Applied Energy xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

# Energy-efficient solvent regeneration in enzymatic reactive absorption for carbon dioxide capture

Mathias Leimbrink[a,*], Stephanie Sandkämper[a], Leigh Wardhaugh[b], Dan Maher[b], Phil Green[b], Graeme Puxty[b], Will Conway[b], Robert Bennett[b], Henk Botma[b], Paul Feron[b], Andrzej Górak[a,c], Mirko Skiborowski[a]

[a] TU Dortmund University, Laboratory of Fluid Separations, Emil–Figge–Straße 70, 44227 Dortmund, Germany
[b] CSIRO Energy, PO Box 330, Newcastle, NSW, Australia
[c] Lodz University of Technology, Faculty of Process and Environmental Engineering, Department of Environmental Engineering, Wólczanska 213, Lódz 90-924, Poland

## HIGHLIGHTS

- Extensive experimental investigation of solvent regeneration with loaded MDEA solutions.
- Innovative IR analytic method successfully applied to loaded MDEA solutions.
- Developed model showed good agreement with experimental data.
- 40% improvement in energy requirement compared to MEA as baseline solvent.

## ARTICLE INFO

*Keywords:*
Solvent regeneration
Pilot scale testing
Rate-based modeling
Energy efficiency
Carbon capture
Enzyme carbonic anhydrase

## ABSTRACT

Although recent studies on the application of enzyme-catalyzed reactive absorption of carbon dioxide ($CO_2$) with thermodynamically favorable solvents such as tertiary amine N-methyldiethanolamine (MDEA) have demonstrated competitiveness with kinetically favorable solvents such as primary amine monoethanolamine (MEA), experimental data on the desorption of $CO_2$ in MDEA are scarce. However, these data are necessary to validate the energetic benefit expected from an enzyme-catalyzed reactive absorption process with an aqueous MDEA solvent. To bridge this gap, the current work presents the experimental results of aqueous MDEA solvent regeneration at the pilot scale with consideration of different solvent flow rates, $CO_2$ loadings and applied reboiler duties. Furthermore, a process model that accurately describes the experimental data was developed to evaluate the energy requirements in a closed-loop absorption-desorption process. For this purpose, the desorption process model was extended using a previously validated enzymatic reactive absorption model to determine the energy efficiency of the overall enzymatic reactive absorption-desorption process. Although the MEA benchmark process requires a specific reboiler duty of approximately $3.8\ MJ\cdot kg_{CO_2}^{-1}$, it was found that this value could be reduced by more than 40% to $2.13\ MJ\cdot kg_{CO_2}^{-1}$ with use of the enzymatic reactive absorption process based on aqueous MDEA solvent.

## 1. Introduction

A strong decrease in the greenhouse gas emissions from various industrial processes, especially fossil-fueled power plants, is a major climate goal that is expected to occupy academia, industry and policy-making in the coming decades [1]. The need to reduce greenhouse gas (GHG) emissions such as carbon dioxide ($CO_2$) by 80–95% before 2050 relative to the 1990 emissions has been proposed by the European Union as a roadmap to a low-carbon economy [2]. Innovative process concepts and novel routes must be developed to meet this ambitious goal while simultaneously enabling reliable and environmental-benign generation of target products and services. In addition, existing plants must be retrofitted with efficient technologies capable of mitigating climate relevant emissions [3]. In this scenario, post-combustion carbon

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*Abbreviations:* $CO_2$, carbon dioxide; CSIRO, Commonwealth Scientific and Industrial Research Organisation; DI, deionized; DOR, degree of regeneration; GHG, greenhouse gas; IR, infrared; MDEA, N-methyldiethanolamine; MEA, monoethanolamine; $N_2$, nitrogen; NEQ, non-equilibrium; PCC, post combustion carbon dioxide capture; PDF, process development facility; PLSR, partial least-squares regression; SRD, specific reboiler duty; VLE, vapor-liquid-equilibrium

[*] Corresponding author.

*E-mail address:* mathias.leimbrink@tu-dortmund.de (M. Leimbrink).

http://dx.doi.org/10.1016/j.apenergy.2017.10.042
Received 20 June 2017; Received in revised form 7 September 2017; Accepted 6 October 2017
0306-2619/

Please cite this article as: Leimbrink, M., Applied Energy (2017), http://dx.doi.org/10.1016/j.apenergy.2017.10.042

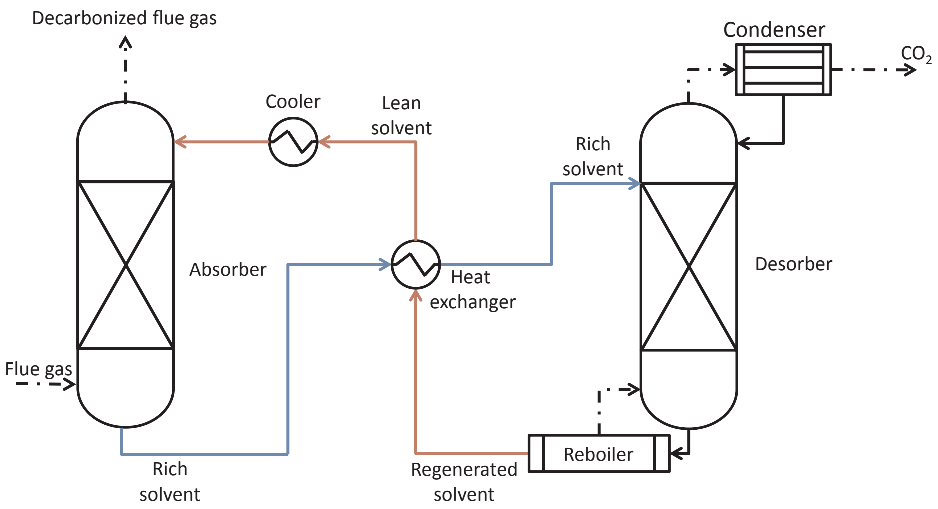

**Fig. 1.** Simplified process scheme of typical amine-based reactive absorption processes.

dioxide capture (PCC) represents the most mature mitigation technology for simple and effective retrofit of existing power plants.

Currently, most PCC processes use amine-based reactive absorption in capture unit operation [4]. Industrial PCC plants are few in number, and most are located in North America where the captured $CO_2$ can be used in enhanced oil recovery. A simplified process scheme the amine-based reactive absorption process is shown in Fig. 1. However, as recently noted by the International Energy Agency, a large discrepancy still exists between the planned reductions in GHG emissions and the currently applied PCC processes that consequently endanger the achievement of global climate goals [5]. The major reason for this lack of application is the large difference between the capture costs of $CO_2$ and the value of $CO_2$ certificates. Although the latter concept was originally introduced to promote $CO_2$ capture, it is currently its biggest handicap. Therefore, to increase the number of PCC applications, more energy-efficient $CO_2$ capture processes must be developed to make capture costs more competitive compared with $CO_2$ certificate prices. Among the few currently applied amine-based reactive absorption processes, which use primary or piperazine promoted amine solvent systems, the high energy requirement for solvent regeneration is an important factor because it could add up to 80% to the costs of electricity [6,7].

Despite its fairly detrimental thermodynamic properties, especially low cyclic loadings and high heat of reaction, monoethanolamine (MEA) is accepted as a baseline solvent because it offers high absorption rates that lead to reduced equipment size. Nevertheless, other solvents such as tertiary amines offer much higher $CO_2$ loading capacities and lower heat of reactions, thus enabling significant potential for energy requirement reductions [8,9]. According to Oexmann and Kather [10], the energy requirement usually supplied by the reboiler ($Q_{reb}$) can be described as the sum of three main contributors:

$$Q_{reb} = Q_{sens} + Q_{des,CO_2} + Q_{vap,H_2O} \tag{1}$$

- $Q_{sens}$: Sensible heat used to increase the solvent temperature from the desorber inlet temperature (rich solvent) to the desorber outlet temperature (regenerated solvent temperature).
- $Q_{des,CO_2}$: Heat of $CO_2$ desorption (non-ideal mixing + heat of dissolution + heat of reaction).
- $Q_{vap,H_2O}$: Heat of evaporation used to produce the portion of water steam that serves as a stripping agent for $CO_2$ and does not recondense along the length of the column but is ultimately condensed in the top condenser.

In addition to fine tuning of the column pressure and liquid-to-gas ratios, $Q_{sens}$ can be optimized primarily by reduction of the solvent flow rate because a certain temperature difference between inlet and outlet streams of a desorber column is inevitable due to the underlying separation principle of reactive absorption, which is exploitation of the temperature-dependent solubility of $CO_2$ [10]. The solvent flow rate can be reduced if the $CO_2$ loading capacity of the solvent is increased. The other two contributors can also be considered as important factors of influence when aiming for more energy-efficient solvent regeneration and thus lowering the energy requirement and capture costs associated with $CO_2$ capture.

Referring to the detailed energetic assessment reported by Feron [11], the potential improvement in the energy performance of $CO_2$ capture processes is quite large. Therefore, significant reductions in the energy requirement can be expected from future generations of innovative absorption-based capture technologies, and according to Feron, bicarbonate forming solvents such as tertiary amines and alkali-carbonates offer a promising alternative [11]. In particular, tertiary amine N-methyldiethanolamine (MDEA) has several advantageous thermodynamic properties compared with primary amines, e.g., MEA and is known to operate well based on industrial experience from other acid gas removal processes [12]. It is worth mentioning that development of novel energy-efficient solvents such as 1-diethylamino-2-propanol [13,14] or the application of acid solid catalysts that facilitate amine-based desorption processes [15–17] can further contribute to reductions in the energy requirement for $CO_2$ capture processes.

MDEA has a significantly lower absorption enthalpy ($\Delta H_{abs,CO_2} \approx 55\ kJ\cdot mol_{CO_2}^{-1}$) compared with the value for MEA (approx. $\Delta H_{abs,CO_2} \approx 85\ kJ\cdot mol_{CO_2}^{-1}$) [18]. As clearly explained by Oexmann and Kather, a solvent with a low absorption enthalpy alone does not always lead to improved energy efficiency [10]. However, MDEA exhibits favorable temperature-dependent $CO_2$ solubility, which enables significant reductions in the amount of steam needed as a stripping agent in the desorber (lower $Q_{vap,H_2O}$) as well as high cyclic loading capacities that consequently reduce the required solvent flow rate [8,19].

Despite such promising thermodynamic properties, absent a promoter such as piperazine, aqueous MDEA is usually not considered as a viable option for $CO_2$ separation from flue gases due to slow reaction kinetics, which currently limit its application to processes with high $CO_2$ partial pressures (e.g., natural gas sweetening) [12]. To make MDEA ratewise competitive in a $CO_2$ capture from power plant flue gas scenario, several research groups have successfully demonstrated that high reaction rates can be achieved using carbonic anhydrase enzyme as a biocatalyst [9,20–26]. Although the majority of these studies have investigated the absorption performance of enzyme-accelerated absorption solvents, virtually no attention has focused on actual experimental evidence and evaluation of the assumed energy-efficient solvent regeneration. Therefore, the current work addresses this lack of