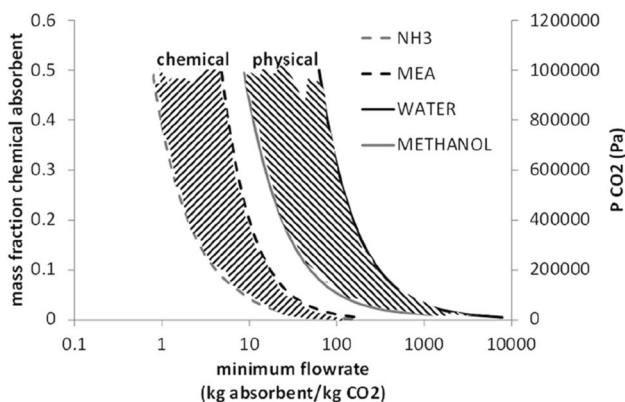
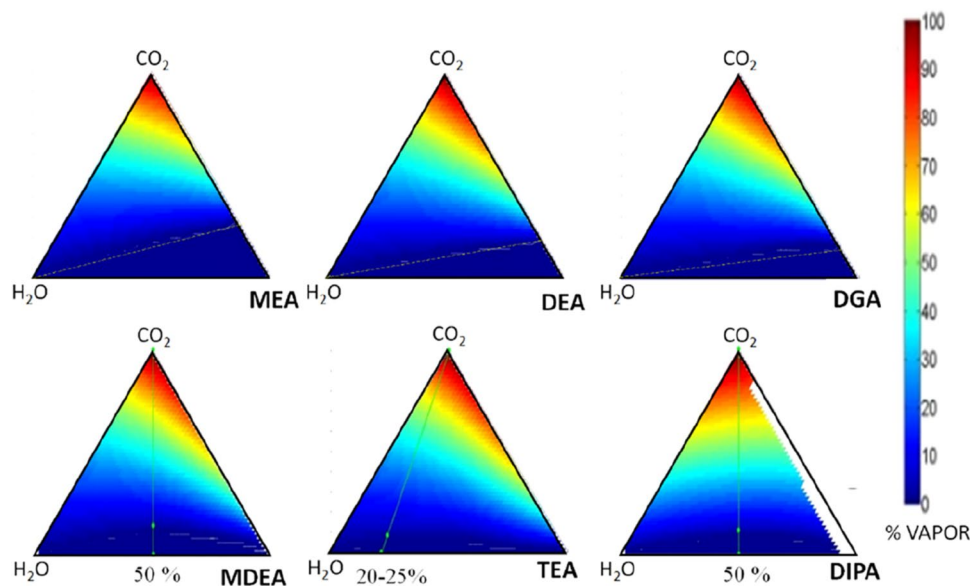
its characteristics (Ong et al. 2020) or by biomass torrefaction to produce artificial biochar mines (Thengane and Bandyopadhyay 2020). However, there is some scepticism about keeping valuable products buried underground. Under the Paris agreement of limiting the global average temperature rise to 2 degrees Celsius, special focus is paid to CO<sub>2</sub> capture techniques. It is expected that cost-effective carbon capture would contribute significantly to most CO<sub>2</sub> decrease scenarios according to the European Commission (2018).

There are several techniques to collect concentrated CO<sub>2</sub> from thermal plants: post-combustion, pre-combustion and oxy-combustion. Some techniques can be highlighted such as ultra-supercritical pulverised coal (USC PC) and natural gas combined cycle (NGCC) power plants with CO<sub>2</sub> capture. Focusing on post-combustion processes, there are various techniques like membrane separation (Brunetti et al. 2010), adsorption (Gautam 2020), calcium or chemical looping (Cormos 2020), precipitation (Moioli et al. 2019), cryogenic separation, absorption and combinations of those. Nevertheless, the most used technology to capture CO<sub>2</sub> at industrial level, which is the basis of comparison for any novel alternative technique, is the absorption: 90% of the carbon captured in large-carbon capture facilities in operation corresponds to absorption. Around the world, the main alternative for large-carbon capture facilities is the chemical absorption using aqueous alkanolamines, such as MDEA, PZ/MDEA for high partial pressure CO<sub>2</sub> meanwhile for low partial pressure of CO<sub>2</sub> MEA or proprietary aqueous amine solutions such as Cansolv, KS-1, etc. (Yamada 2021) are used. Mendez-Alvarez et al. (2016) pointed out that MEA and MDEA have a large operation window compared to other alkanolamines (Fig. 1).

Nevertheless, in USA the physical absorption is the most relevant technique, using propylene carbonate or proprietary solvents such as Selexol, Rectisol. (Yamada 2021). Physical absorption avoids the energy consumption related to the reaction enthalpy during solvent regeneration, but the required solvent flow rate becomes impractical for low CO<sub>2</sub> partial pressures such as for power plants' flue gas (Fig. 2). According to Burnard (2020a), two main barriers must be overcome to spread the use of carbon capture: the high capital expenditure and lack of revenue generation for the low commercial value of CO<sub>2</sub>. Policy incentives and regulatory actions must be put in place urgently to overcome these two barriers.

The implementation and improvement of any industrial process requires a reference process considered as the Best Available Technique and in fact the chemical absorption with aqueous MEA has been taking this role for low partial pressure CO<sub>2</sub> capture for the last half century. European Best Practice Guidelines for CO<sub>2</sub> Capture Technologies indicate that the 30% wt MEA solvent scrubbing post-combustion CO<sub>2</sub>-capture process used in a number of

**Fig. 1** Operation window for some alkanolamines, calculated with OLI® (Mendez-Alvarez et al. 2016)



**Fig. 2** Minimum solvent flow rate for chemical and physical CO<sub>2</sub> absorption at 20 °C (Sala et al. 2014)

industrial applications is considered the benchmark technology (CESAR 2018). However, despite climate change, CO<sub>2</sub> pollution is currently not included as a key environmental issue in the BREF documents (European Commission 2017).

The chemical absorption consists of capturing the gas by cycles of chemical absorption–desorption. Unfortunately, this process comes with a high recycling solvent flowrate and energy demand. Many reports point out that a MEA alkanolamine system to capture 90% CO<sub>2</sub> from a power plant flue gas can consume 30% of the power produced, which is translated into a CO<sub>2</sub> capture cost of 40–100 €/t CO<sub>2</sub> (Merkel et al. 2010). A more favourable scenario is obtained with an energy return of 85% when combined heat and power plants are retrofitted with post-combustion carbon capture (Morales-Mora et al. 2019) or the carbon capture unit also produces electricity (Li et al. 2018). An option to avoid the

solvent recovery costs is to use the collected ammonia as fertilizer, e.g. Bonet-Ruiz et al. (2015) or He et al. (2017). Despite the drawbacks and improvements proposed, chemical absorption with alkanolamines has the greatest potential to reduce emissions (Figuerola et al. 2008).

### Alternative aqueous alkanolamines to MEA

Alkanolamines are compounds that have both hydroxyl (-OH) and amino (-NH<sub>2</sub>) groups. The basicity of the amino group allows the chemical capture of CO<sub>2</sub> due to its acidic character. Alkanolamines are the most common chemical absorbers for CO<sub>2</sub> capture. MEA chemical absorption is the dominant technology to industrially capture CO<sub>2</sub> from power plants exhaust gases up to now, but novel amine absorbents are expected to provide more efficient processes. There is an intense research to find alternative solvents that decrease the energy consumption of aqueous MEA solvent recovery and being less prone to degradation, e.g. Alaba et al. (2017). Besides of alternative aqueous alkanolamines, there are many other alternatives assessed in the literature such as alkanolamines in non-aqueous solvents, ionic liquids, amine functionalized deep eutectic solvents, enhanced with solid catalysts. Salting out effect suggests that physical absorption is not the only mechanism through which CO<sub>2</sub> is absorbed after full theoretical amine loading (Wanderley et al. 2018). However, the enhanced processes compare their advantages versus the aqueous alkanolamines, which are the most mature for treating flue gas. As the literature available is very extensive, this study focuses only on the aqueous alkanolamines because these are the basis of comparison for any other solvent used, and other alternatives will be assessed in future work.

There are many experimental CO<sub>2</sub> equilibrium data available for aqueous alkanolamines (Table 1) and some of their mixtures (Table 2). These data are not only useful to know the load of CO<sub>2</sub> on the alkanolamine but also to estimate the enthalpy of absorption using the simplified Gibbs–Helmholtz equation (Mathias 2016). Substituting the CO<sub>2</sub> fugacity by its partial pressure and assuming a low CO<sub>2</sub> fraction in the gas phase, then the enthalpy of absorption is estimated based on the variation of the CO<sub>2</sub> partial pressure with the inverse of the temperature (Eq. 1). A desorption parameter related with the desorption column heat duty is particularly useful for the ranking of alternative alkanolamines (Zhang et al. 2020a, b).

$$\frac{d(\ln(P_{\text{CO}_2}))}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_{\text{abs}}}{R} \quad (1)$$

In the literature, there are many studies that claim certain aqueous alkanolamines are better than MEA. Besides the commercially available alkanolamines, the computer-aided molecular design is a powerful tool to propose novel solvents suitable for CO<sub>2</sub> capture (Papadopoulos et al. 2016). There is a large number of proposed solvents for CO<sub>2</sub> capture in the literature, for many of them there is some experimental gas liquid equilibrium or calorimetric data, for some of them there are pilot plant experiments but very few have been tested at larger capacity units and lengthier campaigns. Pilot plant and industrial operating data are not always published in the available literature although many studies are available.

Morgan et al. (2018) perform a study for a 10 t CO<sub>2</sub>/h pilot plant, and Feron et al. (2017) run a pilot plant for 1000 h, and both provide a review of previous studies about MEA pilot plants. In pilot plant experiments, Akram et al. (2020) determined that using 40% MEA, the reboiler duty drops by up to 14% compared to the commonly used 30% MEA concentration. Enhanced packings, e.g. (Flechsigg et al. 2018), and flexible operation of MEA columns, e.g. (Cormos et al. 2019), are also under study. In the literature, DEA (secondary amine) or MDEA (tertiary amine) are claimed to have a higher absorption capacity, higher resistance to corrosion and lower exergy lost than MEA (Chowdhury et al. 2013). The corrosion resistance and degradation to harmful compounds, e.g. nitrosamines (Mazari et al. 2019), are out of the scope of the present study.

Although most of the attention at pilot scale is devoted to MEA, there are also some promising pilot plant studies about DEA/PZ for CO<sub>2</sub> rich gases, e.g. Dubois et al. (2017) or Laribi et al. (2019), or about MEA/DEA at ratio 4:1, Idem et al. (2006). Śpiewak et al. (2015) claim the use of AMP/Pz based on process development unit runs; later on, pilot plant runs were performed with MEA solutions as a recognized

baseline solvent suitable for future comparative purposes (Stec et al. 2016) and nowadays the pilot plant study focuses on the methanation of the amine-absorbed CO<sub>2</sub> (Chwoła et al. 2020). Nwaoha et al. (2019) successfully substituted the toxic PZ by 1,5-diamino-2-methylpentane (DA2MP) in pilot plant experiments for the industrially used MDEA/PZ mixture.

Many other aqueous alkanolamines have been proposed based on laboratory experiments. For example, Barzagli et al (2019) determine experimentally, using pure CO<sub>2</sub>, that AMP and its mixtures reach higher loads than MEA and the enthalpy of absorption is smaller according to simplified Gibbs–Helmholtz equation. Many studies identify alkanolamines with a lower absorption enthalpy than MEA, e.g. for DEEA and DMEA are –47.0 and –48.6 kJ/mol, respectively (Xiao et al. 2016) and for 1DMA2P and MEA are –31.7 and –84.3 kJ/mol, respectively (Liu et al. 2017). It is also possible to combine several types of alkanolamines, the purpose of the combination being to take advantage of each compound, e.g. (Xiao et al. 2021). Gómez-Díaz et al. (2021) prove that DMEA/MEA mixture load does not depend on its ratio and DMEA has a faster reaction rate. Therefore, although the MEA is recognized as a proven suitable solvent for CO<sub>2</sub> capture at large scale, many promising alternatives are claimed in the literature.

Process optimization and modification based on rigorous simulations show that the energy consumption of a reference MEA chemical absorption of CO<sub>2</sub> can be decreased; both for MEA or aqueous alkanolamines mixtures are attained similar regeneration reductions between 5 and 40% (Hosseini-Ardali et al. 2020). There are many simulation results that point out some aqueous alkanolamine mixtures outperforming MEA, not only from the energy point of view but also due to their higher stability, e.g. MDEA/PZ. Among the aqueous alkanolamines, some of them present the advantage to produce a phase split of the rich solvent stream (Papadopoulos et al. 2019). The phase poor in CO<sub>2</sub> is recycled directly to the absorption column, decreasing the flow rate of rich CO<sub>2</sub> phase fed to the distillation column. Examples of solvents with phase change behaviour are N,N-dimethylcyclohexylamine (DMCA), methylcyclohexylamine (MCA) and 2-amino-2-methyl-1-propanol (AMP) (Tzirakis et al. 2019), or mixtures such as MAPA/DEEA (3-(methylamino)propylamine/2-(diethylamino)ethanol). The computer-aided molecular design allows the screening and proposal of novel solvents suitable for CO<sub>2</sub> absorption (Papadopoulos et al. 2020a). A novel very promising solvent proposed by computer-aided molecular design is the S1N (N1-cyclohexylpropane-1,3-diamine), for which laboratory experiments corroborate its suitability when mixed with other alkanolamines, e.g. DMCA, (Papadopoulos et al. 2020b). The phase split solvent is proved to be advisable from economic (Zarogiannis et al. 2020a), environmental

**Table 1** Operating conditions data for the prediction of CO<sub>2</sub> solubility in alkanolamine and alkanolamine mixtures

Alkanolamine	Temperature, K	CO <sub>2</sub> partial pressure, kPa	Amine concentration, %	CO <sub>2</sub> loading, $\alpha$	References
AMP	298–328	0.41–1,449	23.5–46.0	0.19–1.1	Dash et al. (2011)
	313–353	3.94–336.6	30	0.28–0.9	Seo and Hong (1996)
	313.2	1.25–144	28	0.4–0.9	Roberts and Mather (1988)
	313.2	0.89–151.9	28	0.4–0.9	Yang et al. (2010)
	313, 343	0.16–5,279	18.8	0.03–1.65	Teng and Mather (1990)
	313–393	6–983.5	30	0–0.97	Tong et al. (2012)
	303–328	0.31–1,472	40, 50	0.24–1.04	Dash et al. (2011)
	293–353	1.59–94	18.76, 28.14	0.13–0.94	Tontiwachwuthikul et al. (1991)
AEEA	303–323	1.11–794.67	15	0.060–1.407	Guo et al. (2013)
DEA	313–353	4.85–357.30	30	0.40–0.73	Seo and Hong (1996)
	298–348	4.85–357.30	47.78	0.0–1.09	Sidi-Boumedine et al. (2004)
	323–366	0.40–3,798.00	25	0.10–1.13	Barreau et al. (2006)
	323	7.00–3,370.00	19.2	0.45–1.13	Jong et al. (1972)
	338.5–366.9	32.00–767.00	25	0.40–0.79	Lawson and Garst (1976)
DGA	323–373	1.58–4,720	60	0.13–0.62	Martin et al. (1978)
DIPA	313–343	107–4,064	45	0.52–1.05	Haghtalab et al. (2014)
	313–343	91.20–3,826.6	30	0.89–1.14	Haghtalab and Talavaki (2017)
	313–373	2.7–5,888	33.63	0.07–1.11	Isaacs et al. (1977)
MDEA	298–373	0.78–140.40	50	0.01–0.49	Park and Sandall (2001)
	298–348	2.70–4,559.50	48.88, 25.73	0.0–1.30	Sidi-Boumedine et al. (2004)
	297.7	0.02–1.64	23.63	0.02–0.26	Lemoine et al. (2000)
	313	0.18–92.80	22.9	0.04–0.84	Austgen et al. (1991)
	313	0.28–89.90	22.9	0.06–0.80	Chung et al. (2010)
	323	6.00–434.00	50	0.10–0.89	Dicko et al. (2010)
	298–373	73.97–747.78	35.00, 50.00	0.03–0.32	Pacheco et al. (2000)
MEA	303–323	0.90–335.90	6.70–19.00	0.35–1.16	Kumar and Kundu (2012)
	303–353	0–50.65	12.00–15.00	0.017–0.577	Tzirakis et al. (2019)
PZ	313–343	0.03–40.00	4.7	0.16–0.96	Bishnoi and Rochelle (2000)
	313	451–3948	14.7	0.32–0.72	Haghtalab et al. (2014)
	354–464.8	28–2,583	29.80–40.59	0.23–0.45	Xu and Rochelle (2011)
	313–343	29–40,200	4.7	0.16–0.96	Bishnoi and Rochelle (2000)
	313	5,800–7,500	15–60	0.34–0.86	Nguyen et al. (2010)
TEA	313–353	1.43–153.40	26.5	0.03–0.53	Chung et al. (2010)
AMMONIA	335–395	0.01–1,000	20.4	1	Lu et al. (2017)
AMP + PZ	293.15–323.15	0.127–140.4	AMP: 8.9–38/PZ: 0.87–8	0.1511–0.9405	Jahangiri and Hassankiadeh (2019) Dash et al. (2011)
DEA + AMP	313.15–373.15	22–2,838	DEA: 20–25/AMP: 5–10	0.3370–1.2	Murrieta-Guevara et al (1998)
DEA + MDEA	313.15–393.15	0.4–2,833.6	DEA: 10–32.5/MDEA: 10–35	0.038–1.119	Murrieta-Guevara et al. (1998)
DIPA + AEEA	313.15–343.15	105–3,819.7	DIPA: 20.25/AEEA: 5–10	0.5837–1.251	Haghtalab and Talavaki (2017)
MDEA + MEA	313.15–373.15	1.12–2,080	MDEA: 12–24/MEA: 6–18	0.1880–1.015	Li and Shan (1992)
MDEA + PZ	313–375.15	0.033–95.78	MDEA: 22.6–47.6/PZ: 0.4–21.3	0.027–0.37	Ghalib et al. (2017) Chen et al. (2011)
			Bishnoi and Rochelle (2002)		
MEA + DAP	315.15–333.15	13.24–215.46	MEA: 10–12.5/DAP: 2.5–5	0.220–0.711	Khodadadi et al. (2019)
DIPA + AMP + PZ	313.15–343.15	112.9–3,709.7	DIPA: 24–36/AMP: 7–13/ PZ: 2–8	0.5020–1.091	Haghtalab and Talavaki (2017)

**Table 2** Alkanolamines and ammonia concentration

Substance	Concentration (%)
MEA	30
AMP	30
DGA	60
AEEA	30
DEA	30
DIPA	33
DPTA	30
MDEA	35
TEA	18
PZ	30
NH <sub>3</sub>	20.4

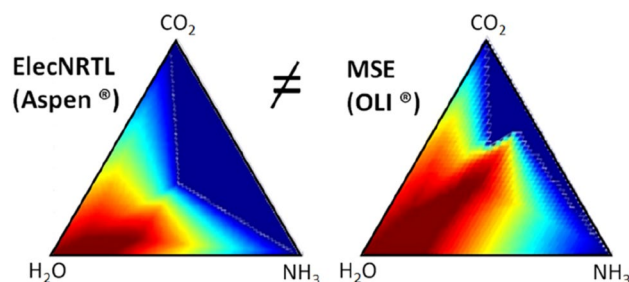
(Shavaliyeva et al. 2021) and operational (resilient to disturbances) (Zarogiannis et al. 2020b) points of view.

This study proposes a fast method that, based solely on experimental data of vapour–liquid equilibrium of CO<sub>2</sub> gas, compares alternatives with MEA in terms of required flow-rate and energy consumption. This method has been applied to several alkanolamines whose experimental gas liquid equilibrium data are available in the literature (DEA, TEA, DIPA, MDEA, DGA, AEEA, PZ, AMP, NH<sub>3</sub>) and some of their mixtures (Table 1). Table 1 compiles the operating conditions of temperature, CO<sub>2</sub> partial pressure, amine concentration and CO<sub>2</sub> load in which each experimental study has been performed. Some aqueous alkanolamines have been extensively studied in the literature by many authors and for some others there is only a single study. The aqueous alkanolamines for which there are not enough experimental points according to the number of model parameters to be properly regressed have not been considered. Although an exhaustive literature review retrieving a vast number of experimental data points has been performed in this study, some interesting alkanolamines may have been missed. However, the proposed method is fast and simple enough to be applied to them in further studies.

## Method

### Standard model equations for alkanolamines gas liquid equilibrium

Assessment of alkanolamine absorbents capture performance is crucial to decrease the carbon footprint of many processes. There are several activity coefficients models useful for electrolyte mixtures such as Pitzer or ElectNRTL



**Fig. 3** Ammonia operation window according to ElecNRTL and MSE models: no solids or vapours are generated when the absorption is on the dark red region of concentrations

that are implemented in commercial simulation software, e.g. Aspen Plus®. Aspen Plus® allows also to use the MSE or Aqueous models based on Debye–Hückel model from the software specific for electrolytes OLI®. MSE model implemented in OLI® allows very accurate calculations for electrolyte systems but is not easy to generate a novel alkanolamine at user level. The activity models such as ElectNRTL require to determine many tens of unknown parameters before modelling. Figure 3 shows that the absorption operation window without solids or vapours using the parameters readily implemented in ElectNRTL of Aspen Plus® appreciably differs from the operation window calculated using MSE of OLI® (Mendez-Alvarez et al. 2016). The activity coefficients complex models are not suitable when limited experimental data are available, then the regressed parameters have little physical relevance, then this drawback is overcome using simplified shortcut methods including the simplified Gibbs–Helmholtz equation (Jiang et al. 2018). OLI® software is used in the present study to solve the exergy balances.

The present study proposes a simple and effective surrogated model that with a small number of parameters and based solely on few CO<sub>2</sub> gas liquid equilibrium experimental data are able to estimate an energy parameter and minimum solvent flow rate required for each solvent. The proposed method is intended to simplify the assessment of CO<sub>2</sub> capture performance, but the regressed CO<sub>2</sub> vapour liquid equilibrium model also is useful for the absorption column design.

### Surrogate model equations for gas liquid equilibrium

Plesu et al. (2018) proposed an equation able to accurately represent the CO<sub>2</sub> gas-liquid equilibrium on aqueous MEA available in the literature, in the CO<sub>2</sub> load range between 0.2 and 0.4 (Eq. 2). The equation neglects the alkanolamine mass

percentage and a value close to the calorimetric determined enthalpy of absorption for MEA for the temperature dependent term is obtained, i.e.  $-88$  kJ/mol vs  $-84$  kJ/mol. The equation has a poor regression of the experimental data at high temperatures and loads, i.e. when the CO<sub>2</sub> partial pressure is higher and deviates from ideality.

$$\ln P_{\text{CO}_2} = 32.95 + 14.96 (\alpha) - 88.081 \left( \frac{1}{RT} \right) \quad (2)$$

This empirical correlation that relates the molar composition and the temperature with the CO<sub>2</sub> partial pressure is computationally inexpensive due to its simplicity, but the main drawback is its low dimensionality which translates into its limited validity range (Carranza-Abaid et al. 2020). In this study, the dimensionality and validity range of the equation is extended. The extension of the previous equation to further alkanolamines including mixtures implies the addition of two parameters to the previous equation, which depend on the alkanolamine mass percentage (Eq. 3). A broad range of CO<sub>2</sub> gas liquid equilibrium data is regressed. The model assumes that the dependence of the CO<sub>2</sub> partial pressure on the inverse of the temperature does not depend on the composition. This rough approach is applied for sake of simplicity. The absorption energy term of the equation loses its physical meaning and does not correspond to the experimental calorimetric absorption energy. Nevertheless, it is expected to be an averaged value of the enthalpy of absorption providing an insight of the energy consumption for the rich solvent recovery.

$$\text{LN } P_{\text{CO}_2} = \text{Intersection} + X_1 \cdot (\alpha) + \Delta H_{\text{abs}} \cdot \left( \frac{1}{RT} \right) + S1 + S2 \quad (3)$$

$$S1 = \sum_{n=0}^{\text{no alk}} X_n \cdot (\% \text{wt Alkanolamine}) \quad (4)$$

$$S2 = \sum_{m=0}^{\text{no alk}} X_m \cdot (\% \text{wt Alkanolamine} \cdot (\alpha)) \quad (5)$$

In this proposed model equation, the partial pressure of CO<sub>2</sub> ( $P_{\text{CO}_2}$ ) is expressed in Pa, the heat absorption in J/mol ( $\Delta H_{\text{abs}}$ ), the gas constant ( $R$ ) is  $8.314 \text{ m}^3 \cdot \text{Pa}/(\text{K} \cdot \text{mol})$ , temperature ( $T$ ) is measured in Kelvin,  $X_i$  are the regressed parameters of the surrogate model, %wt Alkanolamine is the amine mass percentage and “ $\alpha$ ” is the CO<sub>2</sub> load (expressed as the ratio of mols CO<sub>2</sub> absorbed divided by mols alkanolamines necessary for the absorption). The equation is not only providing insights on the energy consumption according to the  $\Delta H_{\text{abs}}$  term but also on the solvent required according to the load term (Eq. 6).

$$\frac{d(\ln P_{\text{CO}_2})}{d\alpha} = X1 + \sum (X_m \cdot \% \text{wt Alkanolamine}) \quad (6)$$

## Mass and exergy balances

CO<sub>2</sub> absorption process scheme is composed mainly of two main sections: the CO<sub>2</sub> absorption and the solvent recovery (Fig. 4). The main unit of the process is the absorption column where the spontaneous absorption of CO<sub>2</sub> towards the equilibrium takes place. Therefore, in this section there is no appreciable energy consumption and usually operates at a rather low temperature around 40 °C to promote the CO<sub>2</sub> absorption. The energy is mainly consumed in the solvent recovery section. The solvent recovery is not spontaneous, and the main energy of the process is consumed at a distillation column reboiler to reverse the CO<sub>2</sub> absorption. The flowsheet is completed with other unit operations such as heat exchangers for heat recovery and a decanter in case of phase split. Nevertheless, for sake of simplicity, the present study focuses only on the minimum flow rate of solvent to the absorption column.

The main streams considered in the mass balances are pointed up in accordance with Fig. 4. The carbon is captured from the exhaust gases (stream 1) collecting a treated gas stream (stream 2) at the top of the absorption column. An aqueous stream containing the alkanolamine is fed at the top of the absorption column, generating a stream of solvent enriched in CO<sub>2</sub> (stream 5). The CO<sub>2</sub>-rich solvent is fed to a distillation column whose purpose is to separate pure CO<sub>2</sub> collected by the distillate (stream 6) and the CO<sub>2</sub> lean solvent stream (stream 4) collected at the bottoms and recycled to the absorption column. The input exhaust gas stream generated from the combustion with an air excess is composed in volume by 79% N<sub>2</sub>,  $x$  % CO<sub>2</sub> and (21- $x$ ) % O<sub>2</sub>, where in this study a  $x = 10\%$  vol CO<sub>2</sub> is assumed.

The minimum solvent flow rate is calculated according to the method proposed by Sala et al (2014) assuming

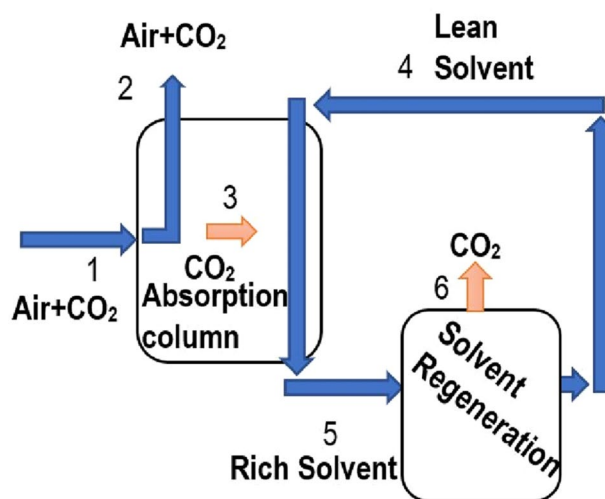


Fig. 4 Typical basic process flowsheet for CO<sub>2</sub> absorption

an infinite number of stages. Assuming infinite number of equilibrium stages for the absorption column, at absorption column top, CO<sub>2</sub> concentration in the treated exhaust gases output (stream 3) is in equilibrium with the CO<sub>2</sub> concentration present in the lean solvent output stream from the distillation column (stream 4). On the other hand, at absorption column bottoms, the feed exhaust gas to the absorption column is in equilibrium with the concentration of CO<sub>2</sub> present in CO<sub>2</sub> rich solvent. Contrary to Sala et al (2014) where the equilibrium was retrieved from a model, in this study, both CO<sub>2</sub> equilibrium information is retrieved from literature experimental equilibrium data. N<sub>2</sub> and O<sub>2</sub> are not absorbed, and therefore, their flow rates at the input (stream 1) and output (stream 2) gas streams are the same.

For a given concentration of solvent in water, all flow rates and compositions of the streams are calculated according to the mass balances described in more detail in the following section. The entropy and enthalpy of these streams required to calculate the exergy balances are determined with OLI® software.

## Mass balances

The mass balances are solved assuming a calculation basis of 100 mol/s for the exhaust gas feed to the system with a 5 to 25% in volume CO<sub>2</sub> and a recovery of 70% of CO<sub>2</sub>. Most of the studies use a recovery of 90%, but this is an artificial cap (Burnard 2020b). The process is operated at 1 atm, and all the streams are at this pressure.

According to the Dalton Law, the partial pressure of CO<sub>2</sub> at the exhaust gas is calculated. The CO<sub>2</sub> load (relationship between the composition of CO<sub>2</sub> in a determined stream and total alkanolamine—Eq. 7) in the liquid stream (stream 5) in equilibrium with the input exhaust gas is retrieved from experimental equilibrium data.

$$\alpha_5 = \frac{w_5^{\text{CO}_2}}{w_T^{\text{ALK}}} = X1 \quad (7)$$

A similar procedure is applied to the top of the absorption column. Establishing a CO<sub>2</sub> recovery of 70%, the amount of CO<sub>2</sub> that leaves the system can be assessed. The air is not absorbed. According to the Dalton Law, the CO<sub>2</sub> partial pressure at the gas phase at the top of the column is also calculated. According to the experimental data of CO<sub>2</sub> equilibrium, the load in the liquid phase at the top of the column is determined (Eq. 8).

$$\alpha_4 = \frac{w_4^{\text{CO}_2}}{w_T^{\text{ALK}}} = X2 \quad (8)$$

The alkanolamine flow rate in the lean and rich solvent streams is the same and therefore with the previous CO<sub>2</sub> load

expressions and the CO<sub>2</sub> mass balance, the molar minimum flowrate of alkanolamine is calculated (Eq. 9). Notice that the minimum alkanolamine flowrate depends on the difference of load values between the top and bottom of the adsorption column. The mass percentage of alkanolamine in the aqueous solution provides the water flow rate (Eq. 10). The available experimental data with a mass fraction of solvent closer to 30% have been chosen (Table 2), nevertheless for DGA the available experimental data are at 60% and for TEA is at 18%. The absorption column exergy balance is performed for all the compounds at 40 °C except for the di-isopropanolamine (DIPA) whose experimental data are only available at 50 °C. The mass balance is solved directly on experimental data instead of using the regressed values due to the uncertainties associated with the regression parameters.

$$w_T^{\text{ALK}} = \frac{w_{5,\text{CO}_2} - w_{4,\text{CO}_2}}{\alpha_5 - \alpha_4} = \frac{w_{6,\text{CO}_2}}{\alpha_5 - \alpha_4} \quad (9)$$

$$w_T^{\text{water}} = w_T^{\text{ALK}} \cdot \frac{MW(\text{ALK})}{MW(\text{water})} \cdot \frac{(100 - x) \text{ g water}}{\times \text{g ALK}} \quad (10)$$

## Results

Many of the main aqueous alkanolamines studied in the literature for CO<sub>2</sub> absorption are critically compared and ranked according to the minimum solvent flow rate required and an energetic parameter provided by the proposed model regression. The literature review indicates that the benchmark process used in the literature to compare any novel exhaust gases CO<sub>2</sub> capture technology is the chemical absorption with MEA. It is expected that the present study results help to decide if the MEA absorption is a proper candidate to be proposed as the Best Available Technique (BAT). When a process is proposed as BAT in the BREFs does not imply that there are no other more efficient or advantageous techniques. The BAT process defines a base line of comparison for any novel technique implemented that should be at least better than the BAT. It is expected that the present results provide some light on the carbon capture and help to include the CO<sub>2</sub> as contaminant in the BREFs.

## Surrogate model

The surrogate model proposed (Eq. 3) correlates the CO<sub>2</sub> gas liquid experimental data in general with good correlation coefficients (Tables 3, 4 and 5). However, in some cases such as for TEA or MEA + DAP the correlation is worse. Table 4 presents the regressed parameters for single aqueous alkanolamines and Tables 5 and 6 for binary



**Table 3** Parameters of surrogate model for single aqueous alkanolamines

Alkanolamine	Int	$\alpha$	$\Delta H_{\text{abs}}$ , J/mol	% wt Alk	% wt Alk. $\alpha$	$R^2$
AEEA	14.06	12.888	-59,234	0.0489	-0.0609	0.976
AMP	30.26	5.212	-66,348	-0.0185	0.070	0.865
DEA	17.68	9.947	-36,925	0.079	-0.036	0.932
DGA	23.76	-	-59,128	-	0.30	0.902
DIPA	22.00	8.661	-46,117	0.057	-0.012	0.955
MDEA	24.90	6.496	-49,186	0.046	-0.011	0.898
MEA	14.96	6.633	-27,745	-0.059	0.182	0.977
PZ	19.25	10.09	-50,128	0.235	-0.281	0.959
TEA	22.59	-0.808	-38,331	-0.0234	0.375	0.736

**Table 4** Parameters of surrogate model for binary mixtures of alkanolamines

Alkanolamine	Int	$\alpha$	$\Delta H_{\text{abs}}$ , J/mol	% wt Alk. 1	% wt Alk. 2	% wt Alk. 1 $\alpha$	% wt Alk.e 2 $\alpha$	$R^2$
AMP+PZ	14.58	-1.7	-21,558	-0.660	-0.239	0.767	0.261	0.865
DEA+AMP	19.08	-	-47,869	-	-0.068	0.210	0.225	0.827
DEA+MDEA	20.31	8.71	-57,749	0.032	0.055	-0.047	-0.035	0.974
DIPA+AEEA	14.19	-	-36,770	-	-0.229	0.245	0.350	0.920
MDEA+MEA	19.47	-	-56,023	-0.189	-	0.679	0.268	0.954
MDEA+PZ	22.74	0.96	-65,012	-0.007	-0.067	0.366	0.181	0.919
MEA+DAP	9.02	-	-36,717	0.391	-	0.428	0.775	0.784

**Table 5** Parameters of the surrogate model for ternary mixtures of alkanol amines

Alkanolamine	Int	$\alpha$	$\Delta H_{\text{abs}}$ J/mol	% wt Alk. 1	% wt Alk. 2	% wt Alk. 3	% wt Alk. 1 $\alpha$	% wt Alk. 2 $\alpha$	% wt Alk. 3 $\alpha$	$R^2$
DIPA+AMP+PZ	7.25	-	31,405	0.14	-	-	0.117	0.482	-	0.928

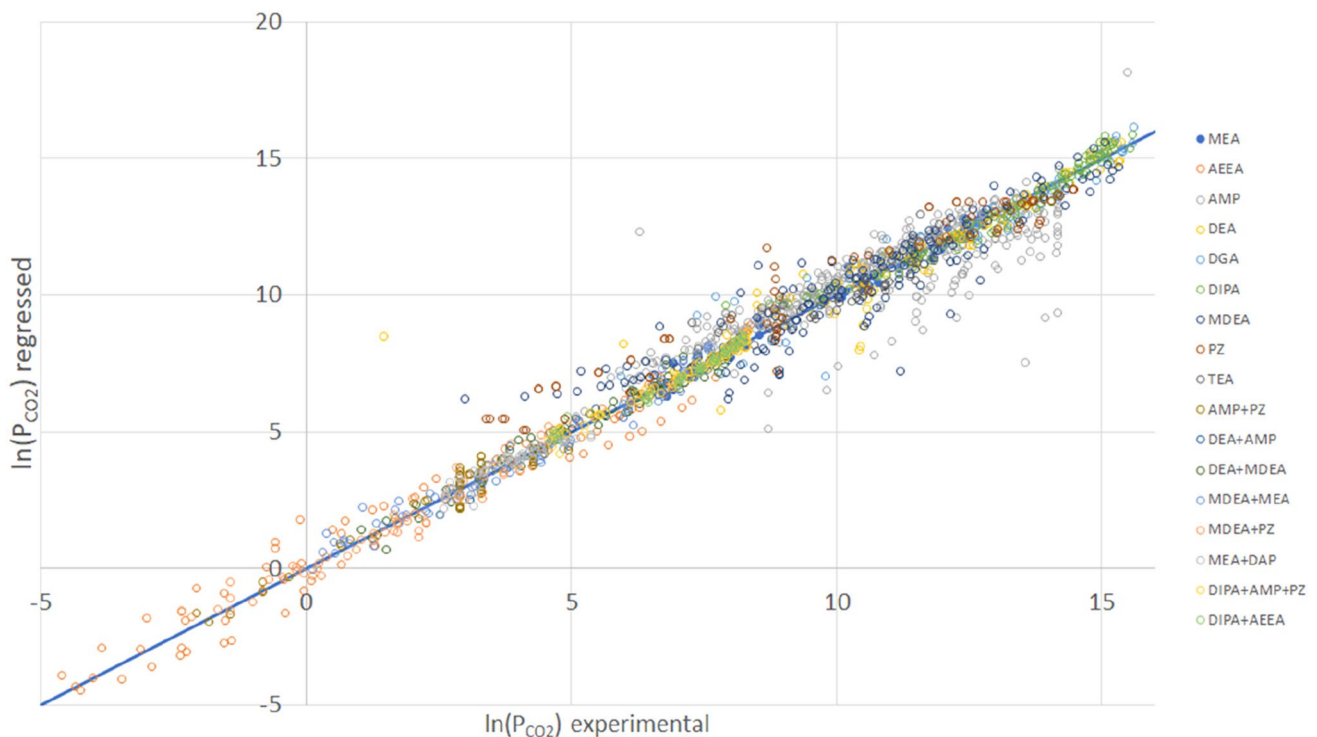
**Table 6** Mass balance results: minimum solvent flow rate for a 5 to 25% CO<sub>2</sub> in exhaust gas, considering a 70% CO<sub>2</sub> recovery

% CO <sub>2</sub>	Molar ratio solvent/gaseous input										
	MEA	NH <sub>3</sub>	DGA	AMP	PZ	MDEA	DEA	AEEA	DPTA	DIPA	TEA
5	14.74	6.86	8.52	20.53	20.29	21.64	24.37	24.95	29.88	28.21	34.36
10	15.62	7.27	10.24	20.85	21.04	21.77	24.9	26.28	30	30.14	34.87
15	16.51	7.69	11.95	21.17	21.79	21.91	25.42	27.61	30.12	32.06	35.39
20	17.40	8.1	13.67	21.49	22.54	22.04	25.95	28.94	30.24	33.99	35.9
25	18.28	8.52	15.38	21.8	23.29	22.17	26.47	30.27	30.37	35.91	36.42

and ternary mixtures. For some alkanolamines mixtures, there are not enough experimental data at different conditions to fit all the model parameters. The Pareto diagram is presented in Fig. 5, showing a random scatter of points at both sides of the diagonal, proving that the model is able to regress properly the gas liquid equilibrium experimental data for all the alkanolamines. Although more parameters would be included in the model, small deviations from the model are unavoidable due to experimental errors.

### Regeneration stream flow rate

The minimum solvent stream flow rate determines the pumping energy and cost related to the equipment and piping diameters. According to the minimum solvent flow rate results, MEA is on a top position together with ammonia (Table 6). DGA is also at a top position, but it is important to notice that no experimental data for 30% alkanolamine were available for DGA and a 60% mass fraction is used in



**Fig. 5** Pareto diagram of the experimental data of gas liquid CO<sub>2</sub> equilibrium versus the regressed model

this case (Table 3). NH<sub>3</sub> was also industrially used, but its volatility discouraged its use. Therefore, MEA is a suitable alkanolamine from the required flow rate point of view for diluted exhaust gases absorption. There are some alkanolamines that are able to reach a higher CO<sub>2</sub> load than MEA but in this case what is important is the CO<sub>2</sub> load difference corresponding to the gas liquid equilibrium when the partial pressure of CO<sub>2</sub> varies. The obtained results depend on the CO<sub>2</sub> gas concentration and recovery and thus, higher CO<sub>2</sub> gas concentrations or recoveries affect the calculated minimum flow rate and the alkanolamines ranking. The minimum flow rate of 30% MEA aqueous solution to capture the CO<sub>2</sub> from an exhaust gas with 25% vol CO<sub>2</sub> is lower than the flowrate of any other assessed alkanolamines to capture a 5% vol CO<sub>2</sub>. The exception is the volatile NH<sub>3</sub> and the DGA, whose experimental data are only available for 60% DGA aqueous solution.

It is expected that a lower minimum solvent flowrate is attainable when the parameters associated with the load of the surrogated model become higher. Figure 6 shows that for 30% alkanolamine and higher concentrations, the lowest minimum solvent flowrate corresponds to the use of MEA. Although being the worst choice according to Table 6, TEA seems also a good option for solvents with high alkanolamine concentrations but due to its low correlation coefficient further experimental research of gas liquid equilibrium is required. The results show that PZ

performs better when its mass percentage is low but notice also that PZ regressed parameters provide negative slope values for high % Alkanolamines, which is physically unfeasible.

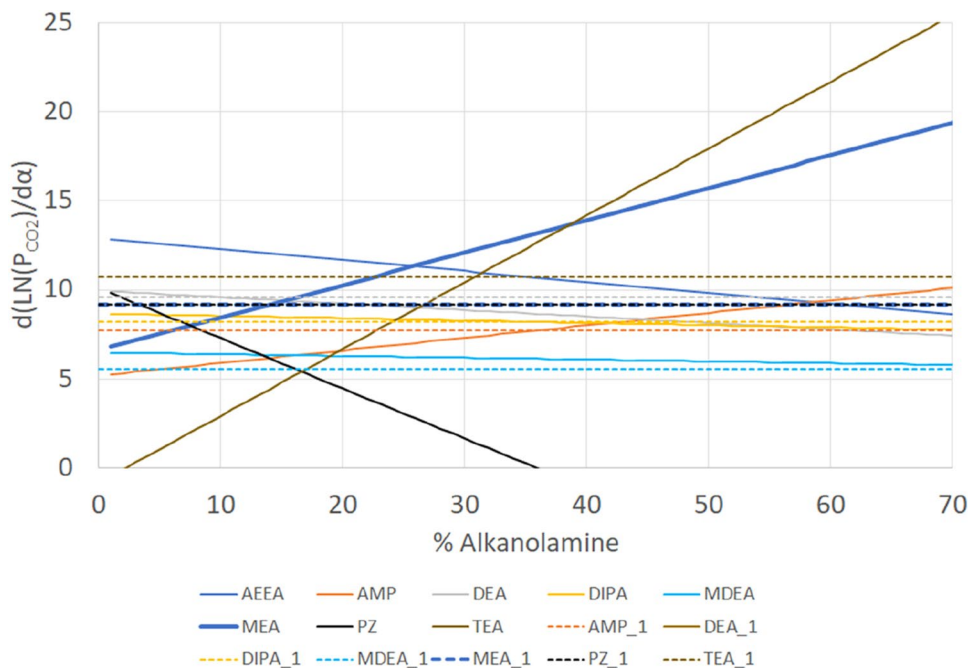
### Energy consumption

Two different approaches are applied in this section for exhaust gases with 10% CO<sub>2</sub> content to identify solvent alternatives outperforming MEA:

- the first approach is based on an exergy balance of the absorption column at 30 °C based on the previous mass balance results and the thermodynamic parameters retrieved from OLI® software;
- the second approach is based on the regression parameters of the proposed surrogate model.

The energy consumption of the carbon capture process by chemical absorption is expected to be related with the exergy lost in the absorption column. The previously mass balances solved for a minimum solvent flow rate are used to perform the exergy balance. The exergy balance on the absorption column depicts some alkanolamines showing better behaviour than MEA (Table 7), for instance the DEA. In case of DPTA, using the experimental equilibrium data where the process takes places spontaneously,

**Fig. 6** Influence of the % of alkanolamine on the minimum solvent flow rate (Alkanolamine\_1 stands for the averaged values with only S1 regression parameter)



**Table 7** Alkanolamine exergy lost

Alkanolamine	Exergy lost J/mol
DGA	$-4.44 \cdot 10^9$
DIPA	$-3.54 \cdot 10^9$
NH <sub>3</sub>	$-3.23 \cdot 10^9$
MEA	$-3.19 \cdot 10^9$
MDEA	$-3.11 \cdot 10^9$
DEA	$-1.15 \cdot 10^9$
DPTA	$3.21 \cdot 10^4$

the value of the exergy is positive which is not in agreement with the fact that the process should be spontaneous. Therefore, thermodynamic parameters implemented in commercial simulation software must be used with caution. Nevertheless, again MEA is in a rather favourable result 1.

Another approach to determine some energy favourable alkanolamines is based on the regressed surrogated model. According to the surrogated model, for the energy the focus is placed on the temperature-dependent parameters as it is expected to provide some hints about the energy consumption, although its value does not correspond to the absorption enthalpy. For instance, MEA energy regressed parameter has a value of  $-28$  kJ/mol versus the  $-84$  kJ/mol enthalpy of absorption (Table 8). The energy regressed parameters are ranked in Table 9, showing that MEA has a lower more favourable value than the other alkanolamines, which is in agreement with the industrial practice. Only the PZ + AMP mixture would have a more favourable parameter. The Pareto diagram between the

**Table 8** Alkanolamines heat absorption

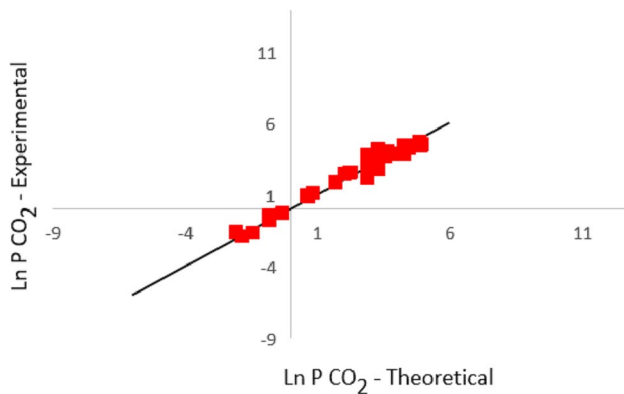
Alkanolamine	Heat absorption, J/mol
PZ + AMP	$-21,558$
MEA	$-27,745$
DIPA + AMP + PZ	$-31,405$
MEA + DAP	$-36,717$
DIPA + AEEA	$-36,770$
DEA	$-36,925$
TEA	$-38,331$
DIPA	$-46,117$
DEA + AMP	$-47,869$
MDEA	$-49,186$
PZ	$-50,128$
MEA + MDEA	$-56,023$
DEA + MDEA	$-57,749$
DGA	$-59,128$
AEEA	$-59,234$
MDEA + PZ	$-65,012$
AMP	$-66,348$

regressed and the experimental CO<sub>2</sub> gas liquid equilibrium for PZ + AMP mixture is shown in Fig. 7, indicating reasonable agreement between the experimental data with the regressed equation (Eqs. 11, 12 and 13).

Although AMP and PZ solvents show worse results at the level of exergy of absorption, when mixed together, they show the best results.

**Table 9** Regressed parameters for the surrogate model without S2 parameter

Alkanolamine	$\alpha$ Operation range	Int	$\alpha$	$\Delta H_{abs}$ J/mol	% wt Alk	$R^2$
AMP	0.2–0.9	27.09	7.72	–62,227	0.4	0.93
MEA	0.4–1.0	15.49	9.16	–35,091	0.11	0.99
MDEA	0.04–0.9	24.02	5.54	–47,405	0.05	0.90
DEA	0.2–0.9	21.71	9.56	–46,658	0.04	0.97
TEA	0.03–0.5	20.01	10.74	–35,969	0.03	0.84
PZ	0.1–1.0	21.29	9.16	–65,295	0.92	0.99
DIPA	0.1–1.1	22.34	8.23	–46,068	0.05	0.98
DGA	0.4–0.8	22.31	13.87	–30,789	–0.10	0.94

**Fig. 7** Experimental data and multiple regression AMP + PZ

$$\text{LN PCO}_2 = 14.58 - 1.7 \cdot (\alpha) - 21558.32 \cdot \left(\frac{1}{RT}\right) + S1 + S2 \quad (11)$$

$$S1 = -0.66 \cdot (\% \text{wt AMP}) - 0.24 \cdot (\% \text{wt PZ}) \quad (12)$$

$$S2 = 0.77 \cdot (\% \text{wt AMP} \cdot (\alpha)) + 0.26 \cdot (\% \text{wt PZ} \cdot (\alpha)) \quad (13)$$

For this mixture, if we assume a total solvent concentration of 30% (23% AMP and 7% PZ), the regeneration flow is 40.15 mol solvent/mol gaseous input, a value much higher as for MEA solvent of 15.62 mol solvent/mol gaseous input (Table 6). Therefore, despite its low value at heat absorption levels, its minimum solvent flowrate is quite high.

The surrogated model including the S1 and S2 parameters has a great influence on the value of the energy regressed parameter, and therefore, the regressions are repeated using only the S1 parameter for single aqueous alkanolamines (Table 9). Without the S2 parameter then the regression correlation of alkanolamines mixtures is rather poor and therefore not performed. The model is not able to regress all the data, and therefore, the regression is performed only in the linearized range of experimental points that is indicated in the table. Although the regressed energy parameter for MEA is still far away from its heat

of absorption, the ranking is still showing that MEA is very favourable. In the case of DGA, using S1 and S2 in the surrogated model leads to unfavourable results, when only S1 is considered then its energy and load regression parameters are more favourable than MEA. Therefore, further experimental gas liquid equilibrium studies on DGA would be interesting to find in which operating conditions DGA could be more advantageous than MEA.

The surrogate model provides a very good regression of experimental CO<sub>2</sub> gas liquid equilibrium, but the energy parameter has only physical meaning for systems at constant composition. However, the lower relative values for MEA in all the regressions indicate that MEA is a good choice, which is in agreement with its nowadays industrial use. Several regressions at different compositions are required for a more precise energy assessment.

Hence, considering both the exergy assessment and the surrogate model parameters, the obtained results indicate that MEA is a suitable choice as benchmark from the energy point of view, although some alkanolamines could outperform MEA.

### Alkanolamines screening

Table 10 indicates that MEA is a good choice to propose it as a BAT, which is in agreement with its nowadays industrial use. Although DGA could require a lower solvent flow rate, a higher energy consumption is expected. However; further, research is required on DGA to find the operating conditions in which this compound could be advantageous. On the other hand, although PZ + AMP mixture would provide an energetically favourable process, its high solvent flow rate discourages its use. Finally, simulation results pointing out that some alkanolamines can have a good performance, e.g. MDEA or DEA, should be taken with caution due to the uncertainties in the thermodynamic data implemented in the commercial simulation software. It is possible that some alternative solvents to MEA are advantageous, therefore further research on this field is required and nowadays

**Table 10** Alkanolamines screening

Alkanolamine	Regeneration stream minimum flowrate (mol solvent/mol gas)	Heat absorption regression parameter (J/mol)	Exergy lost (J/mol)
MEA	15.62	-27,745	-3.19·10 <sup>9</sup>
DGA	10.24	-59,128	-4.44·10 <sup>9</sup>
MDEA	21.77	-49,186	-3.11·10 <sup>9</sup>
DEA	24.90	-36,925	-1.15·10 <sup>9</sup>
PZ+AMP	40.15	-21,558	-

MEA is suitable to be proposed as the best available technique.

### Alkanolamine losses in exhaust gas

A final important point is that some alkanolamine amount can be lost in the exhaust gas phase. Unfortunately, the experimental data available for this situation are very scarce and mainly available for ammonia. This section shows that the previous expression is not only valid for CO<sub>2</sub> gas liquid equilibrium but also for the alkanolamine gas liquid equilibrium. It provides the basis for the application of this model to perform calculations of absorption columns design.

The design of a physical absorption column for low concentration of absorbed compound (e.g. < 10% vol as for CO<sub>2</sub> in exhaust gas combustions) can be easily performed assuming a constant gas flow rate (linear operating line, Eq. 14) and the Henry's law to define the equilibrium line (Eq. 15). NRTL and UNIQUAC thermodynamic models without dissociation are also suitable to describe the physical equilibrium but not the chemical one (Rosa et al. 2021). Solving the integral of Eq. 16 between the mass fraction of the absorbed/desorbed compound at the exhaust gas input and output streams provides the number of transfer units (NTU) of the absorption column (Eq. 16).

$$\text{Operating line: } Y_i = Y_{i1} + \frac{L}{G} \cdot (X_i - X_{i0}) \quad (14)$$

$$\text{Henry's law (physical absorption) : } Y_i^* = H \cdot X_i \quad (15)$$

$$\text{NTU} = \int_{y_0}^{y_1} \frac{dy}{y - y^*} \quad (16)$$

where  $Y_i$  is the mass fraction of compound  $i$  in the gas phase,  $X_i$  is the mass fraction of compound  $i$  in the liquid phase,  $L/G$  is the ratio of liquid and gas mass flow rates,  $Y_{i1}$  is the mass fraction of compound  $i$  in gas output and  $X_{i0}$  is the mass fraction of compound  $i$  in liquid input,  $Y_i^*$  mass fraction of compound  $i$  in the gas phase in gas liquid equilibrium with  $X_i$ ,  $H$  is the Henry's constant characteristic for each compound at a fixed temperature.

The chemical absorption is performed in an equivalent way, but using an expression derived from the proposed regression model instead of Henry's law. For a fixed alkanolamine mass percentage and temperature, Eq. 3 leads to an exponential relation between the liquid and gas equilibrium fractions according to Eq. 17, where  $A$  and  $B$  are the parameters derived from the proposed model.

$$\text{Chemical Absorption: } Y_i^* = e^{A+B \cdot X_i} \quad (17)$$

The pilot plant at Munmorah power station (test serie 5) is used as illustrative example for chemical absorption column design (Yu et al. 2011). The first step is to retrieve the CO<sub>2</sub> and NH<sub>3</sub> gas liquid experimental data available in the literature and regress the proposed equilibrium model for CO<sub>2</sub> (Eq. 18) and NH<sub>3</sub> (Eq. 19). The data for CO<sub>2</sub> correlation are retrieved from Qi et al. (2015), Jilvero et al (2015), Kurz et al (1995), Otsuka et al (1960) and Verbrugge (1973); the NH<sub>3</sub> gas liquid equilibrium is only available in the last two references. The correlation coefficients obtained for the regressed models are of 0.92 and 0.89 for CO<sub>2</sub> and NH<sub>3</sub>, respectively.

$$\text{LN PCO}_2 = 26.97 + 9.53 \cdot (\alpha) + 61599.09 \cdot \left( \frac{1}{8.314 \cdot T} \right) + 0.04 \cdot \% \text{ NH}_3 \quad (18)$$

$$\text{LN PNH}_3 = 20.50 - 4.49 \cdot (\alpha) - 29910.99 \cdot \left( \frac{1}{8.314 \cdot T} \right) + 0.16 \cdot \% \text{ NH}_3 \quad (19)$$

The operating conditions assumed, based on the pilot plant data, are the following:

- Adiabatic absorption, operated at atmospheric pressure and constant temperature of 17.5 °C (pilot plant operates between 101–105 kPa and 15–20 °C)
- Gas inlet: 760 kg/h flow rate with 8.5% vol CO<sub>2</sub> (37.74% CO<sub>2</sub> removal)
- Gas outlet: assumed exhaust gas molar composition of 8.5% CO<sub>2</sub>, 10% O<sub>2</sub>, 78% N<sub>2</sub> and 3.5% H<sub>2</sub>O and free of NH<sub>3</sub> (pilot plant composition ranges between 8.5–12% CO<sub>2</sub>, 6.5–10% O<sub>2</sub>, 76–78% N<sub>2</sub>, 3–6% H<sub>2</sub>O, 190–280 ppm SO<sub>2</sub>, 200–330 ppm NO, < 10 pp NO<sub>2</sub>).
- Liquid inlet (rich solvent): 8,040 kg/h flow rate with 4.5% wt NH<sub>3</sub> (pilot plant operates between 2–5% wt NH<sub>3</sub>)

- Liquid outlet (lean solvent): 4.5% wt NH<sub>3</sub> and 0.3 CO<sub>2</sub> load (pilot plant operates between 0.2–0.5 load)

Eqs. 18 and 19, for  $T=290.15$  K and % NH<sub>3</sub>=4.5% wt NH<sub>3</sub> in liquid phase, depend only on the load ( $\alpha$ ) which, due to the constant % NH<sub>3</sub>, provides the mass fraction of CO<sub>2</sub> in the liquid phase. These equations lead to Eqs. 20 and 21, where the gas molar fraction is calculated by applying Dalton law:

$$Y_{\text{CO}_2}^* = e^{1.66+0.82 \cdot X_{\text{CO}_2}} \quad (20)$$

$$Y_{\text{NH}_3}^* = e^{8.83-0.39 \cdot X_{\text{CO}_2}} \quad (21)$$

The number of transfer units of the absorption column is calculated based on the CO<sub>2</sub> data, i.e. using the  $X_{\text{CO}_2}$  in the exhaust gas inlet and outlet (this last calculated from the CO<sub>2</sub> recovery) and the previous equations (Eqs. 14, 16 and 20). Assuming a gas inlet free of ammonia and with the number of transfer units of the column already calculated, the procedure is repeated to calculate the mass fraction of NH<sub>3</sub> at the gas outlet (Eqs. 14, 16 and 21). The calculated amount of NH<sub>3</sub> lost is of 3.67 kg/h which is in good agreement with the experimental value determined in the pilot plant that was around 3 kg/h.

## Conclusions

A novel shortcut model that regresses a surrogate equation and requires a limited amount of gas liquid CO<sub>2</sub> experimental data is proven to be useful to compare and screening of alkanolamines. The minimum solvent flow rate is calculated by applying the CO<sub>2</sub> mass balance and assuming the liquid CO<sub>2</sub> gas liquid equilibrium is reached at both ends of the absorption column. Therefore, the load and the energy parameter of a novel surrogate model are used as key performance indicators related with the minimum solvent flowrate and energy consumption, whose values are compared to the aqueous MEA which is used as reference. MEA minimum flowrate is 15.62 mol solvent/mol gas and its heat of absorption regression parameter is  $-27,745$  J/mol. Some alkanolamines perform better than MEA in some respects, for example DGA requires less solvent flow rate or PZ + AMP mixture has a more favourable energy parameter but requires higher solvent flow rate. MEA-based CO<sub>2</sub> capture processes are the leading technology for the CO<sub>2</sub> capture from fossil fuel combustion power plants. The literature review and regression results prove that MEA chemical absorption is a suitable benchmark for other solvents, sustaining its inclusion in BREF documents as best available

technique and CO<sub>2</sub> should be included as a contaminant in BREF documents. As future work, the method should be applied to a larger number of solvents and identify alternative solvents to MEA, whose operating conditions of use are more advantageous.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s10098-021-02143-7>.

**Acknowledgements** Author Alexandra Elena Plesu Popescu is a Serra Hünter fellow. The authors acknowledge the valuable contribution of master students Alan Chavarria, Diana Medina, Enric Selfa, Toni Peiró and Jesús García from University of Barcelona (Master of Environmental Engineering) for their support to the bibliographic review, data mining and surrogate model development during their master thesis research.

**Funding** Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature.

## Declarations

**Conflict of interest** The authors declare no conflict of interest.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

## References

- Akram M, Milkowski K, Gibbins J, Pourkashanian M (2020) Comparative energy and environmental performance of 40 % and 30 % monoethanolamine at PACT pilot plant. *Int J Greenh Gas Control* 95:102946. <https://doi.org/10.1016/j.ijggc.2019.102946>
- Alaba PA, Sani YM, Olupinla SF, Daud WWW, Isah YM, Enweremadu CC, Ayodele OO (2017) Toward N-nitrosamines free water: formation, prevention, and removal. *Crit Rev Environ Sci Technol* 47(24):2448–2489. <https://doi.org/10.1080/10643389.2018.1430438>
- Alaba PA, Mazari SA, Farouk HU, Sanni SE, Agboola O, Lee CS, Abnisa F, Aroua MK, Daud WMAW (2020) Harvesting electricity from CO<sub>2</sub> emission: opportunities. *Int J Pr Eng Man-GT In Press*, Challenges and Future Prospects. <https://doi.org/10.1007/s40684-020-00250-2>
- Austgen DM, Rochelle GT, Chen CC (1991) Model of vapor–liquid equilibria for aqueous acid gas-alkanolamine systems. 2. Representation of H<sub>2</sub>S and CO<sub>2</sub> solubility in aqueous MDEA and CO<sub>2</sub> solubility in aqueous mixtures of MDEA with MEA or DEA. *Ind Eng Chem Res* 30(3):543–555. <https://doi.org/10.1021/ie00051a016>
- Aviso KB, Janairo JIB, Promentilla MAB, Tan RR (2019) Prediction of CO<sub>2</sub> storage site integrity with rough set-based machine learning.

- Clean Technol Environ Policy 21(8):1655–1664. <https://doi.org/10.1007/s10098-019-01732-x>
- Barreau A, Blanchon le Bouhelec E, Habchi Tounsi KN, Mougin P, Lecomte F (2006) Absorption of H<sub>2</sub>S and CO<sub>2</sub> in alkanolamine aqueous solution: experimental data and modelling with the electrolyte-NRTL model. *Oil Gas Sci Technol* 61(3):345–361. <https://doi.org/10.2516/ogst:2006038a>
- Barzagli F, Giorgi C, Mani F, Peruzzini M (2019) Comparative study of CO<sub>2</sub> capture by aqueous and nonaqueous 2-amino-2-methyl-1-propanol based absorbents carried out by <sup>13</sup>C NMR and enthalpy analysis. *Ind Eng Chem Res* 58(11):4364–4373. <https://doi.org/10.1021/acs.iecr.9b00552>
- Bishnoi S, Rochelle GT (2000) Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. *Chem Eng Sci* 55(22):5531–5543. [https://doi.org/10.1016/S0009-2509\(00\)00182-2](https://doi.org/10.1016/S0009-2509(00)00182-2)
- Bishnoi S, Rochelle GT (2002) Thermodynamics of piperazine/methyldiethanolamine/water/carbon dioxide. *Ind Eng Chem Res* 41(3):604–612. <https://doi.org/10.1021/ie0103106>
- Bonet-Ruiz A-E, Plesu V, Bonet J, Iancu P, Llorens J (2015) Preliminary technical feasibility analysis of carbon dioxide absorption by ecological residual solvents rich in ammonia to be used in fertigation. *Clean Technol Environ Policy* 17(5):1313–1321. <https://doi.org/10.1007/s10098-015-0950-9>
- Brunetti A, Scura F, Barbieri G, Drioli E (2010) Membrane technologies for CO<sub>2</sub> separation. *J Membr Sci* 359(1–2):115–125. <https://doi.org/10.1016/j.memsci.2009.11.040>
- Burnard K (2020a) IEGHG Technical Report 2020–08: Future Role of CCS Technologies in the Power Sector. International Energy Agency (IEA) Greenhouse Gas R&D Programme. <https://ieaghg.org/ccs-resources/blog/new-ieaghg-report-global-future-role-of-power-ccs-technologies> Accessed 7 January 2021
- Burnard K (2020b) IEGHG Technical Report 2020–07: Update Techno-Economic Benchmarks for Fossil Fuel-Fired Power Plants with CO<sub>2</sub> Capture. International Energy Agency (IEA) Greenhouse Gas R&D Programme. <https://ieaghg.org/publications/technical-reports/reports-list/9-technical-reports/1041-2020-07-update-techno-economic-benchmarks-for-fossil-fuel-fired-power-plants-with-co2-capture> Accessed 7 January 2021
- Carranza-Abaid A, Svendsen HF, Jakobsen JP (2020) Surrogate modelling of VLE: integrating machine learning with thermodynamic constraints. *Chem Eng Sci X* 8:100080. <https://doi.org/10.1016/j.cesx.2020.100080>
- Cebrecuan D, Cebrecuan V, Ionel I (2020) Modeling and performance analysis of subcritical and supercritical coal-fired power plants with biomass co-firing and CO<sub>2</sub> capture. *Clean Technol Environ Policy* 22(1):153–169. <https://doi.org/10.1007/s10098-019-01774-1>
- CESAR (2018) 2011-D2.4.3-APPROVED- project 7th Framework Programme. Collaborative Project-GA No. 213569. European Best Practice Guidelines for CO<sub>2</sub> Capture Technologies—EBTF -2011.03.08.doc [https://zenodo.org/record/1312801#YBRA\\_hYo-Uk](https://zenodo.org/record/1312801#YBRA_hYo-Uk) Accessed 7 January 2021 <https://doi.org/10.5281/zenodo.1312801>
- Chen X, Closmann F, Rochelle GT (2011) Accurate screening of amines by the Wetted Wall Column. *Energy Procedia* 4:101–108. <https://doi.org/10.1016/j.egypro.2011.01.029>
- Chowdhury FA, Yamada H, Higashii T, Goto K, Onoda M (2013) CO<sub>2</sub> capture by tertiary amine absorbents: a performance comparison study. *Ind Eng Chem Res* 52(24):8323–8331. <https://doi.org/10.1021/ie400825u>
- Chung PY, Soriano AN, Leron RB, Li MH (2010) Equilibrium solubility of carbon dioxide in the amine solvent system of (triethanolamine + piperazine + water). *J Chem Thermodyn* 42(6):802–807. <https://doi.org/10.1016/j.jct.2010.02.005>
- Chwoła T, Spietz T, Więclaw-Solny L, Tatarczuk A, Krótki A, Dobras S, Wilka A, Tchórz J, Stec M, Zdeb J (2020) Pilot plant initial results for the methanation process using CO<sub>2</sub> from amine scrubbing at the Łaziska power plant in Poland. *Fuel* 263:116804. <https://doi.org/10.1016/j.fuel.2019.116804>
- Cormos CC (2020) Energy and cost efficient manganese chemical looping air separation cycle for decarbonized power generation based on oxy-fuel combustion and gasification. *Energy* 191:116579. <https://doi.org/10.1016/j.energy.2019.116579>
- Cormos AM, Burca M, Ilea F, Cristea MV (2019) Process control strategy of amine-based post-combustion CO<sub>2</sub> capture systems. *Chem Eng Trans* 76:757–762. <https://doi.org/10.3303/CET1976127>
- Dash SK, Samanta AN, Bandyopadhyay SS (2011) (Vapour + liquid) equilibria (VLE) of CO<sub>2</sub> in aqueous solutions of 2-amino-2-methyl-1-propanol: New data and modelling using eNRTL-equation. *J Chem Thermodyn* 43(8):1278–1285. <https://doi.org/10.1016/j.jct.2011.03.016>
- Dicko M, Coquelet C, Jarne C, Northrop S, Richon D (2010) Acid gases partial pressures above a 50 wt% aqueous methyldiethanolamine solution: experimental work and modelling. *Fluid Phase Equilib* 289(2):99–109. <https://doi.org/10.1016/j.fluid.2009.11.012>
- Dubois L, Laribi S, Mouhoubi S, De Weireld G, Thomas D (2017) Study of the post-combustion CO<sub>2</sub> capture applied to conventional and partial oxy-fuel cement plants. *Energy Procedia* 114:6181–6196. <https://doi.org/10.1016/j.egypro.2017.03.1756>
- European Commission (2017) Kick-off meeting for the drawing up of the best available techniques (bat) reference document for common waste gas treatment in the chemical sector. [https://eippcb.jrc.ec.europa.eu/sites/default/files/2019-11/WGC\\_BREF\\_KoM%20IM%20Report%20May18\\_1.pdf](https://eippcb.jrc.ec.europa.eu/sites/default/files/2019-11/WGC_BREF_KoM%20IM%20Report%20May18_1.pdf) Accessed 10 December 2020
- European Commission (2018) Communication from the commission to the European parliament, the European council, the council, the European economic and social committee, the committee of the regions and the European Investment Bank. A Clean Planet for all A European strategic long-term vision for a prosperous, modern, competitive and climate neutral economy. COM/2018/773 final. <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52018DC0773> Accessed January 2021
- European commission (2020) Climate change. [https://ec.europa.eu/clima/change/consequences\\_en](https://ec.europa.eu/clima/change/consequences_en) Accessed 10 December 2020
- Feron PHM, Cousins A, Gao S, Liu L, Wang J, Niu H, Yu H, Li K, Cottrell A (2017) Experimental performance assessment of a mono-ethanolamine-based post-combustion CO<sub>2</sub>-capture at a coal-fired power station in China. *Greenh Gases* 7(3):486–499. <https://doi.org/10.1002/ghg.1654>
- Figuerola JD, Fout T, Plasynski S, McIlvried H, Srivastava RD (2008) Advances in CO<sub>2</sub> capture technology—the U.S. Department of Energy’s Carbon Sequestration Program. *Int J Greenh Gas Control* 2:9–20. [https://doi.org/10.1016/S1750-5836\(07\)00094-1](https://doi.org/10.1016/S1750-5836(07)00094-1)
- Flechsigs S, Sohr J, Schubert M, Hampel U, Kenig EY (2018) Rate-based modelling of CO<sub>2</sub> absorption with sandwich packings. *Chem Eng Trans* 69:169–174. <https://doi.org/10.3303/CET1869029>
- Gautam SS (2020) Effects of geometric and heat transfer parameters on adsorption–desorption characteristics of CO<sub>2</sub>-activated carbon pair. Article in Press, *Clean Techn Environ Policy*. <https://doi.org/10.1007/s10098-020-01866-3>
- Ghalib L, Ali BS, Ashri WM, Mazari S, Saeed IM (2017) Modeling the effect of piperazine on CO<sub>2</sub> loading in MDEA/PZ mixture. *Fluid Phase Equilib* 434:233–243. <https://doi.org/10.1016/j.fluid.2016.10.022>
- Gómez-Díaz D, Muñoz-Mouro A, Navaza JM, Rumbo A (2021) Diamine versus amines blend for CO<sub>2</sub> chemical absorption. *AIChE J* 67(1):e17071. <https://doi.org/10.1002/aic.17071>

- Guo C, Chen S, Zhang Y (2013) Solubility of carbon dioxide in aqueous 2-(2-aminoethyl)ethanol (AEEA) solution and its mixtures with N-methyldiethanolamine/2-amino-2-methyl-1-propanol. *J Chem Eng Data* 58(2):460–466. <https://doi.org/10.1021/je301174v>
- Haghtalab A, Talavaki MBZ (2017) Measurement of carbon dioxide solubility in aqueous diisopropanolamine solutions blended by N-(2-aminoethyl) ethanolamine + piperazine and density measurement of solutions. *J Nat Gas Sci Eng* 46:242–250. <https://doi.org/10.1016/j.jngse.2017.07.023>
- Haghtalab A, Eghbali H, Shojaeian A (2014) Experiment and modeling solubility of CO<sub>2</sub> in aqueous solutions of Diisopropanolamine + 2-amino-2-methyl-1-propanol + Piperazine at high pressures. *J Chem Thermodyn* 71:71–83. <https://doi.org/10.1016/j.jct.2013.11.025>
- Hashemi A, Pajoum Shariati F, Sohani E, Azizi S, Hosseinifar SZ, Delavari Amrei H (2020) CO<sub>2</sub> biofixation by *Synechococcus elongatus* from the power plant flue gas under various light–dark cycles. *Clean Technol Environ Policy* 22(8):1735–1743. <https://doi.org/10.1007/s10098-020-01912-0>
- He Q, Yu G, Tu T, Yan S, Zhang Y, Zhao S (2017) Closing CO<sub>2</sub> loop in biogas production: recycling ammonia as fertilizer. *Environ Sci Technol* 51(15):8841–8850. <https://doi.org/10.1021/acs.est.7b00751>
- Hosseini-Ardali SM, Hazrati-Kalbibaki M, Fattahi M, Lezsovits F (2020) Multi-objective optimization of post combustion CO<sub>2</sub> capture using methyldiethanolamine (MDEA) and piperazine (PZ) bi-solvent. *Energy* 211:119035. <https://doi.org/10.1016/j.energy.2020.119035>
- Idem R, Wilson M, Tontiwachwuthikul P, Chakma A, Veawab A, Aroonwilas A, Gelowitz D (2006) Pilot plant studies of the CO<sub>2</sub> capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO<sub>2</sub> capture technology development plant and the boundary dam CO<sub>2</sub> capture demonstration plant. *Ind Eng Chem Res* 45(8):2414–2420. <https://doi.org/10.1021/ie050569e>
- Isaacs EE, Otto FD, Mather AE (1977) Solubility of Hydrogen sulfide and carbon dioxide in an aqueous diisopropanolamine solution. *J Chem Eng Data* 22(1):71–73. <https://doi.org/10.1021/je60072a004>
- Jahangiri A, Hassankiadeh MN (2019) Effects of piperazine concentration and operating conditions on the solubility of CO<sub>2</sub> in AMP solution at low CO<sub>2</sub> partial pressure. *Sep Sci Technol* 54(6):1067–1078. <https://doi.org/10.1080/01496395.2018.1524907>
- Jiang K, Li K, Puxty G, Yu H, Feron PHM (2018) Information derivation from vapour–liquid equilibria data: a simple shortcut to evaluate the energy performance in an amine-based postcombustion CO<sub>2</sub> capture. *Environ Sci Technol* 52(18):10893–10901. <https://doi.org/10.1021/acs.est.8b03512>
- Jilvero H, Jens KJ, Normann F, Andersson K, Halstansen M, Eimer D, Johnsson F (2015) Equilibrium measurements of the NH<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system—measurement and evaluation of vapour–liquid equilibrium data at low temperatures. *Fluid Phase Equilib* 385:237–247. <https://doi.org/10.1016/j.fluid.2014.11.006>
- Jong IL, Otto FD, Mather AE (1972) Solubility of carbon dioxide in aqueous diethanolamine solutions at high pressures. *J Chem Eng Data* 17(4):465–468. <https://doi.org/10.1021/je60055a015>
- Khodadadi MJ, Abbasi M, Riahi S, Shokrollahzadeh H (2019) Investigation on kinetics of carbon dioxide absorption in aqueous solutions of monoethanolamine + 1, 3-diaminopropane. *Sep Sci Technol* 54(17):2800–2808. <https://doi.org/10.1080/01496395.2018.1553984>
- Kumar G, Kundu M (2012) Vapour-liquid equilibrium of CO<sub>2</sub> in aqueous solutions of N-methyl-2-ethanolamine. *Can J Chem Eng* 90(3):627–630. <https://doi.org/10.1002/cjce.20598>
- Kurz F, Rumpf B, Maurer G (1995) Vapor–liquid–solid equilibria in the system NH<sub>3</sub>CO<sub>2</sub>H<sub>2</sub>O from around 310 to 470 K: new experimental data and modelling. *Fluid Phase Equilib* 104(C):261–275. [https://doi.org/10.1016/0378-3812\(94\)02653-1](https://doi.org/10.1016/0378-3812(94)02653-1)
- Laribi S, Dubois L, De Weireld G, Thomas D (2019) Study of the post-combustion CO<sub>2</sub> capture process by absorption-regeneration using amine solvents applied to cement plant flue gases with high CO<sub>2</sub> contents. *Int J Greenh Gas Control* 90:102799. <https://doi.org/10.1016/j.ijggc.2019.102799>
- Lawson JD, Garst AW (1976) Gas Sweetening data: equilibrium solubility of hydrogen sulfide and carbon dioxide in aqueous monoethanolamine and aqueous diethanolamine solutions. *J Chem Eng Data* 21(1):20–30. <https://doi.org/10.1021/je60068a010>
- Lemoine B, Li YG, Cadours R, Bouallou C, Richon D (2000) Partial vapor pressure of CO<sub>2</sub> and H<sub>2</sub>S over aqueous methyldiethanolamine solutions. *Fluid Phase Equilib* 172(2):261–277. [https://doi.org/10.1016/S0378-3812\(00\)00383-6](https://doi.org/10.1016/S0378-3812(00)00383-6)
- Li MH, Shan KP (1992) Densities and solubilities of solutions of carbon dioxide in water + monoethanolamine + N-methyldiethanolamine. *J Chem Eng Data* 37(3):288–290. <https://doi.org/10.1021/je00007a002>
- Li K, Feron PHM, Jiang K, Jones TW, Bennett RD, Hollenkamp AF, Pearson P (2018) Reaction enthalpy conversion in amine based PostCombustion CO<sub>2</sub> capture. *Chem Eng Trans* 69:139–144. <https://doi.org/10.3303/CET1869024>
- Liu H, Gao H, Idem R, Tontiwachwuthikul P, Liang Z (2017) Analysis of CO<sub>2</sub> solubility and absorption heat into 1-dimethylamino-2-propanol solution. *Chem Eng Sci* 170:3–15. <https://doi.org/10.1016/j.ces.2017.02.032>
- Lu R, Li K, Chen J, Yu H, Tade M (2017) CO<sub>2</sub> capture using piperazine-promoted, aqueous ammonia solution: rate-based modelling and process simulation. *Int J Greenh Gas Control* 65:65–75. <https://doi.org/10.1016/j.ijggc.2017.08.018>
- Mahmoodpour S, Rostami B, Emami-Meybodi H (2018) Onset of convection controlled by N<sub>2</sub> impurity during CO<sub>2</sub> storage in saline aquifers. *Int J Greenh Gas Control* 79:234–247. <https://doi.org/10.1016/j.ijggc.2018.10.012>
- Martin J, Otto F, Mather A (1978) Solubility of hydrogen sulfide and carbon dioxide in a diglycolamine solution. *J Chem Eng Data* 23(2):163–164. <https://doi.org/10.1021/je60077a001>
- Mathias PM (2016) The Gibbs–Helmholtz equation in chemical process technology. *Ind Eng Chem Res* 55(4):1076–1087. <https://doi.org/10.1021/acs.iecr.5b03405>
- Mazari SA, Alaba P, Saeed IM (2019) Formation and elimination of nitrosamines and nitramines in freshwaters involved in post-combustion carbon capture process. *J Environ Chem Eng* 7(3):103111. <https://doi.org/10.1016/j.jece.2019.103111>
- Mendez-Alvarez C, Plesu V, Bonet Ruiz AE, Bonet Ruiz J, Iancu P, Llorens J (2016) Distillation energy assessment for solvent recovery from carbon dioxide absorption. *Comput Aided Chem Eng* 38:1917–1922. <https://doi.org/10.1016/B978-0-444-63428-3.50324-6>
- Merkel TC, Lin H, Wei X, Baker R (2010) Power plant post-combustion carbon dioxide capture: an opportunity for membranes. *J Membr Sci* 359(1–2):126–139. <https://doi.org/10.1016/j.memsci.2009.10.041>
- Moioli S, Ho MT, Pellegrini LA, Wiley DE (2019) Application of absorption by potassium taurate solutions to post-combustion CO<sub>2</sub> removal from flue gases with different compositions and flowrates. *Chem Eng Trans* 74:823–828. <https://doi.org/10.3303/CET1974138>
- Morales-Mora MA, Pretelín-Vergara CF, Martínez-Delgadoillo SA, Iuga C, Nolasco-Hipolito C (2019) Environmental assessment of a combined heat and power plant configuration proposal with post-combustion CO<sub>2</sub> capture for the Mexican oil and gas



- industry. *Clean Technol Environ Policy* 21(1):213–226. <https://doi.org/10.1007/s10098-018-1630-3>
- Morgan JC, Soares Chinen A, Omell B, Bhattacharyya D, Tong C, Miller DC, Buschle B, Lucquiaud M (2018) Development of a rigorous modeling framework for solvent-based CO<sub>2</sub> capture. Part 2: steady-state validation and uncertainty quantification with pilot plant data. *Ind Eng Chem Res* 57(31):10464–10481. <https://doi.org/10.1021/acs.iecr.8b01472>
- Murrieta-Guevara F, Rebolledo-Libreros ME, Romero-Martinez A, Trejo A (1998) Solubility of CO<sub>2</sub> in aqueous mixtures of diethanolamine with methyldiethanolamine and 2-amino-2-methyl-1-propanol. *Fluid Phase Equilib* 150–151:721–729. [https://doi.org/10.1016/S0378-3812\(98\)00352-5](https://doi.org/10.1016/S0378-3812(98)00352-5)
- Nguyen T, Hilliard M, Rochelle GT (2010) Amine volatility in CO<sub>2</sub> capture. *Int J Greenh Gas Control* 4(5):707–715. <https://doi.org/10.1016/j.ijggc.2010.06.003>
- Nwaoha C, Tontiwachwuthikul P, Benamor A (2019) CO<sub>2</sub> capture from water-gas shift process plant: comparative bench-scale pilot plant investigation of MDEA-PZ blend vs novel MDEA activated by 1,5-diamino-2-methylpentane. *Int J Greenh Gas Control* 82:218–228. <https://doi.org/10.1016/j.ijggc.2019.01.009>
- Ong SH, Tan RR, Andiappan V (2020) Optimisation of biochar-based supply chains for negative emissions and resource savings in carbon management networks. *Clean Technol Environ Policy*. <https://doi.org/10.1007/s10098-020-01990-0>
- Otsuka E, Yoshimura S, Yakabe M, Inoue S (1960) Equilibrium of the NH<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system. *Kogyo Kagaku Zasshi* 62:1214–1218
- Pacheco M, Kaganoi S, Rochelle GT (2000) CO<sub>2</sub> absorption into aqueous mixtures of diglycolamine® and methyldiethanolamine. *Chem Eng Sci* 55(21):5125–5140. [https://doi.org/10.1016/S0009-2509\(00\)00104-4](https://doi.org/10.1016/S0009-2509(00)00104-4)
- Papadopoulos AI, Badr S, Chremos A, Forte E, Zargiannis T, Seferlis P, Papadokostantakis S, Adjiman CS, Galindo A, Jackson G (2016) Computer-aided molecular design and selection of CO<sub>2</sub> capture solvents considering thermodynamics. *Mol Syst Des Eng* 1:313–334. <https://doi.org/10.1039/C6ME00049E>
- Papadopoulos AI, Tzirakis F, Tsivintzelis I, Seferlis P (2019) Phase-change solvents and processes for postcombustion CO<sub>2</sub> capture: a detailed review. *Ind Eng Chem Res* 58(13):5088–5111. <https://doi.org/10.1021/acs.iecr.8b06279>
- Papadopoulos AI, Shavaliyeva G, Papadokostantakis S, Seferlis P, Perdomo FA, Galindo A, Jackson G, Adjiman CS (2020b) An approach for simultaneous computer-aided molecular design with holistic sustainability assessment: application to phase-change CO<sub>2</sub> capture solvents. *Comput Chem Eng* 135:106769. <https://doi.org/10.1016/j.compchemeng.2020.106769>
- Papadopoulos AI, Perdomo FA, Tzirakis F, Shavaliyeva G, Tsivintzelis I, Kazepidis P, Nessi E, Papadokostantakis S, Seferlis P, Galindo A, Jackson G, Adjiman CS (2020a) Molecular engineering of sustainable phase-change solvents: from digital design to scaling-up for CO<sub>2</sub> capture. *Chem Eng J*. <https://doi.org/10.1016/j.cej.2020.127624>
- Park MK, Sandall OC (2001) Solubility of carbon dioxide and nitrous oxide in 50 mass % methyldiethanolamine. *J Chem Eng Data* 46(1):166–168. <https://doi.org/10.1021/je000190t>
- Plesu V, Bonet J, Bonet-Ruiz AE, Chavarria A, Iancu P, Llorens J (2018) Surrogate model for carbon dioxide equilibrium absorption using aqueous monoethanolamine. *Chem Eng Trans* 70:919–924. <https://doi.org/10.3303/CET1870154>
- Qi G, Wang S, Lu W, Yu J, Chen C (2015) Vapor–liquid equilibrium of CO<sub>2</sub> in NH<sub>3</sub>-CO<sub>2</sub>-SO<sub>2</sub>-H<sub>2</sub>O system. *Fluid Phase Equilib* 386:47–55. <https://doi.org/10.1016/j.fluid.2014.11.015>
- Ritchie H, Roser M (2020) CO<sub>2</sub> and greenhouse gas emissions. *Our World in Data* <https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions>. Accessed 10 December 2020
- Roberts BE, Mather AE (1988) Solubility of CO<sub>2</sub> and H<sub>2</sub>S in a hindered amine solution. *Chem Eng Commun* 64(1):105–111. <https://doi.org/10.1080/00986448808940230>
- Rosa LPS, Cruz N, Costa GMN, Pontes KV (2021) A comparative study of thermodynamic models to describe the VLE of the ternary electrolytic mixture H<sub>2</sub>O-NH<sub>3</sub>-CO<sub>2</sub>. In Press, *Chem Prod Process Model*. <https://doi.org/10.1515/cppm-2020-0101>
- Sala M, Bonet J, Plesu V, Bonet-Ruiz AE, Iancu P, Llorens J (2014) Minimum gas/liquid flow rate for absorption columns. *Chem Eng Trans* 39:241–246. <https://doi.org/10.3303/CET143904>
- Salman B, Nomanbhay S, Foo DCY (2019) Carbon emissions pinch analysis (CEPA) for energy sector planning in Nigeria. *Clean Technol Environ Policy* 21(1):93–108. <https://doi.org/10.1007/s10098-018-1620-5>
- Seo DJ, Hong WH (1996) Solubilities of carbon dioxide in aqueous mixtures of diethanolamine and 2-amino-2-methyl-1-propanol. *J Chem Eng Data* 41(2):258–260. <https://doi.org/10.1021/je950197o>
- Shavaliyeva G, Kazepidis P, Papadopoulos AI, Seferlis P, Papadokostantakis S (2021) Environmental, health and safety assessment of post-combustion CO<sub>2</sub> capture processes with phase-change solvents. *Sustain Prod Consum* 25:60–76. <https://doi.org/10.1016/j.spc.2020.07.015>
- Sidi-Boumedine R, Horstmann S, Fischer K, Provost E, Fürst W, Gmehling J (2004) Experimental determination of carbon dioxide solubility data in aqueous alkanolamine solutions. *Fluid Phase Equilib* 218(1):85–94. <https://doi.org/10.1016/j.fluid.2003.11.014>
- Śpiewak D, Krótki A, Spietz T, Stec M, Więclaw-Solny L, Tatarczuk A, Wilk A (2015) PDU-scale experimental results of CO<sub>2</sub> removal with Amp/Pz solvent. *Chem Process Eng* 36:39–48. <https://doi.org/10.1515/cpe-2015-0003>
- Stec M, Tatarczuk A, Więclaw-Solny L, Krótki A, Spietz T, Wilk A, Śpiewak D (2016) Demonstration of a post-combustion carbon capture pilot plant using amine-based solvents at the Łaziska power plant in Poland. *Clean Technol Environ Policy* 18(1):151–160. <https://doi.org/10.1007/s10098-015-1001-2>
- Teng TT, Mather AE (1990) Solubility of CO<sub>2</sub> in an AMP solution. *J Chem Eng Data* 35(4):410–411. <https://doi.org/10.1021/je00062a010>
- Thengane SK, Bandyopadhyay S (2020) Biochar mines: Panacea to climate change and energy crisis? *Clean Technol Environ Policy* 22(1):5–10. <https://doi.org/10.1007/s10098-019-01790-1>
- Tong D, Trusler JPM, Maitland GC, Gibbins J, Fennell PS (2012) Solubility of carbon dioxide in aqueous solution of monoethanolamine or 2-amino-2-methyl-1-propanol: experimental measurements and modelling. *Int J Greenh Gas Control* 6:37–47. <https://doi.org/10.1016/j.ijggc.2011.11.005>
- Tontiwachwuthikul P, Meisen A, Lim CJ (1991) Solubility of carbon dioxide in 2-amino-2-methyl-1-propanol solutions. *J Chem Eng Data* 36:130–133. <https://doi.org/10.1021/je00001a038>
- Tzirakis F, Tsivintzelis I, Papadopoulos AI, Seferlis P (2019) Experimental measurement and assessment of equilibrium behaviour for phase change solvents used in CO<sub>2</sub> capture. *Chem Eng Sci* 199:20–27. <https://doi.org/10.1016/j.ces.2018.12.045>
- Verbrugge P (1973) Vapour–liquid equilibria of the ammonia–carbon dioxide–water system. Ph.D. Dissertation, Delft University
- Wanderley RR, Evjen S, Pinto DDD, Knuutila HK (2018) The salting-out effect in some physical absorbents for CO<sub>2</sub> capture. *Chem Eng Trans* 69:97–102. <https://doi.org/10.3303/CET1869017>
- Xiao M, Liu H, Idem R, Tontiwachwuthiku P, Liang Z (2016) A study of structure–activity relationships of commercial tertiary amines for post-combustion CO<sub>2</sub> capture. *Appl Energy* 184:219–229. <https://doi.org/10.1016/j.apenergy.2016.10.006>
- Xiao M, Cui D, Yang Q, Liang Z, Puxty G, Yu H, Li L, Conway W, Feron P (2021) Role of mono- and diamines as kinetic promoters

- in mixed aqueous amine solution for CO<sub>2</sub> capture. *Chem Eng Sci* 229:116009. <https://doi.org/10.1016/j.ces.2020.116009>
- Xu Q, Rochelle GT (2011) Total pressure and CO<sub>2</sub> solubility at high temperature in aqueous amines. *Energy Procedia* 4:117–124. <https://doi.org/10.1016/j.egypro.2011.01.031>
- Yadav VG, Yadav GD, Patankar SC (2020) The production of fuels and chemicals in the new world: critical analysis of the choice between crude oil and biomass vis-à-vis sustainability and the environment. *Clean Technol Environ Policy* 22(9):1757–1774. <https://doi.org/10.1007/s10098-020-01945-5>
- Yamada H (2021) Amine-based capture of CO<sub>2</sub> for utilization and storage. *Polym J* 53(1):93–102. <https://doi.org/10.1038/s41428-020-00400-y>
- Yang ZY, Soriano AN, Caparanga AR, Li MH (2010) Equilibrium solubility of carbon dioxide in (2-amino-2-methyl-1-propanol + piperazine + water). *J Chem Thermodyn* 42(5):659–665. <https://doi.org/10.1016/j.jct.2009.12.006>
- Yu H, Morgan S, Allport A, Cottrell A, Do T, McGregor J, Wardhaugh L, Feron P (2011) Results from trialling aqueous NH<sub>3</sub> based post-combustion capture in a pilot plant at Munmorah power station: absorption. *Chem Eng Res Des* 89:1204–1215. <https://doi.org/10.1016/j.cherd.2011.02.036>
- Zarogiannis T, Papadopoulos AI, Seferlis P (2020a) Efficient selection of conventional and phase-change CO<sub>2</sub> capture solvents and mixtures based on process economic and operating criteria. *J Clean Prod* 272:122764. <https://doi.org/10.1016/j.jclepro.2020.122764>
- Zarogiannis T, Papadopoulos AI, Seferlis P (2020b) Off-design operation of conventional and phase-change CO<sub>2</sub> capture solvents and mixtures: a systematic assessment approach. *Appl Sci* 10(15):5316. <https://doi.org/10.3390/app10155316>
- Zhang P, Li M, Lv C, Zhang Y, Wang L, Fu D (2020a) Effect of partial pressure on CO<sub>2</sub> absorption performance in piperazine promoted 2-diethylaminoethanol and 1-dimethylamino-2-propanol aqueous solutions. *J Chem Thermodyn* 150:106198. <https://doi.org/10.1016/j.jct.2020.106198>
- Zhang R, Zhang Y, Cheng Y, Yu Q, Luo X, Li C, Li J, Zeng Z, Liu Y, Jiang X, Hu XE (2020b) New approach with universal applicability for evaluating the heat requirements in the solvent regeneration process for postcombustion CO<sub>2</sub> capture. *Ind Eng Chem Res* 59(7):3261–3268. <https://doi.org/10.1021/acs.iecr.9b05247>

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

## Authors and Affiliations

Alexandra Elena Plesu Popescu<sup>1</sup>  · Àgata González<sup>1</sup> · Joan Llorens<sup>1</sup> · Jordi Bonet<sup>1</sup>

<sup>1</sup> Department of Chemical Engineering and Analytical Chemistry, Faculty of Chemistry, University of Barcelona, c/ Martí i Franquès 1, 6th Floor, 08028 Barcelona, Spain