Comparison of aqueous and non-aqueous alkanolamines solutions for carbon dioxide desorption in a microreactor

Babak Aghel [a], Sasan Sahraie [a], Ehsan Heidaryan [b], *

[a] Department of Chemical Engineering, Faculty of Energy, Kermanshah University of Technology, Kermanshah, Iran
[b] Department of Chemical Engineering, Engineering School, University of São Paulo (USP), Caixa Postal 61548, São Paulo, SP, 05508-000, Brazil

ABSTRACT

An experimental study of CO_2 desorption from aqueous and non-aqueous saturated alkanolamine solutions carried out in a tubular microreactor, consisting of a stainless steel microtube with an internal diameter of 800 μm and a total length of 35 cm. We tested a total of six solvent mixtures of water or methanol with monoethanolamine, diethanolamine, or activated methyl diethanolamine in a broad range of operational conditions, including temperature (50—100 °C), rich solvent flow rate (0.5—4.5 ml/min), and amine concentration in the solvent (10 and 50% w/w). CO_2 desorption was thoroughly characterized with respect to the mass transfer rate and energy consumption, and both were expected to improve with the use of a microreactor due to short diffusion distances and a larger surface-to-area ratio. An increase in the operating temperature or concentration of the amine resulted in a higher percentage of desorption and enhanced mass transfer rates, as shown by the local mass transfer coefficient based on the liquid phase values herein disclosed. Increasing the rich solvent flow rate also increased the local mass transfer coefficient values (80%—95%); however, the overall percentage of CO_2 desorption reduced (25%—35%) due to shorter residence times in the microreactor. Similarly, the energetic desorption efficiency improved for all the solutions with increasing temperature (65—75% reduction) and concentration of amine in the solvent (20—35% reduction), yet again decreasing with an increasing flow rate of rich solvent (5—15%). Compared to the literature values for the packed columns and microreactors, our data showed the overall energy consumption up to an 88% reduction in specific CO_2 desorption, demonstrating great potential for the intensification of solvent-mediated, energetically demanding CO_2 desorption. In addition, the results showed that the energy consumption for CO_2 desorption was reduced by 73% by choosing a non-aqueous in preference to an aqueous alkanolamine solvent.

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1. Introduction

The current urgency in controlling CO_2 emissions has triggered a growing interest in Carbon Capture and Storage (CCS) [1] technologies. CO_2 is the undesirable byproduct with a relevant greenhouse effect [2], resulting in the combustion of biomass or fossil fuels. CO_2 is also naturally present in natural gas, which must be removed due to the possible thermal reduction of the fuel and the chemical degradation of the transmission lines [3]. Various methods have been proposed for the separation of CO_2, including cryogenic distillation [4], adsorption [5], and membranes [6], yet solvent absorption [7—10] remains the preferred method for CO_2 capture, which consists of selectively absorbing CO_2 with a given solvent mixture in a gas-liquid contacting system. Regarding solvent selection, alkanolamine-based solvents are the most commonly used for presenting high solubility to CO_2 [11—13]. However, solvent recovery (which is driven by a temperature increase of the solvent mixture) is very demanding energetically, representing about 70% of energy and operating costs [14,15]. Therefore, there is a major need to reduce energy consumption in solvent recovery to increase the efficiency and sustainability of CO_2 solvent capturing.

There are two possible approaches to optimize solvent recovery. The first involves using devices offering improved gas-liquid contacting, thereby leading to superior mass transfer rates. Among modern and optimal mass transfer devices, microchannels are a key technology [16—18]. Microchannels increase the massive transfer of mass with the ability to create a much higher interface area

* Corresponding author. Department of Chemical Engineering, Engineering School, University of São Paulo (USP), São Paulo, SP, 05508-000, Brazil.
E-mail address: heidaryan@engineer.com (E. Heidaryan).

between phases than conventional mass transfer devices, and they reduce thermal losses in the thermal recovery unit with high heat transfer capability [19–21]. A second solution involves using solvents that require less energy input for solvent recovery. Today, the most commonly used alkanolamine solvents for CO_2 absorption are monoethanolamine (MEA), diethanolamine (DEA), and methyl diethanolamine (MDEA) [22–24].

One of the most affordable and cheapest solvents for alkanolamines is water; however, other studies suggested using some organic solvents, such as methanol (MeOH) or ethanol instead of water [25–27]. MeOH has a thermal capacity and boiling point much lower than water, enabling the rich solvent to be recovered even with hot water in the thermal recovery unit.

So far, CO_2 absorption by alkanolamine methanol-based solvents has been mainly focused on conventional mass transfer devices, such as packed bed columns. Gao et al. [26] studied CO_2 absorption experimentally in a system including filled absorption and desorption columns and showed that the MEA-MeOH solvent had a higher CO_2-absorption rate and lower energy consumption than MEA.

An exception is the work of Nguyen et al. [28], who explored a microvascular system with capillaries smaller than 300 μm, and Liu et al. [29], who studied CO_2 desorption from a rich solvent of MDEA. These studies have explored the effects of different parameters, including MDEA concentration, desorption temperature, solvent flow rate, and solvent load on the CO_2 desorption rate, and they have reported that the CO_2 desorption rate is very sensitive to the desorption temperature. CO_2 desorption was almost in equilibrium after approximately 7 s, indicating the benefit of using a microreactor for the rapid release of CO_2.

In another study, Liu et al. [30] also investigated experimentally the heat transfer and energy consumption per CO_2 emitted from a rich solution of MDEA in a microreactor. The results showed that the heat transfer coefficient is strongly dependent on the applied heat flux. The solvent flow rate was the most important variable affecting the thermal flux, followed by the desorption temperature, amine concentration in the solvent, and amine load.

As the performance of CO_2 desorption processes depends strongly on the contact between two phases, in this study, a tubular, microreactor system has been used. The main innovation was the use of microreactor technology as a mass and heat transfer booster in the removal of CO_2 from amine solutions. A further change of this work was the use of aqueous and non-aqueous alkanolamine solutions (MEA, DEA, and a-MDEA) in a tubular microreactor. The effect of the temperature, flow rate of rich amine, amine concentration, and amine loading on the percentage of CO_2 desorption and the total mass transfer coefficient inside the reactor was studied to evaluate the operational conditions that led to significant improvements in mass transfer and reduction on energy demand for solvent regeneration. It should be noted that, although investigating the hydrodynamics in the microreactor would provide crucial information for a better understanding of the overall solvent-desorption process, our evaluation was limited to specific aspects of the chemical and mass transfer aspects of the desorption process.

2. Experiments and methodology

2.1. Materials

We sourced sulfuric acid from Kimia Pars Co., 98% HCl from Merck Co., 99% sodium sulfate from Kimia Pars Co., and methyl orange reagent from the French Biochem Co. A-MDEA with a purity of 85% (45% MDEA, 40% PZ and 15% water) was sourced from BASF Co., 99.9% MEA and DEA were sourced from Shazand Petrochemical Co., 99.9% Methanol was also used with Merc standard. Table 1 shows the properties of the materials used in this study.

2.2. Experimental setup

The apparatus in Fig. 1 was used to desorb the CO_2 from an amine solvent. This system includes an 800 μm-diameter stainless steel tube with a length of 35 cm as a microreactor. An electric coil heater was used around the tube to apply the desired temperature. A dimmer and a power analyzer GM86 model from the Chinese company BENETECH with an uncertainty of 1 W were installed to adjust the temperature and measure the power consumption of the heater over the power supply of the heater. The insulation was applied to reduce the thermal losses around the steel tube and coil. An SP1000HPM syringe pump manufactured by Fanavaran Nano-Meghyas, Tehran, Iran, with an uncertainty of ±3%, was used to pump the solvent.

In the first stage, to study the desorption in the microreactor, it was necessary to saturate the amine solution with CO_2 to assess the maximum loading capacity of the prepared amines solution. It was carried out in a chamber at ambient temperature with an uncertainty of ±0.1 °C and specific pressure with an uncertainty of ±20 kPa by injecting carbon dioxide and giving enough time to saturate the amine with the mentioned solvent loading. The system was initially purged with inert N_2 for several minutes to remove any gaseous contaminants that could be present. Saturation was considered complete by observing the evolution of CO_2 bubbles into the aqueous amine solution. The amount of amine load at the input of the micro-reactor was measured at the start of the test, although some of the amine load decreased due to physical desorption. Also, the results of the measurement of the amine load showed that after reaching the ambient temperature, the amine load did not change significantly and remained nearly constant.

By pumping the CO_2-rich amine into the microreactor operated horizontally through a syringe pump and applying the operational temperature, the solvent inside the microreactor became two phases. It introduced the two-phase separator from the outlet side of the microreactor. The gas (mainly CO_2) was released from the upper part of this two-phase separator, and the amine was emitted from the lower part of the separator (CO_2-free).

Generally, due to the occurrence of a flashing phenomenon in phase separator, some separation might occur. However, this was discarded because no separation was observed downstream of the tubular microreactor. Moreover, the phase separator was insulated completely to avoid heat losses. Fig. 1 shows a schematic of the desorption system.

The CO_2 loading in the liquid samples was determined by the standard method given by the Association of Official Analytical Chemists (AOAC) using a Chittick apparatus [31]. According to this method, a specific volume of liquid is added to the conical flask with methyl orange as an indicator. Then the sulfuric acid solution from a burette is added to the liquid sample. The sulfuric acid solution contains 200 g of sodium sulfate and 40 ml of concentrated sulfuric acid in 800 ml distilled water. By adding the sulfuric acid solution, CO_2 is released from the solution and exits the flask. The CO_2 loading of the liquid sample is obtained by measuring the volume of CO_2 and calculated as follows:

$$\alpha_{CO_2} = \frac{mol_{CO_2}}{mol_{Amine}} \tag{1}$$

while the number of moles of the Amine is calculable by $C_{Amine} \times V_{Amine}$, the number of the CO_2 moles can be returned using its released volume.

Since MeOH and water were evaporated at a high temperature,

Table 1
Physical properties of materials used.

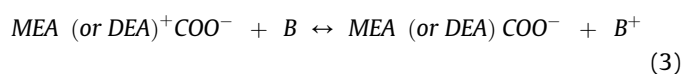| Material	Chemical formula	Molecular weight gr/mol	Purity	Boiling point °C at 760 mm Hg
MEA (Monoethanolamine)	C_2H_7NO	61.08	99.9 vol%	170
DEA (Diethanolamine)	$C_4H_{11}NO_2$	105.14	99.9 vol%	280
MDEA (Methyldiethanolamine)	$CH_3N(C_2H_4OH)_2$	119.16	-	247
PZ (Piperazine)	$C_4H_{10}N_2$	86.14	-	146
HCl (Hydrochloric acid)	HCl	36.46	98 vol%	85
Sodium sulfate	Na_2SO_4	142.04	99 wt%	1429
Methanol	CH_3OH	32.04	99.9 vol%	64.7
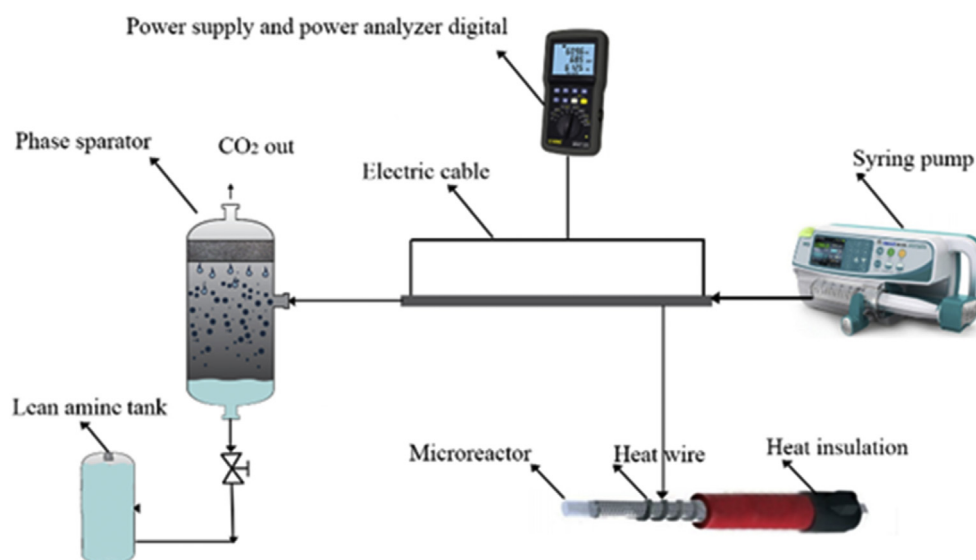
**Fig. 1.** Schematic of the CO_2 desorption operation system.

using titration, the change in the solvent concentration was calculated compared to the amount of amine present in it, and its effect on the amount of the final load was applied. It should be noted that although the basis of separation is a flashing phenomenon, due to the lack of transparency of stainless steel, this flow phenomenon was not studied.

2.3. Determining the rate of mass transfer

The significant contribution of CO_2 absorption by alkanolamine is due to the chemical reaction. The most common stoichiometry of the reaction of type-I and −II alkanol amines, such as MEA and DEA, has been reported as follows [32−37]:

$$MEA \ (or \ DEA) \ + \ CO_2 \ \leftrightarrow \ MEA \ (or \ DEA)^+COO^- \qquad (2)$$

$$MEA \ (or \ DEA)^+COO^- \ + \ B \ \leftrightarrow \ MEA \ (or \ DEA) \ COO^- \ + \ B^+ \qquad (3)$$

In equation (3), B represents the reactive base. This mechanism, known as the Zwitterion mechanism, consists of two steps. In this way, the overall reaction of the primary and secondary amines is as follows:

$$2MEA \ or \ DEA) \ + \ CO_2 \ \leftrightarrow \ MEA \ or \ DEA) \ COO^- \ + \ MEA \ (or \ DEA)^+ \qquad (4)$$
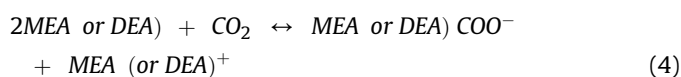
Stoichiometric identification of type III alkanolamines, especially activated tertiary alkanol amines, such as a-MDEA, is slightly more complicated than the stoichiometry of types I and II alkanolamines. The overall a-MDEA reaction with CO_2 is as follows [38−40]:

$$PZ \ + \ MDEA \ + \ CO_2 \ \leftrightarrow \ PZ \ COO^- \ + \ MDEA^+ \qquad (5)$$

PZ is an annular secondary amine, which, as expected, forms the ion of carbamate through the mechanism of Zwitterion. In other words, PZ is weak in protonation. Therefore, it plays a basic role in a parallel and simultaneous reaction of MDEA, which is considered a strong deprotonation form. In other words, the reaction rate of PZ is so high that no other PZ remains for the reaction. For this reason, the mixed-use of MDEA and PZ has the advantage of using high PZ absorption and high absorption capacity of MDEA simultaneously.

The Arrhenius relationship proves that all the reactions are performed at higher temperatures at a higher rate. However, for exothermic reactions, such as CO_2 absorption based on the fact that the reactions of CO_2 absorption are reversible and equilibrium

reactions, increasing the temperature can decrease the reaction product (carbon dioxide-rich amine), although the increase in temperature, based on the Arrhenius relationship due to the increase of the molecular movement, increases both reaction rates. In other words, at a high temperature, the absorption reaction (forward) versus the desorption reaction (backward). Therefore, it is expected that by increasing the temperature, the experimental conditions only favor the desorption operation. The above reactions are true for both the aqueous and non-aqueous media. The only difference between aqueous and non-aqueous solutions is the difference in the reaction rate constant so that non-aqueous solutions (methanol) increase the reaction rate constant slightly [41].

CO$_2$ is absorbed in both chemical and physical forms by aqueous and non-aqueous alkanolamine solutions. According to two-film mass transfer theory (which is schematically shown in Fig. 2), the mass transfer flux is as follows [42]:

$$N_{CO_2}a_V = k_L a_V (x_{b.CO_2} - x_{i.CO_2}) \tag{6}$$

In the above relation, $N_{CO_2}a_V$ and $k_L a_V$ are, respectively, the total mass transfer flux and the local mass transfer coefficient based on the liquid phase. The total transfer mass flux from the CO$_2$ mass equilibrium at the inlet and outlet of the microreactor is as follows [29,43]:

$$N_{CO_2}a_V = \frac{Q_L x_{Amine}}{V_r}(\alpha_{in} - \alpha_{out}) \tag{7}$$

where V_r is the volume of the reactor, and Q_L is the liquid flow rate. By combining the relations (6) and (7), the local volumetric liquid mass transfer coefficient is obtained as follows:

$$k_L a_V = \frac{Q_L x_{Amine}}{V_r} \frac{(x_{b.CO_2} - x_{i.CO_2})}{(\alpha_{in} - \alpha_{out})} \tag{8}$$

In equation (8), $x_{b.CO_2}$ is the molar concentration of CO$_2$ in the liquid phase, which can be obtained by averaging as follows:

$$x_{b.CO_2} = \frac{x_{in.CO_2} - x_{out.CO_2}}{\ln\left(\frac{x_{in.CO_2}}{x_{out.CO_2}}\right)} \tag{9}$$

Also, $x_{i.CO_2}$ is the concentration of CO$_2$ in the liquid phase and the gas-liquid interface. Generally, the concentration of CO$_2$ in the liquid phase and at the gas-liquid interface is in equilibrium with the gas phase. In other words, the concentration of CO$_2$ that can dissolve in the amine solution depends on the partial pressure of CO$_2$ and temperature due to Henry's Law. Therefore, using Henry's law, the concentration of CO$_2$ may calculate as follows [11,29,44]:

$$x_{i.CO_2} \cong x_{eq.CO_2} = \frac{P_{CO_2}}{He} = \frac{(P_t - P_{H_2O})}{He} \tag{10}$$

An important criterion in determining and comparing the rate of chemical and physical absorption is the enhancement factor. The enhancement factor is expressed as the ratio of the chemical absorption rate to the physical absorption rate. The enhancement factor based on the dimensionless quantity of Hata (Ha) is defined as follows [45]:

$$Ha = \frac{k_{L.chem}}{k_{L.phys}} \tag{11}$$

$$E = \frac{Ha}{\tanh(Ha)} \cong Ha \tag{12}$$

Equation (12) is true when the value of Ha is greater than 3. In this case, $\tanh(Ha)$ will become approximately equal to 1. The kinetic study of the CO$_2$ absorption reaction with alkanolamine shows that the local liquid mass transfer coefficient for the chemical reaction is as follows [41,46]:

$$k_{L.chem(for\ MEA\ or\ DEA)} = \sqrt{(k_{MEA\ or\ DEA}^* x_{MEA\ or\ DEA} + k_B^* x_B)D_{CO_2}} \tag{13}$$

$$k_{L.chem(for\ a-MDEA)} = \sqrt{(k_{MDEA}^* x_{MDEA} + k_{PZ}^* x_{PZ})D_{CO_2}} \tag{14}$$

In equation (13), $k_{L.phys}$ is the local liquid mass transfer coefficient for physical absorption, which was obtained as follows [47]:

$$k_{L.phys} = 2\sqrt{\frac{D_{CO_2}}{\pi\tau}} \tag{15}$$

$$\tau = \frac{V_r}{Q_L} \tag{16}$$

In this study, the percentage of CO$_2$ desorption θ was calculated as follows:

$$\theta = \frac{\alpha_{in} - \alpha_{out}}{\alpha_{in}} \tag{17}$$

Accordingly, the CO$_2$ loading, enhancement factor, percentage of CO$_2$ desorption, and local mass transfer coefficient were selected for evaluation of this study.

2.4. Operational conditions
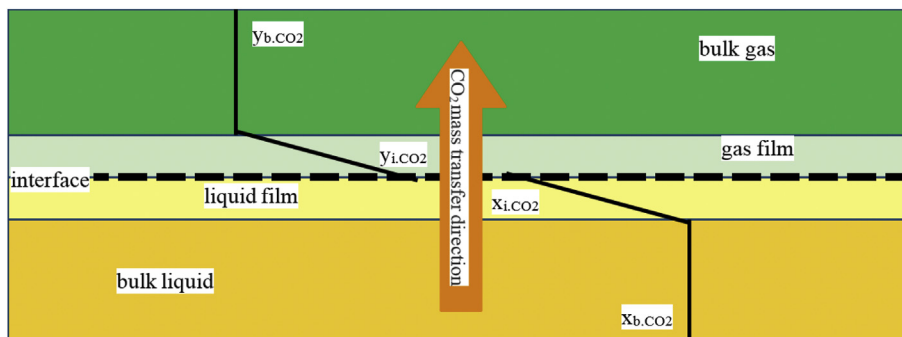
The input liquid phase for the aqueous and non-aqueous

Fig. 2. Schematic of the two-film mass transfer theory CO$_2$ desorption.

Table 2
Operation parameters and their levels for the desorption process.

Parameter	Unit	Value
Temperature	°C	50, 60, 70, 80, 90, 100
flow rate of rich amine	ml/min	0.5, 1.5, 2.5, 3.5, 4.5
Amine Concentration	wt%	10, 20, 30, 40, 50
Pressure	atm	≈ 1
Amine Loading	mol CO_2/mol amine	MEA: 0.48
		DEA: 0.70
		a-MDEA: 0.90

solutions of MEA, DEA, and a-MDEA have a charge of 0.48, 0.70, and 0.95 mol of CO_2 per amine mole, respectively. All experiments are carried out under atmospheric pressure. Due to the wide range of alkanolamines and the presence of methanol, a wide range of temperatures were considered. The temperature varied between 50 and 100 °C.

Regarding the retention times, we tested solvent flow rates from 0.5 to 4.5 ml/min. As based on the Hagen-Poiseuille equation, the pressure drop was estimated at 0.01 bar along the microreactor; the pressure drop has not been measured experimentally. Finally, regarding the conventional operational concentrations, for all solutions, the concentration variation range was considered from 10 to 50%. Table 2 summarizes all the main operational conditions.

3. Results and discussion

3.1. The effect of temperature

It can be inferred from the equilibrium lines that the solvent CO_2 desorption process is driven by temperature. Naturally, increasing temperatures led to larger differences solution in CO_2 loading (Fig. 3-a), between the input and output for all six solvent mixtures tested: MEA-WATER, DEA-WATER, a-MDEA-WATER, MEA-MeOH, DEA-MeOH, and a-MDEA-MeOH (Fig. 3a). At both low (50 °C) and high (100 °C) temperatures, the α values are approximately similar for both aqueous and non-aqueous alkanolamine solutions and only dependent on the alkanolamine solvent used. In terms of percentage CO_2 desorption (Fig. 3-b), the plots showed a concave shape for the aqueous solutions, whereas in the non-aqueous solutions, we observed convex shape plots, with the last being similar to the absorption/desorption equilibrium graph. Due to the lower boiling point of methanol (~65 °C), the most significant jump in CO_2 desorption was seen for the lower temperatures and alkanolamine-methanol mixtures.

Fig. 3-c shows that an increase follows the increase in CO2 desorption in $k_L a_v$. The increase in temperature enhanced the rate of the chemical reaction, which favors the forward reaction. On the other hand, increasing temperatures resulted in more effective molecular penetration in the liquid phase, with the CO_2 dissolved in a rich solvent reaching the gas-liquid interface more easily. We
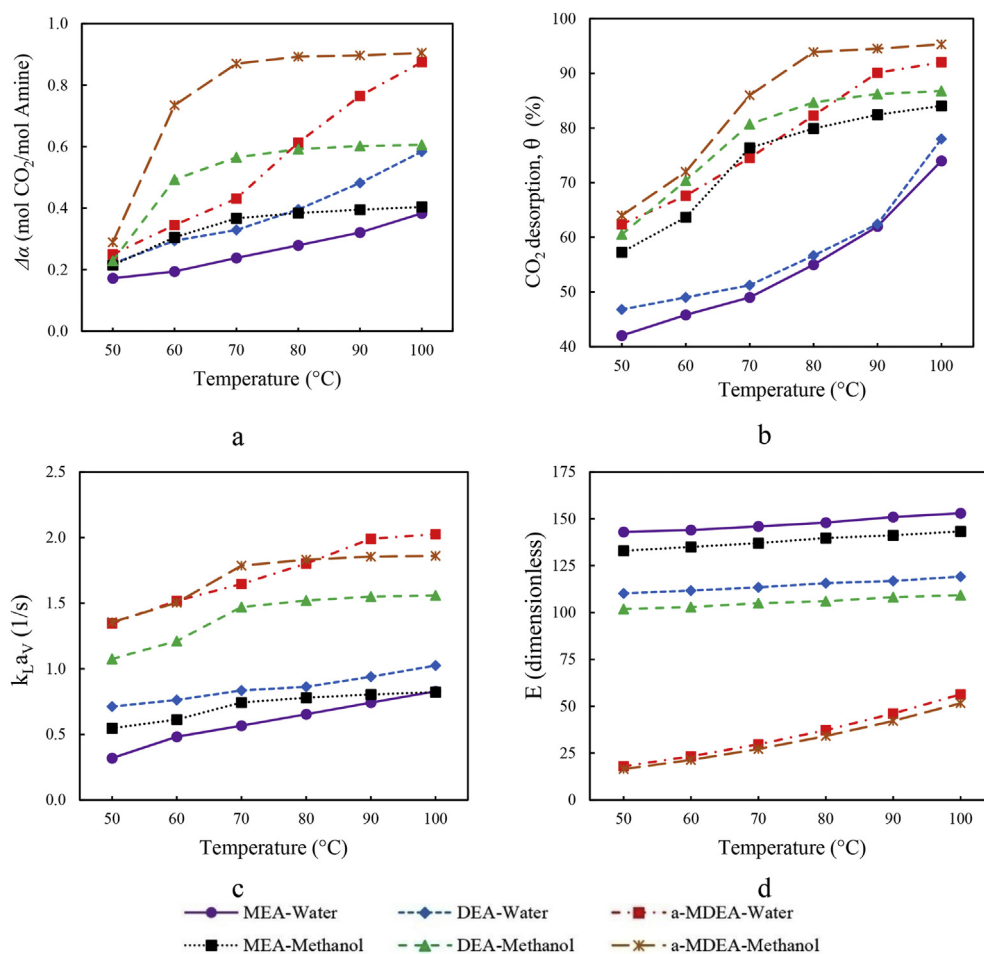
Fig. 3. The effect of temperature on (a) the difference in CO2 loading, α between input and output, (b) the desorption percentage, (c) the liquid-side volumetric mass transfer coefficient, kLav, and (d) the enhancement factor, E. These experiments were conducted using 2.5 ml/min aqueous amine and 30 wt% of amine concentration.

have not analyzed in this study the flow hydrodynamics within the tubular microreactor; however, one can expect intense gas-liquid mixing as dissolved CO_2 was released from the liquid solvent mixture, with decreasing film thickness in the interface. Naturally, $k_L a_v$ increased with an increase in temperature. We estimated the $k_L a_v$ values in the range of 0.3−2.0 in the range of conditions tests, which corresponded with the values reported in the literature [29].

The Enhancement factor, E was found to reduce as CO_2 absorption performance of the solvent mixture improved, meaning physical desorption was improved by increasing the molecular permeability coefficient. We found that E values remained almost independent of temperature for the MEA and DEA solvent mixtures and showed a positive correlation with temperature for the a-MDEA mixtures. Increasing the temperature improves physical and chemical desorption simultaneously, in contrast to the CO_2 absorption process whereby physical desorption occurs alongside chemical desorption.

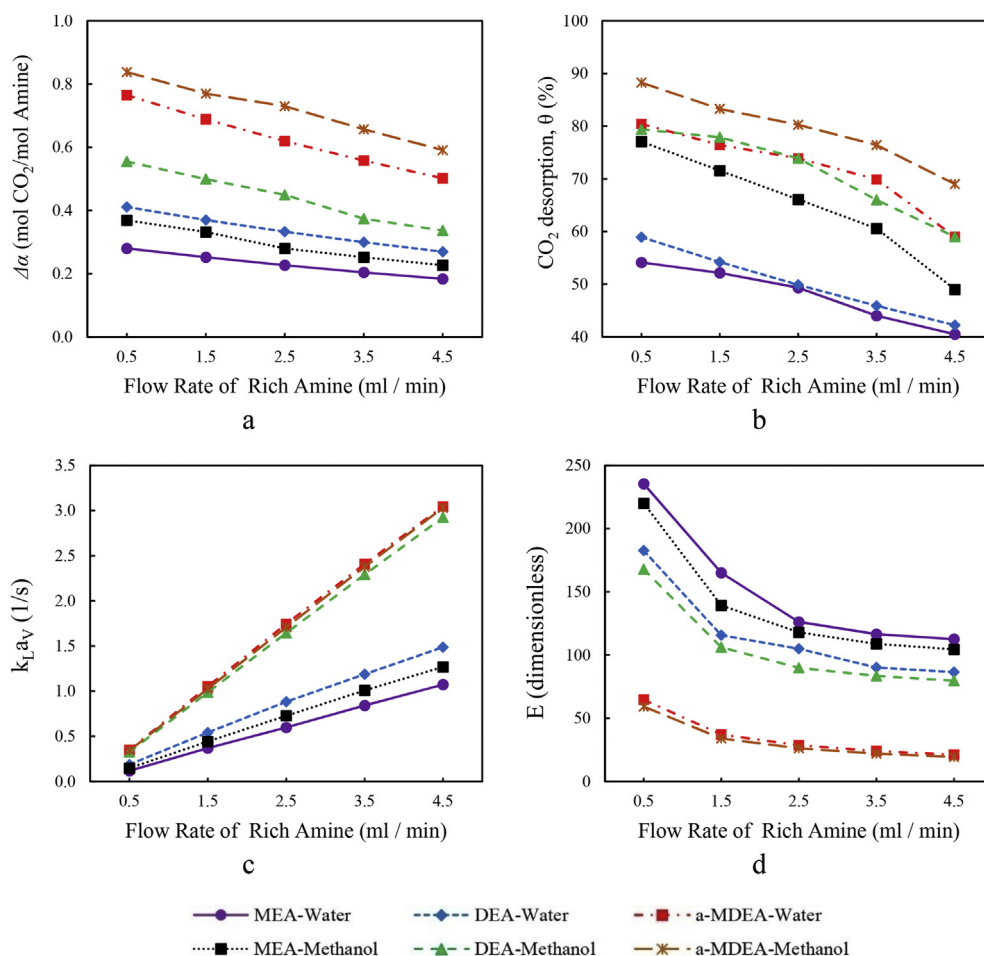### 3.2. The effects of the flow rate of rich amine

Increasing the rich solvent flow rate in the microreactor has the natural consequence of shortening the retention time. Therefore, we observed a negative linear correlation between the flow rate of rich amine, CO_2 loading, and CO_2 desorption (Fig. 4a and b, respectively). The values of $K_L a_v$ increased linearly with the increase in flow rate (Fig. 4c), presumably through an increase in the heat

transfer rate through the wall of the tube. It shows the possibility of increasing the mass transfer for CO_2 desorption in a microreactor system and a more rapidly approaching equilibrium CO_2 concentration given by equation (8). Previous studies [48,49] can justify this behavior that at a low flow rate of rich amine, the mass transfer in the interface of two phases is too weak. However, by increasing the flow rate of rich amine making two phases increased, and the mass transfer coefficient that mainly depends on interface diffusion increased sharply.

The E values decreased with the increasing flow rate for all six solvents mixtures tested (Fig. 4-d), which according to equations (15) and (16), represents an increase in the physical mass transfer coefficient because E represents the ratio of reaction rate to the mass transfer rate, and an increasing mass transfer coefficient causes a decrease E for all six solvents mixtures.

3.3. The effects of amine concentration

In line with the surface-renewal theory for mass transfer, an increasing concentration of amine resulted in a larger number of available amine sites occupied by CO_2, thereby enhancing the difference in CO_2 loading and the CO_2 desorption rate (Fig. 5-a and 5-b, respectively). The $K_L a_v$ values increased linearly with the amine concentration due to the mass transfer driving force (Fig. 5-c). Interestingly, the E values (Fig. 5-d) also increased with the increasing amine concentration for all six tested solvent mixtures.

Fig. 4. The effect of flow rate of rich amine on (a) the input and output difference loading, (b) the desorption percentage, (c) the liquid-side volumetric mass transfer coefficient, and (d) the enhancement factor, based on an 80 °C temperature and 30 wt% the amine concentration.
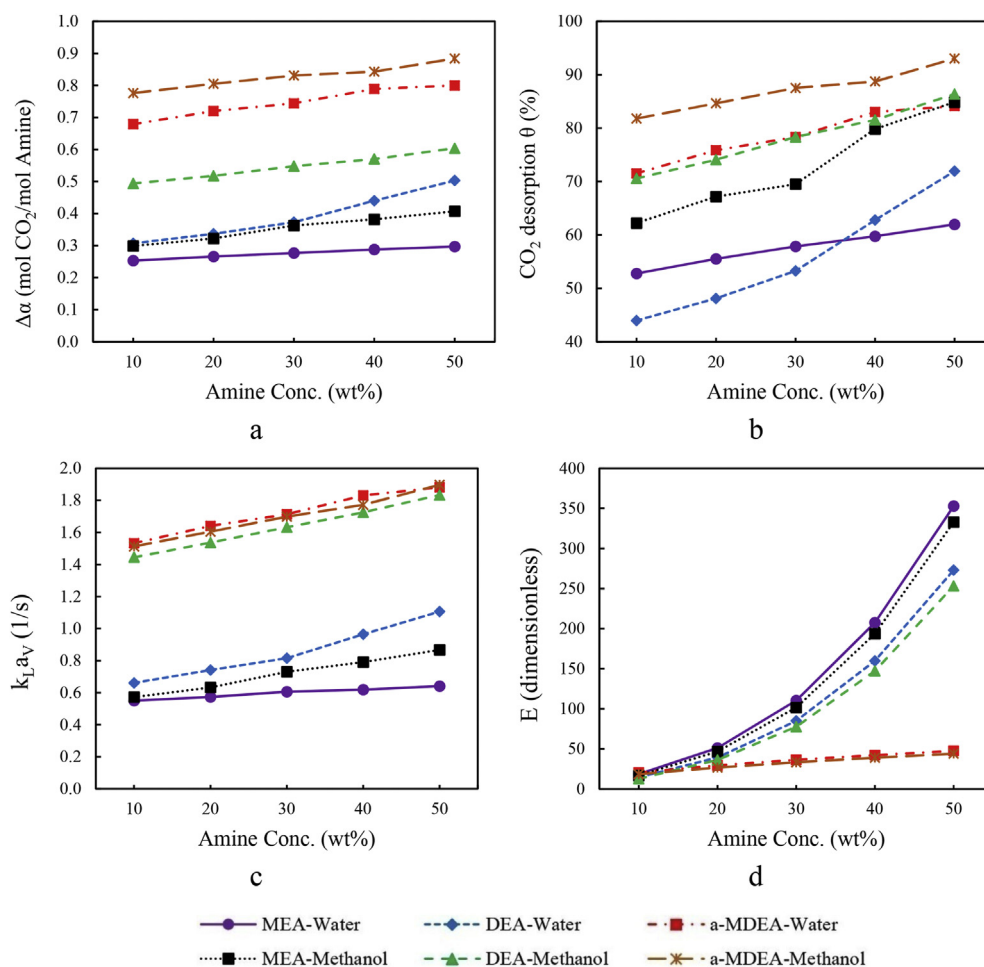
Fig. 5. The effect of amine concentration on (a) the input and output difference loading, (b) the desorption percentage, (c) the liquid-side volumetric mass transfer coefficient, and (d) the enhancement factor, based on 80 °C temperature and 2.5 ml min^{-1} aqueous amine.

By increasing the amine concentration, more active sites have existed; therefore, more CO_2 molecules can absorb, resulting in increasing all criteria of the desorption process.

We observed that the amine concentration had little effect on the mass transfer, with the biggest factor being the type of amine. It has a direct impact on the design of the CO_2 desorption system. In general, a change in the type of amine has a more positive outcome concerning mass transfer compared to increasing the amine concentration. The results in Figure 5c also show that, in general, the DEA-methanol mixture presents a K_La_v value 2–3 times larger than any of the aqueous mixtures tested. According to the literature [50], this behavior can be interpreted by the difference Henry's law constant of CO_2 in MeOH and H_2O.

3.4. Desorption energy consumption

CO_2 desorption is energetically very intensive because the desorption process is driven by rapid changes in the solubility of dissolved CO_2 as the temperature of the solvent changes. Therefore, we calculated the energy efficiency of the desorption process η as the energy consumed per desorbed CO_2:

$$\eta = \frac{Q}{\dot{m}_{CO_2}} \qquad (18)$$

where Q and $\dot{m}_{CO_2}$ are the absolute energy consumed (MJ) and CO_2

desorbed (Kg), respectively. In this setup, an increase in the temperature of the microreactor results in a direct increase to the energy consumed; however, the use of higher temperatures results in an enhanced rate of desorption increasing also the CO_2 desorption. Therefore, the temperature is a reciprocal factor of η.

Fig. 6-a shows that as the temperature increases, the value of η rapidly decreases, more significant for aqueous solvent mixtures. This graph also shows that a further increase in temperature has little benefit concerning CO_2 desorption, only increasing energy consumption for the process.

Increasing the solvent flow rate also, in general, results in increased energy consumption, represented by a linear increase in the η values in Fig. 6-b, where an increase in amine concentration (Fig. 6-c) results in a reduction in η.

3.5. Optimization and comparison

A further experimental run enabled the direct comparison of solvents and testing the effect of methanol and water on the efficiency of CO_2 absorption. Fig. 7-a and 6-b show that in similar operational conditions, non-aqueous alkanolamine solvents perform better in terms of the percentage of CO_2 desorption percentages and the mass transfer coefficient compared to aqueous mixtures. It is linked to larger desorption rates at lower temperatures for non-aqueous alkanolamine solutions. However, the results also show that primary and secondary amines are more appropriate
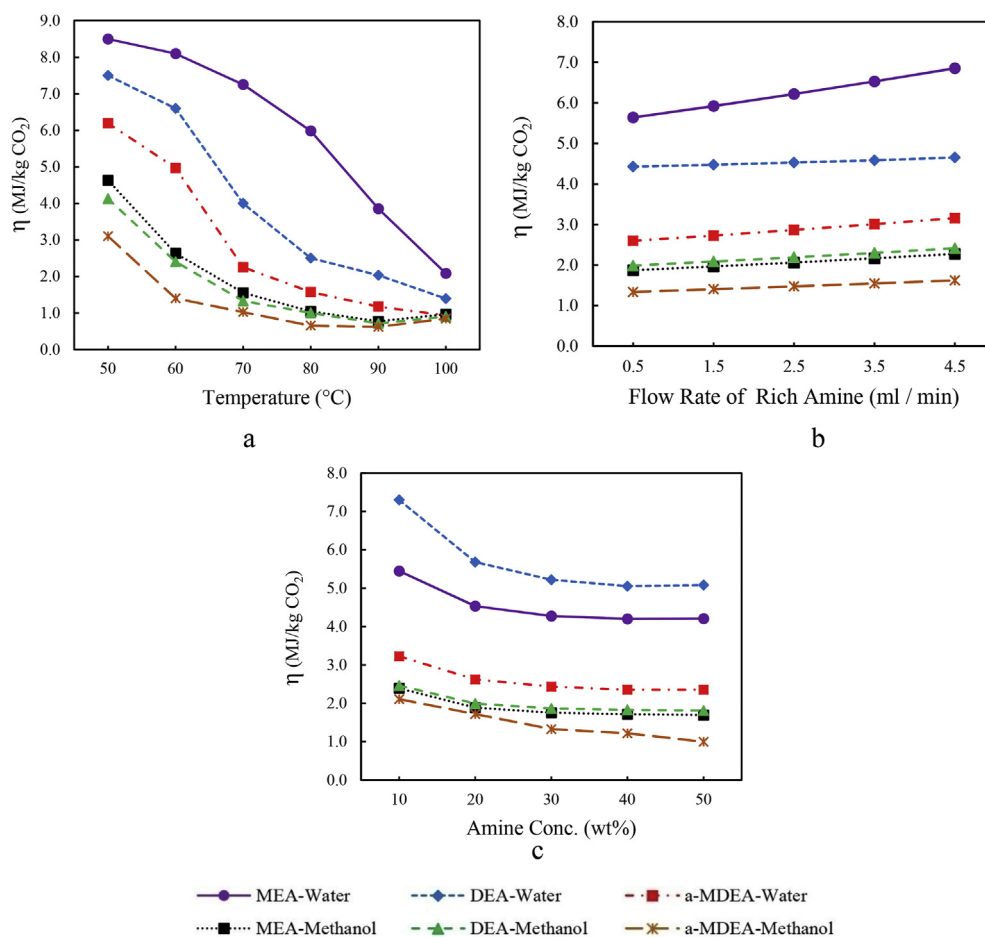
Fig. 6. The effect of different operating conditions on energy consumption.

than a-MDEA, with Fig. 7-c showing that the use of methanol reduces E (less than 5%), which is presumably linked to a difference in the physical properties of methanol and water, such as viscosity and CO_2 solubility, as well as their chemical reaction constants. The enhancement factor is the criterion of the chemical bond in the rate of the absorption and desorption process, and it is therefore responsible for the differences between the chemical bonds of water and methanol and its contribution to the desorption process.

Overall, the biggest impact regarding energy efficiency was found in the replacement of methanol with water (Fig. 7-d), with non-aqueous alkanolamine solutions presenting the η values 2.0–3.5 times lower than the aqueous solutions. The addition of methanol to amine increases the CO_2 desorption rate at lower temperatures by decreasing the solvent boiling point. The operation of CO_2 desorption at low temperatures has the benefit of reducing operating costs. For non-aqueous solutions of MEA, DEA, and a-MDEA, we obtained the η values equal to 0.380, 0.371, and 0.301 MJ/kg CO_2, respectively, therefore one order of magnitude smaller than the values reported for the packed bed columns or the previous microreactor work of Liu et al. [30]. As shown, the use of MeOH instead of water can reduce the amount of η from 50 to 73%, depending on the type of amine.

In Fig. 8, the obtained η values were compared with other studies in literature, demonstrating that the tubular microreactor reduced by around 88% compared to the packed columns (the most common mass transfer device in the CO_2 absorption process) [26,51–53]. It should be mentioned that the type of solvent and the type of reactor can both contribute to reducing the overall energy consumption. However, it is not possible to change the solvent type; only then can the replacement of the reactor system can be effective in reducing energy consumption.

4. Conclusions

By studying CO_2 desorption from aqueous and non-aqueous solutions of alkanolamine (MEA, DEA, and a-MDEA) in a tubular microreactor, we concluded that increasing temperatures led to an increased percentage of the CO_2 desorption percentage and improved mass transfer coefficients. On the other hand, by increasing the rich solvent flow, the percentage of desorption was decreased, and the mass transfer coefficient increased. Despite the higher ability of the aqueous solution of MEA to absorb CO_2, it required a higher energy demand for solvent recovery (>3 MJ/kg CO_2). Consequently, non-aqueous solvent mixtures led to a substantial reduction in energy recovery to <1.5 MJ/kg. In particular, the use of methanol instead of water in the amine mixture reduced desorption energy consumption by about 73%, except for the a-MDEA mixture. In optimal conditions, CO_2 desorption in the microreactor improved the mass transfer efficiency and reduced energy consumption by 88%. These results will inform solvent mixtures and intensified desorption designs to help improve the sustainability and environmental impact of solvent CO_2 capture. Based on successful examples reported in the literature, it is possible to scale-up by numbering up this microreactor approach for CO_2 capture/desorption to achieve the demands of an industrial plant by, for example, designing the device as a packed column.
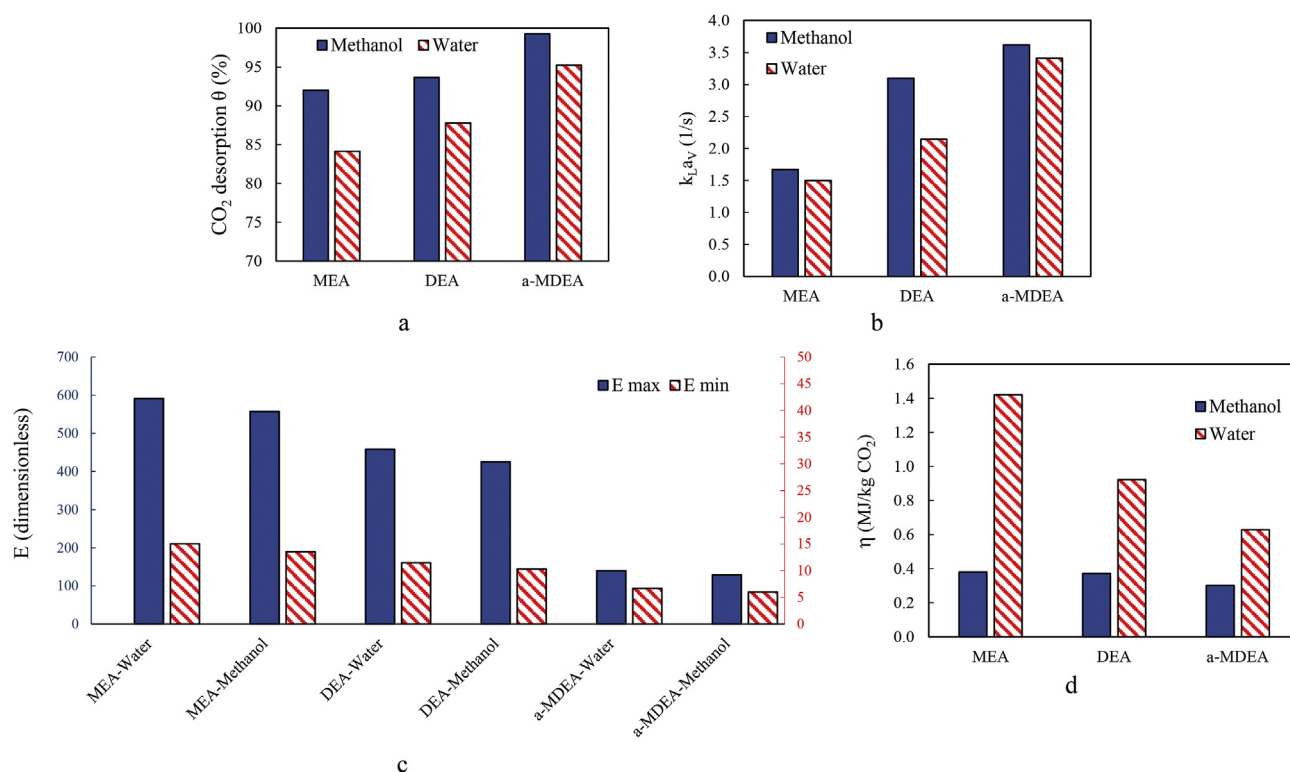
Fig. 7. A comparison of solvents in terms of a) the desorption percentage, b) the mass transfer coefficient based on liquid-phase, c) the enhancement factor, and d) the consumption of energy in optimal operating conditions.
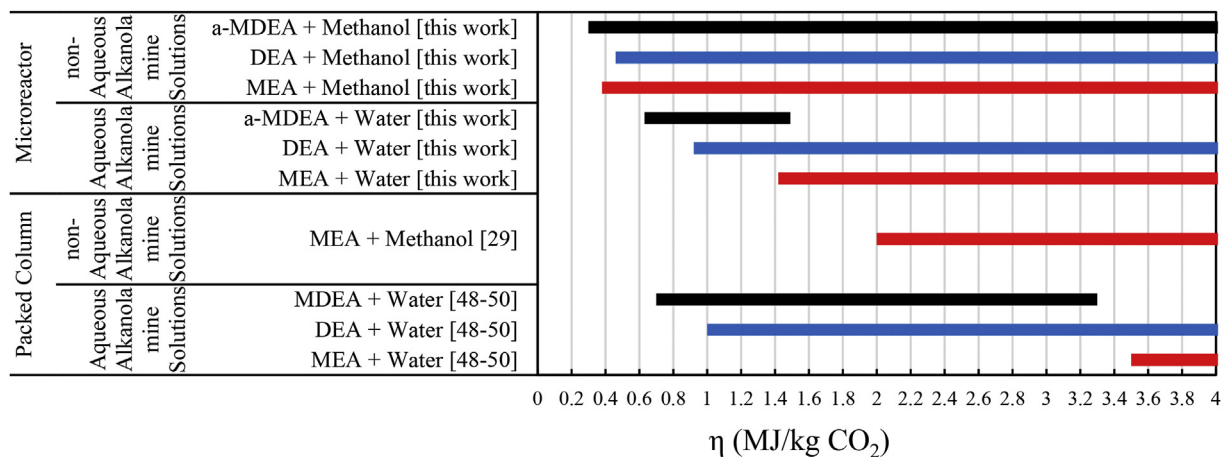
Fig. 8. Comparison of ranges of CO_2 desorption energy consumption (η), achieved by different gas-liquid absorption systems and various solvents.

Future research should explore in-depth the hydrodynamics and detailed thermal analysis in the tubular microreactor to fully understand the underpinning phenomenon responsible for the mass transfer and energetic improvements reported in this study.

Nomenclature

Symbols and abbreviations

a_V	Interfacial area per volume, m^2/m^3
R	Universal gas constant, l.kPa
C	Solution concentration, mol/l
V	Volume, ml
x	Amine mole fraction, $kmol/m^3$
D	Diffusion coefficient, m^2/h
$K_L a_V$	Overall mass transfer coefficient based on liquid phase, 1/h
$k_L a_V$	Liquid-side volumetric mass transfer coefficient, 1/h
N	Mass transfer flux, $kmol.m^{-2}.h^{-1}$
n	Molar flow rate of gas, $kmol.h^{-1}$
Ha	Hata number, dimensionless
He	Henry's law constant, $kPa \cdot l^3/mol$
E	Enhancement factor, dimensionless
P	Total system pressure, kPa
k*	Reaction rate constant
T	Temperature, K

Greek letters

α CO_2 loading, mol CO_2/mol Amine
θ The percentage of absorption, %

Abbreviations

B   Reactive base
He   Henry coefficient
MEA   Monoethanolamine
DEA   Diethanolamine
MDEA   Methyldiethanolamine
PZ   Piperazine
a-MDEA   Activated methyldiethanolamine
MeOH   Methanol
CCS   Carbon capture and storage

Subscripts

g   Gas phase
L   Liquid phase
CO_2 Carbon dioxide
in   Inlet
out   Outlet
chem   Chemical
phys   Physical
Amine   Alkanolamine
r   Reactor
t   Total
eq   Equilibrium

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