

EXPERIMENTAL AND MODELLING STUDIES ON THE ENHANCED ABSORPTION OF CARBON DIOXIDE USING IMMOBILISED AMINES

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Summary

The feasibility of using amine groups immobilised on a solid carrier in the context of carbon dioxide absorption is evaluated. The activating influence of immobilised amines in enhancing the absorption rates of MDEA solutions was demonstrated in a stirred-tank reactor experiments. Further experimental and modelling studies, involving the measurement of individual mass transfer rates and reaction kinetics, are also described. A novel approach for a hybrid cyclic carbon dioxide adsorption-absorption process, which overcomes the shortcomings identified in the original concept, is proposed. Experiments and simulation studies for validating the new proposal are presented.

Keywords

CO₂ capture, process intensification

Introduction

Blends of primary or secondary amines with tertiary amines, such as methyldiethanolamine (MDEA), are frequently used for the removal of CO₂ from gas mixtures [1]. These ‘activated’ amine solutions are advantageous, since they combine high absorptive capacity of tertiary amines with high absorption rates of primary or secondary amines. However, the acceleration of CO₂ absorption via rapid formation of carbamates with primary or secondary amines is usually required only locally within the absorption column. In other parts of the absorption process homogeneous activating additives can give rise to undesirable side-effects, such as increased corrosion or higher energy demands for regeneration. Thus it would seem to be preferable to immobilise the activators on a solid carrier, which would ideally also serve as packing material, within the absorption column. In this way the activators would be localised in those parts of the absorption process in which they are needed and excluded elsewhere.

The formation of carbamate then takes place as a kind of chemical adsorption process through the reaction of CO₂ with the immobilised primary or secondary amines. The activators are regenerated continuously and ‘in-situ’ by the reaction between the flowing aqueous MDEA phase and the carbamate, releasing bicarbonate into the solution flowing over the packing (Figure 1).

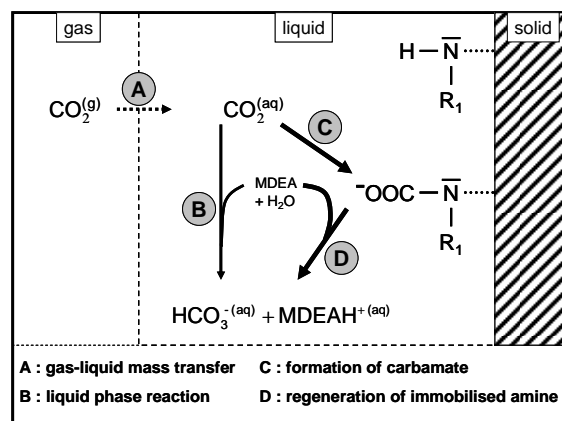


Figure 1: Schematic reaction mechanism for immobilised activators

Stirred-tank reactor experiments

The positive effect of immobilised activators on the absorption behaviour was first demonstrated by means of preliminary batch experiments in an aerated stirred-tank reactor [2]. For the experiments an adsorber resin functionalised with benzyl amine (BA) groups (Lewatit VP OC 1065, Lanxess) was chosen as the immobilised activator material. The resin particles are spherical, with a diameter of 0.5-1 mm, and have a density of 1.092 kg/m³. The concentration of BA groups was determined by titration with 0.1 m HCl to be 0.33 mol/l Lewatit.

As discussed by Schubert, Grünewald and Agar, immobilised activators can enhance the absorption of CO₂ into an aqueous MDEA solution to a similar extent as an equivalent quantity of liquid activators (e.g. diethanolamine) [2]. Further experiments with respect to the regeneration process demonstrated that CO₂ loaded immobilised activators can be regenerated with aqueous MDEA (0.5 M) solution and subsequently exhibit the same absorptive behaviour as the fresh material.

Mass transfer and reaction kinetics

To quantify the various mass transfer and reaction processes occurring in the three-phase system (see figure 1) and identify possible rate-limiting steps, additional experiments were carried out in a gas-solid fixed-bed and a gas-liquid double stirred-cell contactor.

a) Gas-solid fixed-bed

The experiments were carried out in a capillary with a diameter of 4 mm, a length of 1.1 m and a constant fixed-bed void fraction of 0.78. Various reaction conditions were studied, with gas velocities in the range of 0.01 - 0.07 m/s and temperatures between 25 - 55 °C.

The results show that a very high adsorption rate of CO₂ with an instantaneous reaction of CO₂ and the BA groups to carbamate occurs. There were no clear rate-limiting steps to be detected in the mass transport between the gaseous and solid phases. The adsorption was carried out until complete loading of the functionalised adsorber resin was achieved.

b) Gas-liquid double stirred-cell

In a gas-liquid double stirred-cell contactor experiments were carried out to determine the reaction kinetics of dissolved CO₂ with amines immobilised on suspended resin particles. Furthermore, the enhancement of the absorption of CO₂ into an aqueous MDEA solution with the immobilised amines was investigated. The gas-liquid double stirred-cell contactor used (total volume 1.091 l, liquid volume 0.5 l) has the advantage that no liquid phase analysis is required. In each experiment a certain amount of CO₂ is injected rapidly into the reactor and the pressure decrease caused by absorption and reaction is monitored. From this pressure development, the reaction kinetics between the dissolved CO₂ and the suspended immobilised amines was estimated using a simple mathematical model based on the film theory, which was implemented in Aspen Custom Modeller (ACM).

The absorption experiments with an aqueous MDEA solution and suspended immobilised amines showed no enhancement of the absorption rate by the immobilised activators for this kind of gas-liquid contactor. The mathematical model indicates that the gas-liquid mass transfer is the rate-limiting step in this system. According to the film theory, it can be reasoned that - in contrast to the more mobile liquid elements - the suspended

immobilised activator particles do not enhance the reaction rate of CO₂ at the imperfectly mixed phase interface and thus do not influence the absorption favourably.

New approach

Based on the results of the experimentation described, a novel approach is proposed, which exploits the advantages of a periodically operated absorption column. The process can be subdivided into three basic steps:

The first step represents the adsorption of CO₂, in which the rapid formation of carbamate with the immobilised amine groups on the solid carrier takes place. In the second step, the regeneration of the loaded resin with an aqueous solution of a tertiary amine is carried out in order to convert the CO₂ into bicarbonate in the liquid phase. Finally, in the third step, the liquid phase needs to drain off the packing, in order to offer direct contact between the gas and solid phase for the following first step.

The principle feasibility of this concept was validated experimentally: The hydrodynamic behaviour of different shapes, sizes and porosities of an adsorber resin packing were tested on the laboratory scale. The diameter of the packed column used was 100 mm with a packing height of 400 mm. The results show an acceptable pressure drop over the packing and a good mechanical strength of the adsorber resin. For the concept to function correctly, one must ensure both good access of the gas to the activator surface by using hydrophobic properties to enhance run-off and permit extensive carbamate hydrolysis by employing higher regeneration temperatures or sterically hindered activator groups.

In addition to the dynamic and static hold-up, the cycle time and the adsorption capacity were ascertained. The results obtained previously were confirmed by the additional experiments showing a low hold-up and a realistic cycle time.

Simulation studies were carried out on the basis of a dynamic process model of the stepwise cyclically operated separation process. Several parameter sets for the reaction kinetics and the mass transfer were tested. Additionally, the regeneration of the CO₂-loaded aqueous amine solution in a stripping column and the minimum energy demand for the whole process were determined. The results of the modelling study are compared with data from literature for a conventional absorption of CO₂ using an aqueous monoethanolamine (MEA) solution.

References

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