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Absorption of Carbon Dioxide using Enzyme Activated Amine Solution in Columns with Random Packings

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Packed columns with structured or random packings are widely used in gas cleaning processes. Especially columns filled with random packings cover a large part of such applications in industrial practice. However, most of the recent investigation on carbon dioxide absorption from flue gases or other gas sources containing carbon dioxide (CO_2) has been performed in columns equipped with structured packings, mostly due to their low pressure drop compared to other internals. CO_2 usually is absorbed from the gas stream by means of a solvent. Amongst others, amine mixtures have gained a major role as a chemical solvent in this context. Beside the absorption kinetics and capacity, the energy demand for the regeneration of the solvent is a key factor for the operating costs of CO_2 absorption plants.
In previous studies, enzyme activated amines have been studied in lab scale, in order to enhance the absorption kinetics and to reduce the energy demand for regeneration. Besides the small scale, these studies focused almost exclusively on columns with structured packings. Despite the known benefits of structured packings, they can be inferior to random packings for systems with solid content and systems with mass transfer resistance in the liquid phase. Therefore, this work investigates columns at significantly larger scale equipped with random packings and presents the results of an extensive experimental study using the enzyme activated amine solution for the absorption of CO_2. In particular, the different random packings McPac (Maćkowiak 2001) from stainless steel and ENVIPAC from plastic have been studied in a test plant with diameter of d_S=600 mm. Fluid dynamics and mass transfer characteristics have been measured using various liquid and gas loads, packing height and column diameter using the CO_2 inlet concentrations of ≥ 15 vol%.
The experimental results are used for the validation of a process model, implemented in Aspen Plus® simulation software. A good agreement between experimental results and the simulation of the complex, reactive absorption system is established.

1. Introduction

Carbon dioxide (CO_2) is an inert gas, which is generated from natural and anthropogenic sources. In the past years CO_2 was identified as a major contributor to global warming and the burning of fossil fuels releases notable amounts of CO_2 to the atmosphere. As a consequence the 2-Degree Goal was proposed which would result in a strong reduction of CO_2-emissions. Therefore in the last decade much research on separation of CO_2 was done (Morreale&Shi 2015). The reactive absorption of CO_2 with amine solution in packed columns have been already established in industrial scale cleaning of natural gas and is a proven technology. However, the typically used primary amines like Monoethanolamine (MEA) have a high energy demand for regeneration and low capacities due to their reaction mechanism. This results in elevated operating costs and inhibits the industrial scale use for CO_2 absorption from flue gas till now.
The tertiary amine N-Methyldiethanolamine (MDEA) is a promising amine solution because of a lower energy demand for regeneration and lower toxicity than MEA, but offers a poor reaction rate (Eq(1)).

$$\mathrm{CO_2 + R_1R_2R_3N + H_2O \leftrightarrows R_1R_2R_3NH^+ + HCO_3^-} \quad (1)$$

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For this reason much research aimed to use the favorable characteristics of MDEA, but improving the reaction rate (Morreale&Shi 2015). A common approach is a mixture of MDEA with Piperazine or MEA. This increases the reaction rate significant, but unfortunately the energy demand of regeneration as well. A more promising approach is the addition of an enzyme called Carbonic Anhydrase (CA). It has a fundamental function in animals by catalyzing the formation of CO_2 to bicarbonate HCO_3 (Eq(2)). CA enhances the overall reaction rate in an aqueous mixture with MDEA and is biodegradable (Morreale&Shi 2015).

$$\mathrm{CO_2 + H_2O \leftrightarrows HCO_3^- + H^+} \quad (2)$$

The applicability to enhance absorption of CO_2 with an enzyme was successfully investigated in laboratory scale columns with structured packings and is called enzymatic reactive absorption (ERA) (Leimbrink et al. 2017).

Most of the research on CO_2 absorption in packed columns has been performed in columns with structured packings, mainly due to their low pressure drops compared to tray and random packed columns. Anyway, structured packings have drawbacks compared to random packings in systems with solid content and systems with mass transfer resistance in the liquid phase. Therefore, it is worth to study random packings for CO_2 absorption in packed columns.

In the first part of this work the experimental results of ERA in columns with random packings will be presented. The second part will show the implemented model in Aspen Plus® to simulate the ERA and its validation with the experimental results.

2. Experimental set-up

2.1 Test plant

The experimental investigation of the random packings has been performed in an industrial scale DN600 test plant (ENVIMAC 2012) (see Figure 1). The test plant has been used for standardized characterization of column internals for many years and is equipped with industrial standard state-of-the-art measurement devices with a high degree of automatization (Hoffmann et al. 2007, Kunze et al. 2015). Experiments have been performed using MDEA-CA-water absorption system with stainless steel random packings type McPac 1 and random packings made of polypropylene type ENVIPAC 3 (see Table 2).

Figure 1: Picture of DN600 test plant for ERA with random packings.

A flow sheet of the DN600 test plant is shown in Figure 2. Compressed CO_2 is added to an air stream until the feed concentration of 15 vol% is reached. The air stream is pumped in a closed cycle to avoid the release of big amounts of CO_2 to the atmosphere. Measurement of the CO_2 concentration is performed online by an infrared CO_2 analyser, calibrated with a test gas. Concentrations are measured above and underneath the packing. Liquid samples at the inlet and the outlet are taken in order to close the mass balance and to determine MDEA and CO_2 concentration in the liquid phase. Also the pressure drop of the air stream through the packing is measured to determine fluid dynamics and the inlet and outlet temperatures of the fluids are measured. For experiments the slightly preloaded MDEA solution from Tank 1 is pumped by Pump 1 to the top of the column. From there the liquid flows countercurrently through the packing. The loaded MDEA-solution is pumped from the bottom of the column to Tank 2.

In Table 1 the key parameters of the test plant are summarized. The experiments were performed at ambient pressure and at a constant gas and liquid temperature of 298 K. The absorption experiments were done in a broad operational range for gas capacity factor F_V from 1 to 2 $Pa^{0.5}$ and specific liquid loads u_L from 6 to 40 $m^3/(m^2h)$.

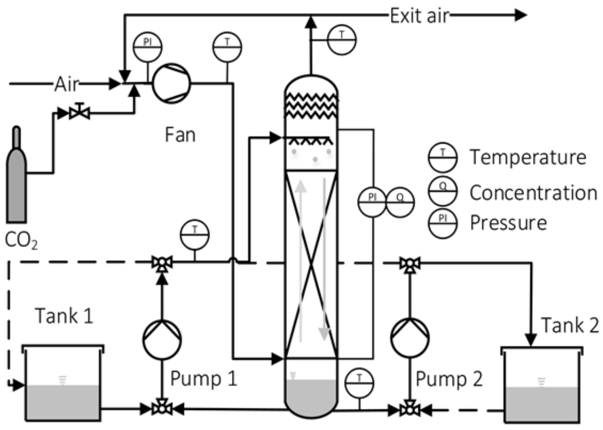

Figure 2: Flow sheet of the DN600 test plant used for ERA with random packings.

Table 1: Characteristics of the DN600 test plant.

Plant	H [m]	d_S [mm]	F_V [$Pa^{0.5}$]	u_L [m/h]	v_{CO_2} [vol%]	p [bar]	T [K]
DN600	3	600	1-2	6-40	~15	1	298

2.2 Random packings

This work examines the ERA in columns with random packings for the first time. For a broader investigation of the packing characteristics with an MDEA solution two highly different random packings are investigated. First, the metal random packing McPac 1, which offers a high specific surface area a_P with high void fraction ε_P and high separation efficiency (see Table 2) and second, the plastic random packing ENVIPAC 3, which offers a high resistance to corrosion, low specific surface area and low pressure drop.

Table 2: Investigated random packings in this work (Maćkowiak 2010).

Packing	Material	d [mm]	a_P [m^2/m^3]	ε_P [-]
McPac 1	Stainless steel	32	185	0.974
ENVIPAC 3	Polypropylene	90	60	0.959

2.3 Enzyme characteristics

In 1933 Carbonic Anhydrase (CA) was isolated from mammal's blood and his importance for CO_2 transportation was realized (Meldrum&Roughton 1933). There are various forms of CA existing and all catalyze the reaction in Eq(2). Main advantages of CA are non-toxicity and biodegradability. Nonetheless it is stable below 60 °C and between pH 5 and 11, a typical operating window of CO_2 absorption processes. Previous studies showed good resistance against gaseous contaminations like Sulphur dioxide, Chlorine or Nitrate (Lu et al. 2011, Morreale&Shi 2015).

2.4 Physical properties of the test system

The physical properties of the studied aqueous 30 wt% MDEA solution with CA is shown in Table 3. It is obvious that the used system have differing properties from water. CA is added to a concentration of 0.2 wt%, which is not affecting the physical properties.

Table 3: Physical properties of aqueous 30 wt% MDEA with enzyme at 25 °C.

System	η_L [Pa s]	σ_L [N/m]	ρ_L [kg/m^3]
30 wt% MDEA-CA	$3 \cdot 10^{-3}$	0.05	1020

3. Experimental results

3.1 Fluid dynamics of MDEA in random packings

Fluid dynamics of the studied packings have been experimentally determined by pressure drop measurements for dry and irrigated packing using the MDEA-CA-water system according to Table 3.
In Figure 3 the pressure drop of the irrigated packing with 30 wt% MDEA solution in packed bed with metal random packing McPac 1 and plastic random packing ENVIPAC 3 is shown for a selected liquid load. Due to their smaller size, the McPac 1 have a sixfold increased pressure drop compared to ENVIPAC 3 under the conditions shown in Figure 3. Also it is obvious that ENVIPAC 3 offers a wider operating window and higher capacity compared to the McPac 1 packing.

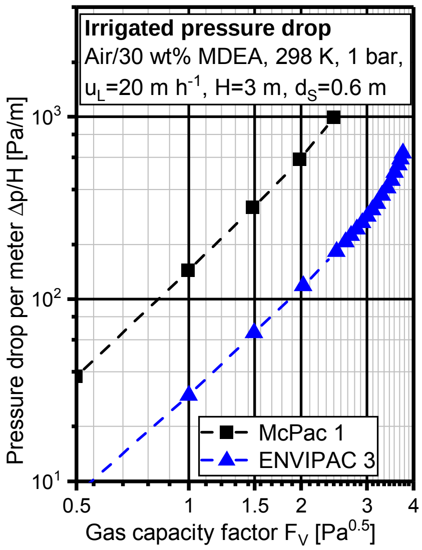

Figure 3: Pressure drop of the irrigated packing per meter $\Delta p/H$ as a function of gas capacity factor F_V at a specific liquid load u_L of 20 m/h in an air/30 wt% MDEA-system for McPac 1 and ENVIPAC 3 in DN600 column.

3.2 Separation efficiency of ERA in random packings

The separation efficiency of a packing affects the packing height that is required to perform a defined separation task. An apparatus that is smaller in terms of volume will reduce the investment and operational costs. To show the applicability of ERA in columns with random packings CO_2 absorption experiments were done in the test plant shown in Figure 1.

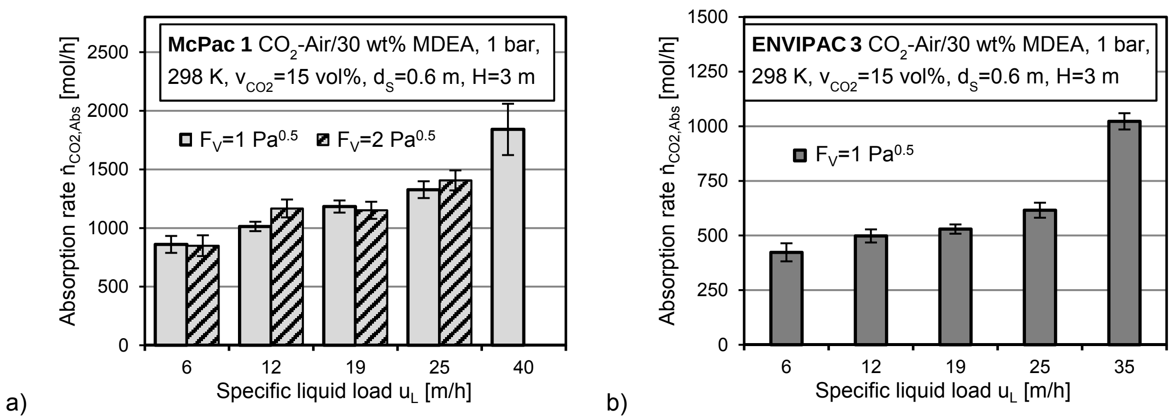

Figure 4: Experimental absorption rate $\dot{n}_{CO_2,Abs}$ of ERA for various specific liquid loads u_L in columns filled with McPac 1 (a) and ENVIPAC 3 (b) packing.

Figure 4 shows the achieved CO_2 absorption rates $\dot{n}_{CO_2,Abs}$ for the column equipped with McPac 1 and ENVIPAC 3 packings. In general, the increase of the specific liquid load u_L raises the CO_2 absorption rate. Due to the threefold higher specific surface area of McPac 1 it shows higher absorption rates, but only doubled absorption rates compared to ENVIPAC 3. Furthermore, McPac 1 and ENVIPAC 3 show a similar trend of absorption rate to specific liquid load ($\dot{n}_{CO_2,Abs} \sim u_L^b$). Because of the liquid side controlled mass transfer, the variation of the gas capacity factor shows negligible effect on the absorption rates.
The mass transfer experiments were repeated several times within the period of almost one year in order to study the stability of the enzyme. The results show high reproducibility which indicated a high stability of the enzyme activity, when stored properly under degradation temperatures of the enzyme.

4. Modelling & experiments

An Aspen Plus® model has been set-up for the absorption of CO_2 in enzyme activated MDEA-solution for structured packings in previous works (Leimbrink et al. 2017). In this work, the model has been extended to random packings. The experimental results from the industrial scale test plant have been used to validate the Aspen Plus® model.

4.1 Modeling of ERA

The model developed earlier is based on a rate-based approach considering the fluid dynamics, mass transfer, reaction kinetics and electrolytes (Kenig et al. 2001). Gas-liquid equilibria data are taken from Rinker et al. (1995) and the property method ELECNRTL is used. For the characterization of the mass transfer in columns with random packings the correlation from Maćkowiak (2015) has been implemented in this work. Reaction and enzyme kinetics are implemented via the power-law (Eq(3)) described in Leimbrink et al. (2017).

$$r = k \cdot T^n \cdot \exp\left(-\frac{E_A}{RT}\right) \prod_{i=1}^{N} c_i \tag{3}$$

Figure 5 shows the schematic flow sheet to implement the test plant into the commercial simulation software Aspen Plus®. To avoid liquid loss due to evaporation, water is added to saturate the incoming gas stream. The liquid stream is preloaded to take into account the dissolved CO_2 before experiment.

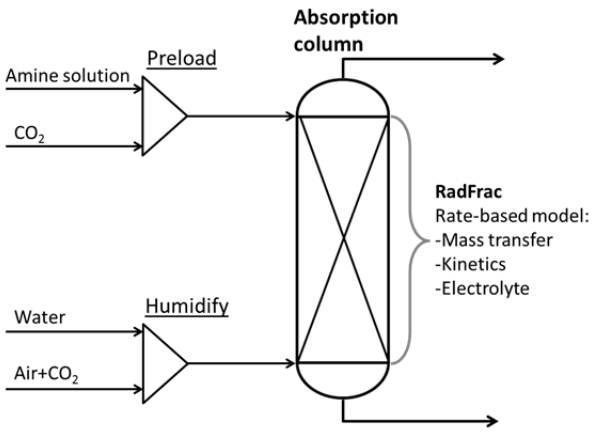

Figure 5: Modelling ERA of CO_2 in aqueous amine solution with rate-based model.

4.2 Comparison with experiments

The developed model has been validated using the experimental results described in chapter 3. The results of the validation are shown in Figure 6, where the experimental absorption rates are plotted against the simulated values. The majority of the simulated points for McPac 1 show a good agreement with a mean percentile deviation $\bar{p}$=15 % of all points (Eq(4)). For the ENVIPAC 3, the model underestimate the absorption rates for all measured point within a mean percentile deviation of $\bar{p}$=12 %, still showing good agreement between experimental and calculated values.

$$\bar{p} = \frac{1}{n} \cdot \sum_{i}^{n} \frac{\left|\dot{n}_{i,Sim} - \dot{n}_{i,Exp}\right|}{\dot{n}_{i,Exp}} \cdot 100\,\% \tag{4}$$

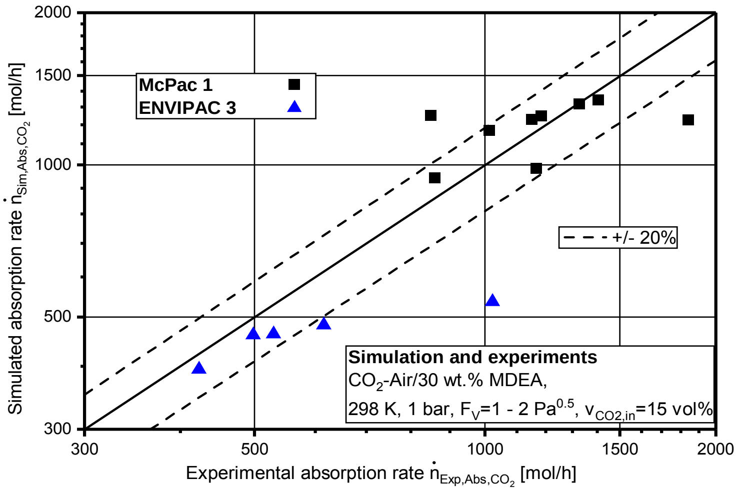

Figure 6: Parity plot of experimental and simulated absorption rates $\dot{n}_{CO_2,Abs}$ of ERA in DN600 test plant for McPac 1 and ENVIPAC 3.

5. Conclusion

The experimental work showed the general applicability of the ERA for the absorption of CO_2 from inertial gases in columns with random packings from metal and plastic and with different sizes. It was shown that the plastic packing ENVIPAC 3 is especially suitable for CO_2 absorption processes at low pressure drops. Due to this fact ENVIPAC 3 is a cost efficient packing in terms of investment costs and operating costs for the CO_2 absorption in large columns. Also, the long-term stability of CA was proven during the test series. The simulated absorption rates with the developed model showed a good agreement with the experimental work.

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