

Mass Transfer Study on Catalytic Structured Packings for Reactive Separations

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This paper deals with a study on mass transfer in modular catalytic structured packing Katapak-SP with the purpose of determining the effective mass transfer area. Information has been gathered by using the chemical absorption method and monitoring the composition profiles along the packed bed. Liquid load ranged between 5 and 27 m³/(m²h). A procedure was developed taking into account the hybrid structure of the packing. The use of correlations for the volumetric mass transfer coefficient available in the literature and of data obtained from targeted experiments allowed choosing the proper operating conditions. A simple model to calculate the effective area is presented. The model is based on the packing geometry and the liquid flow distribution within the hybrid structure of the packing.

1. Introduction

Modular catalytic structured packings are used in an increasing number of industrial applications where reaction and separation (i.e. distillation, absorption, extraction) can be efficiently integrated in single equipment (Aferka et al. 2010). The commercially available Sulzer Katapak-SP packing, under study in this work, is characterized by a hybrid structure made of corrugated sheets of conventional distillation layers (separation elements) and catalytic baskets, i.e. wire gauze envelopes filled with catalyst particles, assembled in alternate sequence (reaction elements). The modular design allows varying the relative size of the separation and reaction zones by placing one or more corrugated sheets in between. This feature allows to arrange the packing to fit the requirements of each specific process, and makes Katapak-SP a highly competitive internal device for reactive separation columns. The ratio between catalytic baskets and corrugated sheets (typically, 1:1, 1:2 or 1:3) identifies the packing configuration (Götze et al., 2001). Modelling attempts have pointed out that rate based models provide better results than stage models in describing reactive separation columns. Besides the kinetics parameters, of particular interest for the improvement of predictive models is the quantification of fluid dynamic related parameters, i.e. pressure drop, liquid hold-up, effective mass transfer area and coefficients (Viva and Brunazzi, 2009a).

In this study, we determined experimentally the effective mass transfer area of Katapak-SP packing for which no data is available in the literature. To the author's knowledge, it is the first time that a chemical absorption method is employed to study a packing with a complex geometrical structure like the Katapak-SP packing. In fact, the hybrid structure determines the flow development inside the packed bed and consequently affects the application of the method. Volumetric mass transfer coefficients from the literature and targeted experiments were used to enable a critical analysis of the measurement method and chose the proper operating conditions.

Then, a simple model based on liquid flow distribution and packing geometry is presented to interpret the measured effective area.

2. Experimental method and setup

Chemical absorption rate data in the fast-reaction regime is frequently employed to determine effective gas-liquid interfacial area in packed columns (Danckwerts, 1970).

Among the large variety of the two-fluid systems, the absorption of CO₂ into NaOH solution is especially proper (Rejl et al. 2009). CO₂ reacts in the liquid phase with NaOH and forms bicarbonate and carbonate. The reaction is of second order and the formation of the bicarbonate ion is the limiting reaction. The value of its equilibrium constant at ambient temperature is large enough to allow considering the reaction as practically irreversible. The kinetics of the system has been extensively studied and characterised (Kolev et al. 2006). Weimer and Schaber (1996) have investigated how the test conditions must be chosen, when studying conventional packings, in order to operate in the desired fast reaction of pseudo-first order condition. They found that using air (i.e. with only some 380 ppmv CO₂), instead of a CO₂ enriched gas stream, has no effect on the reaction regime, and that the method is preferable because this way, the use of chemicals is significantly reduced and more importantly caustic and carbonate concentrations change very slowly. The gas side resistance is limited by operating at high gas velocities (1-2 m/s). Effective gas-liquid interfacial area measurements using air and 0.1-1 molar NaOH solution have been recently reported by Tsai et al. (2011) to characterise structured packing, by Alix et al. (2011) to study a new carbon packing, and by Duss et al. (2010) to optimize the absorber design for post-combustion CCS. Aferka et al. (2011a), used air and 0.3 molar NaOH solution to determine the effective interfacial area of MellapakPlus 752.Y, and the results were used to validate tomographic measurements.

In this paper the technique is applied, for the first time, to determine the effective interfacial area of catalytic structured packing. In particular, two modular configurations of Katapak-SP, i.e. 1:1 and 1:2, have been studied in the nominal size of 100 mm diameter and 200 mm height. They are made of stainless steel, glass particles of 1 mm diameter fill the catalytic baskets. Corrugated sheets are those encountered in MellapakPlus 752.Y. A comprehensive description of the packings geometry is provided in Viva et al. (2011a).

The column has an internal diameter of 100 mm and is 2 m high. It is made of transparent plexiglass. Packed beds are constituted by nine Katapak-SP elements, rotated by 90° with respect to each other. The column was operated at atmospheric pressure and room temperature. Air is supplied by a compressor, pre-humidified and fed at the bottom of the column. A multiple point source distributor was used to feed the liquid at the top of the column. The column is connected to two 500 L capacity storages, one for the fresh solution and one for the used solution, to ensure that the caustic solution concentration is constant during the tests. Nevertheless, liquid samples both at the inlet and the outlet of the packing were taken during the runs. The concentrations of hydroxides and carbonates in the liquid samples were determined by titration with HCl. Also temperature of gas and liquid were accurately measured during the runs. Ionic strength of the solution, hydroxides concentration and temperatures have a significant impact when evaluating the interfacial area (Duss et al., 2010) this is the reason why they need to be accurately measured and monitored.

Gas samples were withdrawn at different locations along the column. Besides monitoring inlet and outlet air streams, samplings were taken directly from the packed portion of the column to avoid end effects (Rejl et al. 2009) and monitor the gas composition profile along the packed bed. The CO₂ concentration was measured by an infrared gas analyzer (Ecocontrol AD 30), calibrated with N₂ for zero point and 590 ppm CO₂/air span gas. The 4-20 mA signal was recorded continuously on a data logger and stored on a PC. This feature allowed the CO₂ concentration to be observed in real-time.

Use of the chemical method with a packing characterized by a hybrid structure like the Katapak-SP packing, requires, among others, the following aspects to be considered:

- Evaluation of the composition and ionic strength of the solution as it flows down the packed bed (model for the liquid flow)
- Large Hatta number throughout the packed bed ($Ha > 3$)
- Limited gas side mass transfer resistance
- Significant variation in CO₂ concentration in the gas phase to limit experimental errors

For the current study we found a satisfactory compromise with the following operating conditions: gas F-factors were comprised between 0.8-1.5 Pa^{0.5} (for each liquid load, the maximum F-factor was fixed by operating at pressure drop below 3-5 mbar/m, so as to work below the gas loading point; some runs were also conducted at higher gas rates and up to the flooding point, to determine the gas effect on the effective area); liquid loads ranged from 5 to 27 m³/(m² h); the feed liquid was a 0.3 molar NaOH solution, some runs with 0.1 and 0.5 molar solutions were also conducted for a validation of the method.

To evaluate the effective interfacial area from the resulting experimental data we used the physico-chemical property values and reaction kinetic constants published by Pohorecki and Moniuk (1988).

The material balance and rate equations on segments (of height dz) were written in Matlab 7.0 and integrated over the packed bed to calculate the composition profiles along the column. The effective interfacial area was assumed to be constant. It is the only parameter to adjust in order to fit the measured CO₂ profile and meet the NaOH concentration in the liquid bulk measured at the column inlet and outlet.

The hybrid structure of the packing determines the gas and liquid flows development inside the packed bed (Viva and Brunazzi, 2009b). Two zones can be distinguished within the packing, the open channels (OC), which correspond to the separation zone where the corrugated sheets are placed, and the catalytic baskets (CB). The mesh size of the wire gauze envelopes ensures easy access of liquid, prevents the particles cross-over and makes the baskets practically impermeable to the gas flow. Hence, it can be reasonable assumed that the gas flows entirely in the separation zone.

In previous studies on the same packings, Viva et al. (2011a) deduced the distribution of liquid flowrate, between the reaction and the separation zones, from hold-up distribution measurements. The liquid specific load, uL , was written as the sum of two contributions:

$$uL = u_{OC} \cdot \Psi_{OC,S} + u_{CB} \cdot \Psi_{CB,S} \quad (1)$$

where u_{OC} and u_{CB} stand for the liquid specific load outside and inside the catalytic baskets, respectively, and Ψ_{OC} and Ψ_{CB} are the superficial fractions on the column cross section occupied by the OC and CB zones (Viva et al. 2011b). Liquid distribution changes with the liquid load and quantitative results are provided Viva et al. (2011c. Aferka et al. (2011b).

In its way down the packed bed, the liquid solution flowing in the separation zone contacts the gas phase and absorbs CO_2 . As a consequence, its composition and ionic strength vary. To model the liquid behaviour, two extreme cases were considered: (a) the liquid is continuously and completely mixed in any packing cross section, (b) the liquid flowing in the separation zone never mixes within the packing with the liquid flowing in the reactive zone.

In regard to the Hatta number criterion, estimates of the physical liquid side mass transfer coefficient (k_{L0}) are needed. Correlations for k_{L0} from the literature (Behrens et al. 2006) were used to calculate Ha number and monitor the values along the packed bed for all the liquid loads. The used correlations predict values of k_{L0} of the order of 10^{-4} and 10^{-5} m/s. Measurements not shown here for brevity, consisting of the desorption of CO_2 from aqueous solutions into air, support these estimates (Navazio, 2014). The worse conditions occur at the higher liquid loads. We found that the use of 0.3 molar NaOH solution allowed us satisfying the large Ha criterion. Additional runs were conducted with 0.5 M solution to check the results.

The gas side mass transfer resistance and its associated errors in the measured contact areas are minimised when dilute caustic solution and high gas velocities are used. For the present study (with the 0.3 molar solution) and with the chosen operating conditions, the gas side resistance affect the calculation of the effective area by less than 4-7 %. The gas-side mass transfer coefficient was calculated from the correlation of Brunazzi et al. (1995) adapted to the Katapak-SP geometry. Furthermore, targeted measurements, not shown here for brevity, consisting of the absorption of SO_2 into caustic solutions have supported this estimate (Viva, 2009).

3. Results and discussion

Figure 1 shows a sketch of the packed section of the column including the location of the gas sampling stations (two for each level). CO_2 concentration axial profiles for Katapak-SP 11 and Katapak-SP 12 are compared: measurements were conducted with the same liquid load ($20 \text{ m}^3/\text{h}/\text{m}^2$) and gas F-factor ($1 \text{ Pa}^{0.5}$). Points are the experimental values while the lines are the calculated profiles. The figure shows that a higher CO_2 mass transfer rate, and hence higher effective area, is obtained for Katapak-SP 12 compared with Katapak-SP 11. This can be explained with the higher specific geometric area of the packing, i.e. 282 and $210 \text{ m}^2/\text{m}^3$, respectively (Viva et al. 2011a). No significant gas effects were observed for F-factors below the gas loading point.

To analyse the measured experimental profiles and hence calculate the effective area, two extreme cases were considered in the modelling of the liquid behaviour: (a) the liquid is continuously and completely mixed in any packing cross section, (b) the liquid flowing in the separation zone never mixes within the packing with the liquid flowing in the reactive zone. Both models were considered and the results for both packings are reported in Figure 2, where the relative percentage difference between the calculated effective area is shown as a function of the liquid load. ae is the area calculated considering model (a), i.e. complete mixing of the liquid in each cross-section, while ae_{NR} is the area calculated considering model (b), i.e. no remix. With the chosen operating conditions, it has been found that both models affect the calculated area by less than 5 %. The worst scenario occurs at low liquid loads and with model (b).

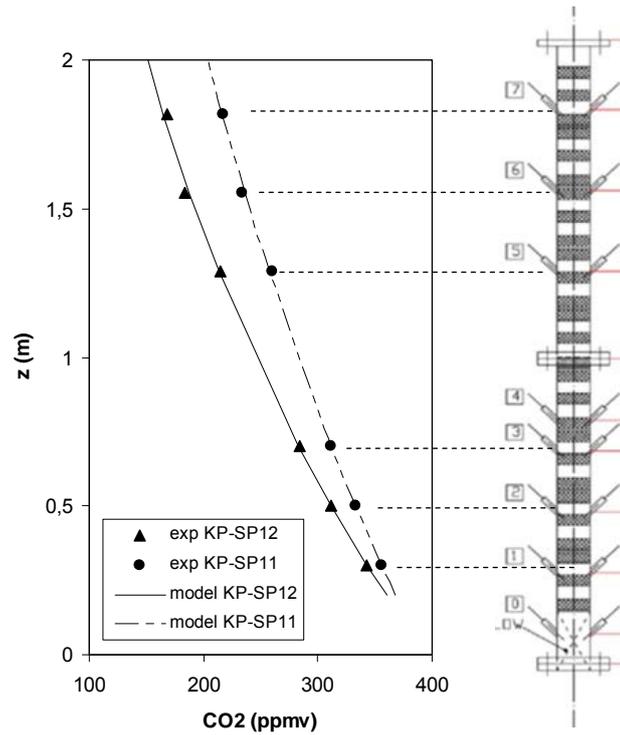


Figure 1: Sketch of the packed section of the column (right) and CO₂ concentration along the column axial coordinate (left). Liquid load = 20 m³/(m²h), F-Factor = 1 Pa^{0.5}

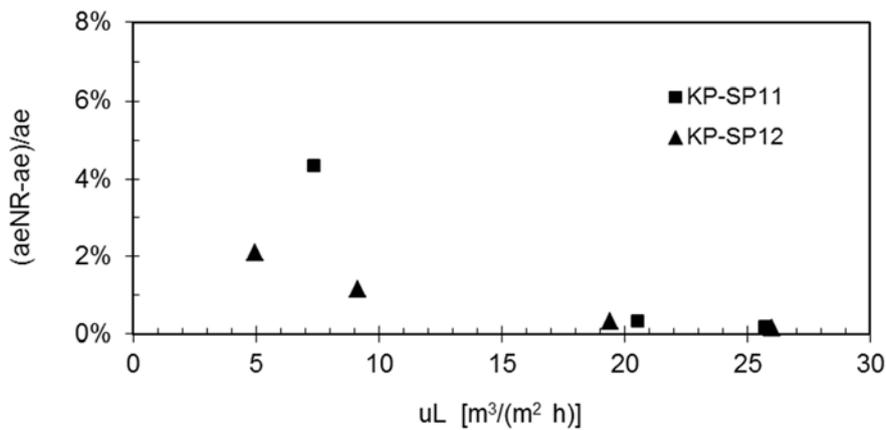


Figure 2: Effect of the liquid flow model on the calculation of the effective area

The influence of both the liquid load and packing type on the effective mass transfer area is summarised in Figure 3, where data for MellapakPlus752.Y are also reported for comparison (Aferka et al., 2011a). Every packing exhibited an increase in effective area with increasing liquid load. For MellapakPlus 752.Y packing this is naturally attributable to a greater portion of the packing being wetted and therefore available to participate in the mass transfer process. A correlation for the fractional area of MellapakPlus packing as a function of liquid load can be easily obtained by interpolation of the experimental data and is represented by the continuous curve shown in Figure 3.

For Katapak-SP the mass transfer process takes place only in the separation zone. Hence, the effective area could be calculated as the sum of two contributions, i.e. the corrugated sheets and wire gauze of the catalytic baskets, therefore:

$$ae = (ae/ag)_{MP,u_{OC}} \cdot ag_{MP_inK-SP} + ae_{WG} \quad (2)$$

where ae is the Katapak-SP effective area for a liquid load of u_L , $(ae/ag)_{MP}$ is the fractional area of MellapakPlus packing for a specific load of u_{OC} , ag_{MP_inK-SP} is the specific geometric area of the corrugated sheets in the Katapak-SP packing, ae_{WG} is the effective area of the wire gauze assumed completely wetted. For any liquid specific load, u_L , the corresponding liquid specific load outside the catalytic baskets, u_{OC} , is determined by Eq(1).

A fairly good agreement is observed in Figure 3 with predictions of Eq(2).

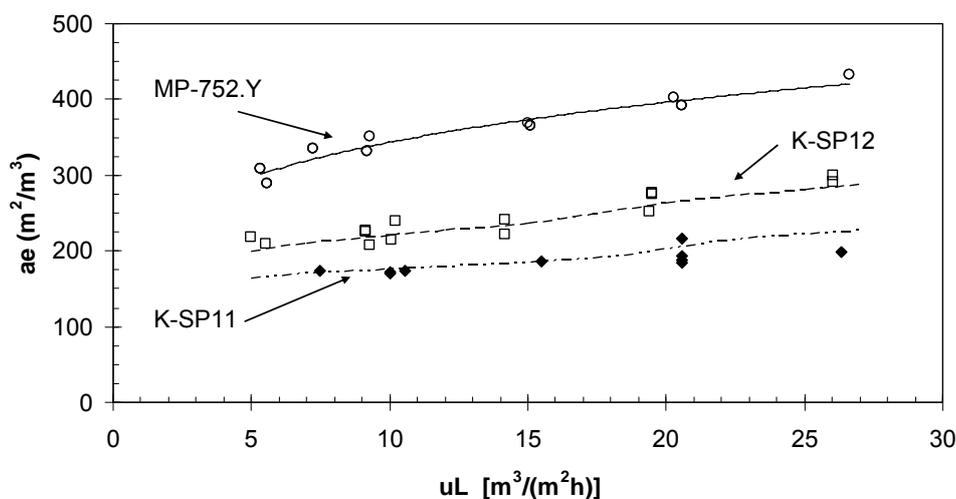


Figure 3: Effective area as a function of liquid load. Comparison between calculated values (lines) and experimental data (points)

4. Conclusions

A study on mass transfer in modular catalytic structured packing Katapak-SP with the purpose of determining the effective mass transfer area was carried out.

A procedure based on chemical absorption was developed to calculate the effective area directly from experimental results. The packing is characterized by a hybrid structure made of separation and reactive zones. Hence, to calculate the effective area from the experimental data two extreme cases were considered in the modelling of the liquid behaviour: (a) the liquid is continuously and completely mixed in any packing cross section, (b) the liquid flowing in the separation zone never mixes within the packing with the liquid flowing in the reactive zone. Both models were considered and their effects on the calculated area quantified. Experiments were carried out for liquid loads ranging from 5 to 27 m³/(m² h) and composition profiles were monitored along the packed bed.

Subsequently, a simple model based on liquid flow distribution and packing geometry is presented which interprets fairly good the measured values.

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