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On the development of new column internals for reactive separations via integration of CFD and process simulation

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Abstract

Reactive separations combining mass transfer with simultaneous chemical reactions impose additional requirements on the applied column internals. Traditionally, reactive separation processes have been optimised via operational parameter adjustment. By this way, a direct influence of the internals geometry and structure cannot be taken into consideration. Therefore, the application of process-specific column internals, rather than of the internals currently available on the market, is desirable. Development of new internals is a major focus of interest in an European project entitled *Intelligent Column Internals for Reactive Separations*. In particular, such development is achieved by the application of modern CFD facilities combined with the rigorous, rate-based process simulation. An important challenge is to provide an opportunity of obtaining hydrodynamic and mass-transfer correlations, necessary for the process description, not only from the experimental measurements, but also directly from the CFD simulations. In this paper, a way to generate virtual correlations is demonstrated for a single-phase flow through structured packings. The rate-based simulation is illustrated with the heterogeneously catalysed synthesis of *n*-hexyl acetate via reactive distillation.

Keywords: New column internals; CFD; Process simulation; Reactive distillation

1. Introduction

Reactive separations are becoming more and more important in several areas of chemical engineering, and one can look forward to rapid progress in this technology sector in the near future [1]. A traditional way to optimise reactive separation processes does not include internals optimisation and is based on the adjustment of operational parameters. However, the type, geometry and structure of internals influence the whole process performance significantly. Consequently, the application of process-specific column internals, rather than of the internals currently available on the market, is required.

This has given an impetus to initiate a large European project, entitled Intelligent Column Internals for Reactive Separations (INTINT) and aimed at principal improvement of the column internals and their fitting to particular reactive separation processes. The key theoretical innovation is the application of modern CFD facilities, in combination with the rigorous, rate-based process simulation approach. This should result in a significant reduction of the number of expensive hydrodynamics experiments. The CFD simulations can be regarded as *virtual experiments* carried out even without really existing externals. CFD should help to predict the performance of the internals by varying their geometrical and structural properties. In the long-term perspective this can even be seen as a principal way towards the *virtual prototyping of internals*.

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This paper suggests a description of the new approach and illustrates the influence of different catalytic internals on reactive distillation of *n*-hexyl acetate from hexanol and acetic acid.

2. CFD modelling

Regarding structured packings made of corrugated sheets (with or without catalytic beds filled with the immobilised granular catalyst), the CFD simulations will hardly replace the real experiments entirely in the near future. Obvious difficulties are caused by the very complex flow patterns of the counter-current gas–liquid film flows, especially above the load point. However, the accuracy of some significant constituents of the hydraulic and mass-transfer correlations can definitely be improved by CFD [2]. In this work, CFD is applied to the calculation of the dry pressure drop as a function of the gas load, which is a prerequisite to the two-phase flow simulation.

The importance of the appropriate representation of the underlying internals geometry is well understood, with special attention on the effect of the corrugation angle [3]. Here rigorous CFD analysis helps to avoid heuristic assumptions about possible structure of the relevant correlation, which are inevitable, both in conventional mechanistic models [4] and in more sophisticated considerations [3].

In this work, CFD simulations of a single periodical sub-volume (one packing crossover, shown in Fig. 1) [5] are used in order to describe the flow pattern in the widely used Sulzer-BX internals, with the standard corrugation angle of 60°. The effects of the tower wall are not included at this stage. The flow is considered as fully established, with the periodic boundary conditions satisfied on the open boundaries. The general-purpose commercial CFD package CFX-4 [6] is used for the simulations.

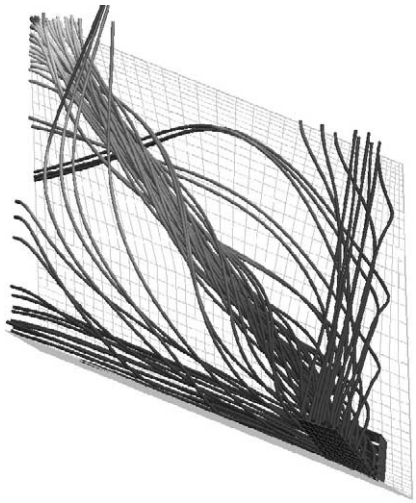

Fig. 2. Flow structure in the free shear layer [5].

The Reynolds number of the gas flow is in the transitional or turbulent flow regime. Therefore, for detailed resolving of mixing layers, a proper choice of the turbulence model and a fine grid is crucial [5].

A reduced resolution of the mixing layer can cause a significant underestimation of the intensity of the diagonal vortex bundle (Fig. 2), of the longitudinal vortices, and consequently of the values of the pressure forces applied to the both walls. At the same time, the resultant of these pressure forces does not

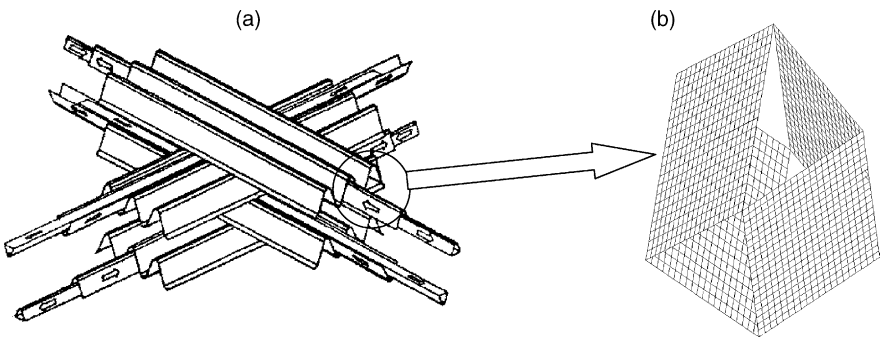

Fig. 1. Schematic representation of a corrugated sheet packing adapted from [2] (a) and a packing crossover (b).

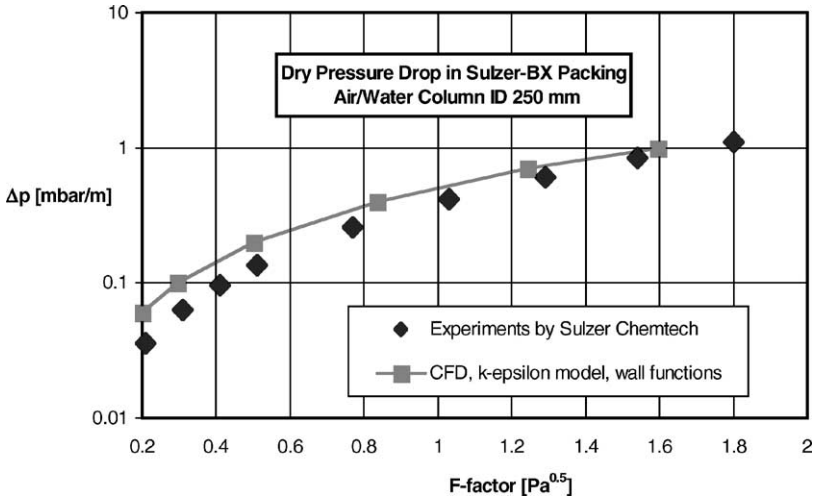

Fig. 3. Calculated and measured dry pressure drop [5].

change significantly. Therefore, it might be tempting to use a coarse grid of only a few thousands of control volumes per crossover for reducing the computation time or including more geometry elements into the computational domain. However, the complicated flow structure, shown in Fig. 2, clearly demonstrates that without proper resolution of the vortex scales responsible for the turbulence generation the resulting flow characteristics can be qualitatively wrong.

When the flow pattern is determined, it is possible to perform a post-processing of the data and estimate important relations between hydrodynamic variables and operational parameters of the process. An example is given in Fig. 3, where the relationship between the dry pressure drop and the gas load is shown. The calculated curve is based on simulations with a grid of 96,000 control volumes inside a crossover. A comparison of simulated results with the correspondent experimental data available from Sulzer Chemtech [7] demonstrates their good agreement. It is worthy of note that such correlations can usually be obtained only by extensive and expensive experimental investigations.

Numerical experiments have revealed a strong pressure drop sensitivity to the corrugation angle value. At the same time, a relatively weak dependence on the accuracy of the grid resolution of the mixing layer has been observed. This phenomenon can be explained by a dominating contribution to the pressure drop from the form drag whose value is a resulting force of two oppositely directed pressure forces which act on the two walls forming the gas channel [5].

The described technique is extended to yield other important correlations, e.g. for residence time distribution and mass-transfer coefficients [8].

3. Rate-based modelling

The final decision on the suitability and performance of newly developed, process-specific column internals should be made based on the simulations of the entire process.

Traditional equilibrium-based models and efficiency approaches are often inadequate for reactive separation processes. To avoid possible significant errors, it is necessary to model separations taking account of actual mass-transfer rates [9,10]. Therefore, in this work a direct account of process kinetics is realised. This approach to the description of a column stage is known as *the rate-based approach* and implies that actual rates of multicomponent mass transport, heat transport and chemical reactions are considered immediately in the equations governing the process phenomena. Mass transfer near the vapour–liquid interface is described via the well known two-film model, whereas the multicomponent diffusion in the films is covered by the Maxwell–Stefan equations

[11]. A detailed model description is given in [10,12,13].

In the rate-based approach, the influence of the process hydrodynamics is taken into account by applying correlations for mass-transfer coefficients, specific contact area, liquid hold-up, residence time distribution and pressure drop. As mentioned above, this correlations are usually obtained experimentally, with really existing internals. If we are able to gain the correlations by the CFD simulations, we can create "virtual internals" and study them prior the manufacturing. This is a key point enabling computer-based optimisation of both internals and the entire process.

4. Case studies

As an example process, the heterogeneously catalysed synthesis of *n*-hexyl acetate from *n*-hexanol and acetic acid via reactive distillation is selected. Reactive distillation experiments have been carried out in laboratory (55 mm diameter) and pilot scale (162 mm diameter) columns [14]. In most of the pilot scale experiments, a visible formation of the by-product 1-hexene was observed. Probable reasons of this phenomenon are higher reaction temperatures, as the pilot column is operated at 0.5 bar, whereas the lab scale column at 0.325 bar, and different residence time behaviour. The boiling points of the pure components at the corresponding pressures are given in Table 1. The lowered pressure is essential in order to prevent the applied catalyst Amberlyst® CSP2 from damage, because of the limited temperature stability of the acidic ion-exchange resin.

For this catalyst, immobilised in bags of the applied catalytic packings Sulzer Katapak®-S and Montz Multipak®, reaction kinetics has been determined in [14]. The kinetics has been adapted to the following activity-based pseudo-homogeneous approach:

$$r_i = \nu_i (k_{\mathrm{fwd}} a_{\mathrm{HEXOH}} a_{\mathrm{HAC}} - k_{\mathrm{bwd}} a_{\mathrm{HEXAC}} a_{\mathrm{H_2O}})$$

where r_i is the reaction rate and ν_i the stoichiometric coefficient of ith component, k_{fwd} and k_{bwd} the reaction rate constants of forward and backward reaction, respectively. This kinetics, however, includes mass transport effects and hence is of a preliminary character. Therefore, as stated in [14], it will be revised in the future. Currently, no kinetic description for the formation of 1-hexene is available. Thus, its influence on the concentration profiles and liquid–liquid separation at pilot scale is accounted for by using a pseudo-feed.

Within a reactive distillation column, the high-boiling *n*-hexyl acetate is obtained as the bottom product, whereas the distillate represents a mixture of all components. Due to the presence of miscibility gaps, a liquid–liquid separation step follows the total condensation of the distillate at the top of the column. The aqueous phase from the decanter is withdrawn completely; on the contrary, only a small part of the organic phase is purged in order to prevent the accumulation of the side-product 1-hexene, whereas the main part is fed back to the column as organic reflux.

For the modelling of thermodynamic equilibrium, NTRL model is used. The Nothnagel equation of state accounts for the non-idealities of the vapour phase due to the dimerisation of acetic acid. The necessary parameters are obtained from the ASPEN Properties Plus™ database and from published data [14].

The characteristics of both investigated column scales and the applied column internals are summarised in Table 2. In both configurations, acetic acid is fed below and *n*-hexanol above the catalytic section of the column, mainly in stoichiometric ratio. The industrial scale Sulzer Katapak®-S 250.Y has a catalyst content of about 25 vol.%. As far as the two laboratory scale packings applied are concerned, the catalyst fraction in Sulzer Katapak®-S Lab is only 15.8 vol.%, whereas in Montz Multipak®-2 it is 27.7 vol.%. Separation efficiency for both lab scale internals is very similar. A detailed information on the applied packings is given in [15].

Table 1
Boiling points (T_b) of pure components at different operating pressures

Component	T_b (°C) at 0.5 bar	T_b (°C) at 0.325 bar
1-Hexene (HEX)	42.9	31.7
Water (H_2O)	81.3	71.0
Acetic acid (HAC)	96.4	84.5
n-Hexanol (HEXOH)	136.6	124.8
n-Hexyl acetate (HEXAC)	146.5	133.0

Table 2
Pilot plant characteristics [14]

	Laboratory scale column	Pilot scale column
Column diameter	50 mm (non-catalytic section), 55 mm (catalytic section)	162 mm
Rectifying section	Not available	2.1 m (MELLAPAK® 500.Y)
Reactive section	2.0 m (Sulzer KATAPAK®-S Lab) or 2.0 m (Montz MULTIPAK®-2)	6.1 m (KATAPAK®-S 250.Y)
Stripping section	1.0 m (Sulzer CY)	3.1 m (MELLAPAK® 500.Y)
Operating pressure	0.325 bar	0.5 bar
Decanter operated at	25 °C	15–25 °C

5. Results and discussion

A comparison between experimental data and simulated concentration profiles for the pilot scale column is shown in Fig. 4. In this experiment, the total feed rate is about 33 kg/h. The bottom product *n*-hexyl acetate is obtained with a purity of 99.5 wt.%.

The liquid-phase profiles demonstrate a strong decrease of *n*-hexanol in the catalytic zone due to the reaction and a corresponding increase of *n*-hexyl acetate towards the bottom of the column. The accumulation of 1-hexene and water at the top of the column is evident.

While the agreement between simulation and experimental results for the lower part of the column is very good, visible differences are present in the upper part of the column. This discrepancy should be attributed to the use of preliminary reaction kinetics and questionable accuracy of some liquid–liquid equilibrium data for the simulation of the decanter.

For the laboratory scale column, the influence of the catalytic internals has been investigated theoretically and experimentally (cf. [14]). The simulated concentration profiles in Fig. 5 illustrate the difference between Sulzer Katapak®-S and Montz Multipak®-2 for the catalytic section of the column. Operating

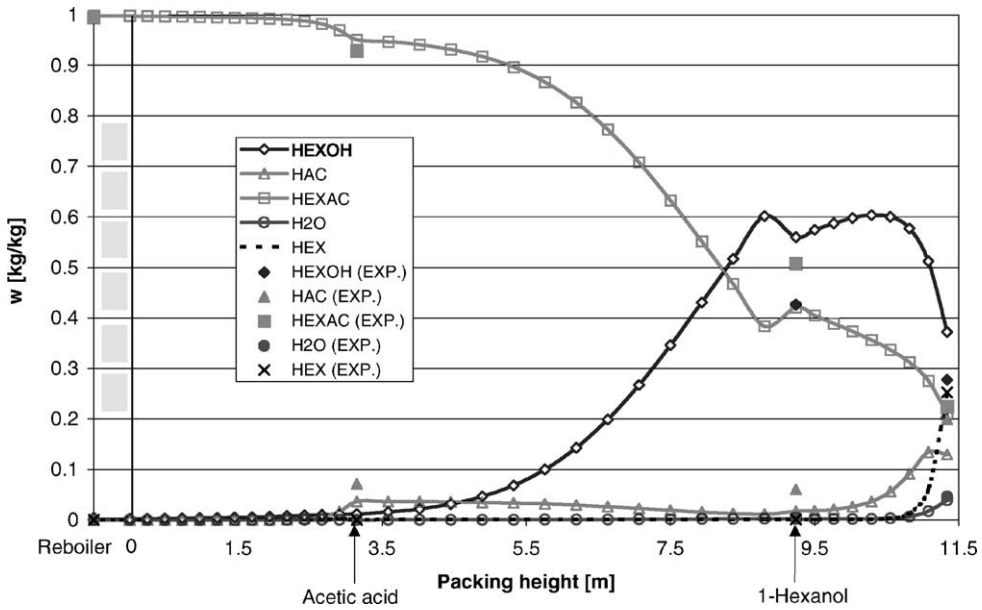

Fig. 4. Liquid-phase concentration profiles for the pilot scale column.

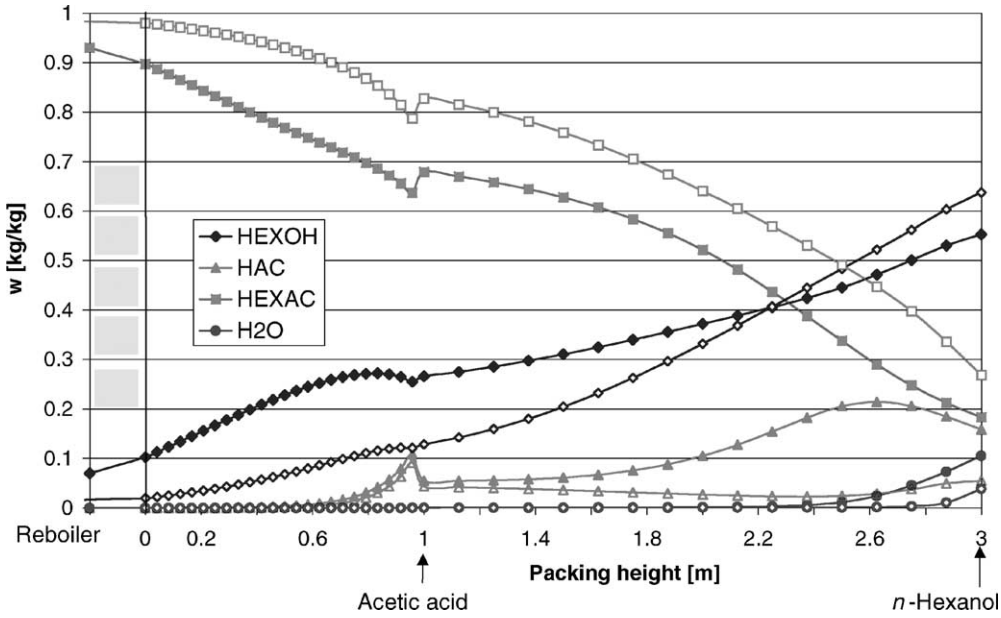

Fig. 5. Concentration profiles for the laboratory scale column obtained with two different catalytic internals at identical operating conditions: Katapak®-S (solid symbols), Multipak®-2 (empty symbols).

conditions are identical, with a heat duty of 1000 W and the total feed rate of about 3 kg/h in stoichiometric ratio.

The predicted conversion of 96% for Multipak®-2 is higher than that for the Katapak®-S laboratory packing (89%), since the catalyst content of Multipak®-2 is almost twice as high. This is mirrored by the higher *n*-hexyl acetate concentration at the bottom of the column. The same behaviour is observed experimentally. The enhanced reaction rate is illustrated by the steeper slope of the *n*-hexanol profile in the catalytic section, between the two feeds.

Such information provides a basis for the process optimisation. For example, one can perform simulations by varying the catalyst content and specific surface area. In a subsequent step, a geometry generated in accordance with the results obtained can be simulated by means of CFD as described above. The correlations for the modified internals can be implemented into the process simulator and allow a final judgement on the overall performance of the new internals. For the system considered in this paper, the development of pilot scale catalytic internals with adjusted residence time distribution, separation and reaction efficiency, could result in a suppression of the undesired side reaction towards 1-hexene.

6. Conclusions

An innovative approach to the design of column internals for reactive separations is proposed, which combines modern CFD facilities and the rate-based simulation approach. CFD should provide the necessary hydrodynamic and mass-transfer correlations and thus reduce the number of required hydrodynamic experiments. This strategy allows the optimisation of column internals without real manufactured internals. The CFD modelling concept is based on the use of small periodical representative elements of the structured packing allowing a very fine grid and sufficient resolution of the flow patterns. As an example, a dry pressure drop correlation for the Sulzer BX packing is obtained via the post-processing procedure. This correlation agrees well with the experimental data.

The developed rate-based model is used for the simulation of the synthesis of *n*-hexyl acetate by

heterogeneously catalysed reactive distillation and yields results which are in reasonable agreement with the experimental data. Further steps should be undertaken to improve the measured reaction kinetics. The influence of the choice of catalytic column internals is illustrated by comparing the performance of the laboratory scale packing Sulzer Katapak®-S Lab and Montz Multipak®-2 for the hexyl acetate synthesis.

Acknowledgements

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