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Comparison of the kinetic promoters piperazine and carbonic anhydrase for CO₂ absorption

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Abstract

Kinetic promoters that catalyse the absorption and desorption of CO₂ can enable the use of solvents with low heat of reaction and slow absorption rate such as MDEA. Mass transfer experiments with 30 wt% MDEA promoted by either 5 wt% piperazine (PZ) or 1.7 or 8.5 g/L enzyme carbonic anhydrase (CA) were conducted in a wetted wall column apparatus at 298 K, 313 K and 328 K for different solvent loadings. The mass transfer of PZ promoted solvents was strongly influenced by the solvent loading as it was steeply decreasing for all temperatures as the solvent loaded; the temperature also increased the mass transfer, the extent was dependent on the solvent loading. CA promoted solvent mass transfer characteristics showed less dependency on the solvent loading and temperature. Lower enzyme concentrations were found to be much slower than MDEA/PZ solvents, whereas high enzyme concentrations were as efficient in capturing CO₂ as a 30 wt% MDEA/5 wt% PZ mixture in terms of overall mass transfer, considering change of mass transfer due to solvent loading over the height of a column.

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1. Introduction

Carbon capture and storage technology (CCS) has the ability to reduce greenhouse gas emissions with almost immediate impact while ensuring a safe and stable energy supply over the next years, by capturing the carbon dioxide from flue gases exiting fossil fuel burning power plants.

The capture of CO₂ from flue gases is a very energy intensive task. The energy demand of the capture process is offset by combustion of fossil fuels which thus reduces the electricity output of the power plant. In this way the cost of CO₂ free electricity is linked to the energy requirement of the post combustion capture process. The capital costs of retrofitting the post combustion capture unit to the power plant will likewise influence the costs. Clearly, both the capital and operating costs should be minimized for an ideal process. The capital costs can be minimized by reducing the equipment sizes, in mass transfer operations this can be done by intensifying the mass transfer. Likewise, for chemical absorption this can be done by increasing the reaction rate of the solvent with CO₂. Higher reaction rates result in higher mass transfer rates when the other process conditions are kept constant. The current solvents of choice are therefore primary and secondary amines since they have faster kinetics with their direct reaction mechanism with CO₂ forming carbamates. The operating costs of the process can be minimised by limiting the energy requirement for pumps, gas compression, and heat requirement of the desorber. Interestingly, the overall energy demand as a fraction of total energy demand of these tasks is very different. For example, the heat requirement for the solvent regeneration in a post combustion CO₂ capture process makes up between 61 and 70 % of the total energy demand, whereas the compression (up to 110 bar) needs between 25 and 33 % of the total energy [1]. When excluding the compression step the overall energy demand of the desorber rises to 90-93% of the total energy demand. The energy requirement in the desorber can be divided into 3 different parts; part of the energy is needed to reverse the CO₂-solvent reaction, this energy is represented by the heat of desorption. Since the vapor stream consists mainly of CO₂ and water, steam needs to be generated in order to maintain the desorber pressure. The steam leaves the desorber on top and is condensed; the energy demand is referred to as latent heat loss. As the solvent is not brought into the desorber at boiling conditions it has to be heated up to the desired temperature, this energy demand is called sensible heat loss. These latter two heat requirements are strongly dependent on the process design and process conditions. The heat of ab-/desorption is solvent dependent, and so choosing a solvent with a lower heat of absorption can likewise reduce the energy demand of the process.

Fast reaction solvents like primary and secondary amines exhibit a higher heat of ab-/desorption than tertiary amines, the group of primary amines have about 30-40% higher heat of absorption than tertiary amine and the secondary amines about 20 to 30% [1].

On the other hand the kinetics of tertiary amines like MDEA are much slower than primary and secondary amines. The use of aqueous MDEA without additives for a post combustion capture process is not feasible as absorptions towers as high as 300 m would be required to achieve 90% capture [2]. The use of kinetic promoters can help increasing the reaction rate and therefore help taking advantage of the low heat of ab-/desorption.

A very efficient promoter is the secondary diamine piperazine (PZ), which is used in BASF's activated methyldiethanolamine (a-MDEA) solvent. Another very efficient promoter that has gained a lot of interest in recent years is the enzyme carbonic anhydrase which catalyzes the reversible hydration of CO₂ forming bicarbonate.

2. Materials and methods

Mass transfer experiments were carried out in a wetted wall column apparatus with MDEA promoted by piperazine or carbonic anhydrase. The experiments were conducted at 298, 313 and 328 K at different solvent loadings.

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