

## RATE-BASED MODELLING AND SIMULATION OF REACTIVE STRIPPING

I. Mueller<sup>1</sup>, E.Y. Kenig<sup>\*1</sup>, M. Kloecker<sup>#1</sup>, T. J. Schildhauer<sup>†2</sup>, F. Kapteijn<sup>2</sup> and J.A. Moulijn<sup>2</sup>

<sup>1</sup>University of Dortmund, Department of Biochemical and Chemical Engineering, Emil-Figge-Str. 70, 44227 Dortmund, Germany

<sup>2</sup>Technical University Delft, DelftChemTech, Reactor & Catalysis Engineering, Julianalaan 136, 2628 BL Delft, The Netherlands

KEYWORDS: integrated process, reactive stripping, esterification, rate-based model

### INTRODUCTION

One of the promising ways for process intensification is to integrate reaction and separation in one single unit. In the past decades, the chemical process industries have shown an increasing interest in the development of such integrated processes. In this respect, *reactive distillation* represents undoubtedly one of the most popular examples. However, reactive distillation is only advantageous for processes where the temperature windows for distillation and reaction coincide. Otherwise, *reactive stripping* may be an interesting alternative. The removal of reaction (by-)products from the liquid phase by means of a sweep gas offers flexibility in process conditions regarding pressure and temperature. In contrast to reactive distillation, reactive stripping can be carried out in both co-current and counter-current operation mode.

The feasibility of reactive stripping in monolithic catalyst supports was successfully demonstrated at pilot scale applying the so-called film-flow monoliths with wide channels (Schildhauer et al., 2005a). The investigated reaction system was the esterification of hexanoic acid with 1-octanol, which is accompanied by the etherification of the alcohol.

Interfacial mass transfer, vapour-liquid equilibrium and reaction are interdependent, and their interactions strongly influence both conversion and selectivity. For such complex processes, rate-based models perform much better than equilibrium models (see e.g., Kenig et al., 2000, Baur et al., 2001). This work presents a rate-based model, which is valid for both co-current and counter-current reactive stripping. The model is validated against experimental data obtained in zeolite coated film-flow monoliths for the esterification of hexanoic acid with 1-octanol, and a good agreement between calculated and measured concentrations is demonstrated.

\*Corresponding author: Tel. +49 231 755-2357; E-mail address: e.kenig@bci.uni-dortmund.de

#Present address: Cognis Deutschland GmbH & Co. KG, P.O. Box 13 01 64, 40551 Duesseldorf, Germany

†Present address: Laboratory for Energy and Material Cycles, Paul-Scherrer-Institut, 5232 Villigen PSI, Switzerland

## EXPERIMENTAL

### SET-UP

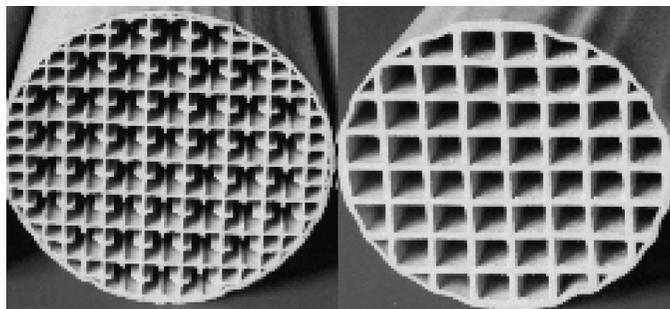
Internally finned middle (IFM) and squared channel (SQ) monoliths (see Figure 1) were coated with zeolite BEA (CP811 E-75 by Zeolyst, Si/Al ratio 150). The general procedure described elsewhere (Nijhuis et al., 2001) has been modified to hold for a half slurry concentration and twofold dip-coating-drying-calcination procedure. This leads to stable catalyst coatings, with an average loading of 25 g BEA on each 50 cm long 25 cpsi monolith piece (diameter 43 mm).

The experiments were carried out in a pilot scale plant (Figure 2). For each experiment, four pieces of coated monoliths were stacked carefully in line and mounted in a 2 m high heated column of 50 mm diameter. The preheated liquid feed was distributed via a spray nozzle. After each pass, the liquid was collected in the liquid-supply vessel and circulated continuously through the reactor (batch-recycle mode). The preheated counter-current nitrogen stream was fed after one pass to a condenser to separate the liquid and then vented. The condensables were collected in a phase separator, from where the water could be tapped off, whereas the organics (mostly cumene) were sent back to the liquid vessel via an overflow. During the experiments, liquid samples were taken from the liquid reactor inlet and outlet. Samples were analysed using a gas chromatograph and a Karl Fischer coulometer to determine concentrations and water content. In this paper, the conversion measured at the reactor inlet for a certain time point is referred to as *reactor inlet conversion*. The difference in conversion between the reactor inlet and outlet samples at the same time point is called *per (single) pass conversion*.

For reactive stripping experiments, about 13 l of liquid was used containing cumene as solvent, tetradecane as internal standard and about 12 mol% of both hexanoic acid and 1-octanol. All experiments were carried out at 160°C and 5 bar absolute pressure.

## RESULTS

Figure 3 shows the 1-octanol conversion for reactor inlet and outlet over the experiment run time. The results are nearly the same for both, IFM and SQ, monolith types (similar



**Figure 1.** Monolithic catalyst supports for film flow operation: IFM (left) and SQ (right)

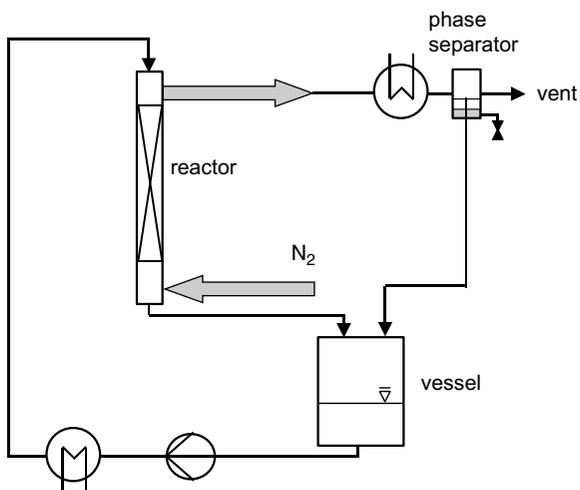


Figure 2. Set-up of experimental pilot plant

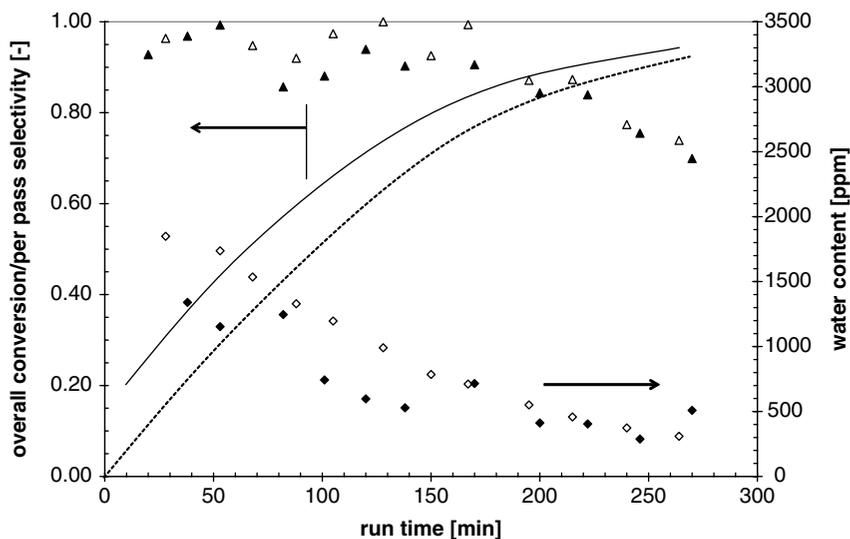


Figure 3. Octanol conversion for reactor inlet (SQ and IFM, dashed line) and outlet (SQ and IFM, solid line), water concentrations (diamonds) and per-single-pass-selectivity (triangles): open symbols, co-current operation (SQ); filled symbols, counter-current operation (IFM)

catalyst mass). Therefore, they are represented by the same lines in Figure 3. It can be observed that the distance between these two lines (the per-single-pass-conversion) does not decrease in the first hour, although the reactant concentration decreases. This can be explained by the inhibition effect of water on the catalyst. The decreasing water concentration (diamonds) leads to an increase of catalyst activity, which compensates the influence of the decreasing reactant concentration. However, at the end of the experiment, the per-single-pass-conversion is decreased by the further lowered reactant concentrations.

While the conversion is similar, the water concentrations and therefore the selectivity for the co-current (SQ, open symbols) and counter-current operation (IFM, filled symbols) show some differences. Especially at a conversion of 50–70%, the water content at the reactor outlet for the co-current operation is higher than for the counter-current one. Since the side reaction, the etherification, is suppressed in this system by high water concentration, the per-pass-selectivity is higher for the co-current operation. This effect is caused by the operation mode and is almost independent of the monolith geometry (Schildhauer et al., 2005a).

## MODELLING

### MODELLING BASIS

As the changes of process variables with time are small and the residence time of both phases within the column is low, the process can be treated as a steady-state process. Therefore, a steady-state rate-based model for the reactive stripping has been recently developed at the University of Dortmund (Klöker et al., 2005). This model takes into account heat and interfacial multi-component mass transfer, chemical reactions and thermodynamic non-idealities. The model has been implemented in the simulation tool Aspen Custom Modeler™. In this work, this model is refined and extended to cover the co-current operation mode.

### KINETICS

For the description of the heterogeneously catalysed reaction, a pseudo-homogenous approach was chosen. The reaction rates of the esterification  $r_{ester}$  (main reaction) and etherification  $r_{ether}$  (side reaction) are described by an adsorption-based approach:

$$r_{ester} = \frac{k_{ester} \cdot C_{acid} \cdot A \cdot m_{cat}}{1 + K_{octanol} \cdot C_{octanol} + K_{eq} \cdot C_{water}}$$

$$r_{ether} = \frac{k_{ether} \cdot C_{octanol} \cdot K_{octanol} \cdot A \cdot m_{cat}}{(1 + K_{octanol} \cdot C_{octanol} + K_{eq} \cdot C_{water})^2}$$

with  $A = 1 - \frac{C_{ester} \cdot C_{water}}{K_{eq} \cdot C_{acid} \cdot C_{octanol}}$  (1)

The constants used in these equations are given in Table 1.

**Table 1.** Kinetic constants (Schildhauer et al., 2006)

|               |                       |                              |
|---------------|-----------------------|------------------------------|
| $k_{ester}$   | $1.98 \times 10^{-7}$ | $\text{m}^3/(\text{gcat s})$ |
| $k_{ether}$   | $2.27 \times 10^{-5}$ | $\text{m}^3/(\text{gcat s})$ |
| $K_{eq}$      | 2.65                  | –                            |
| $K_{octanol}$ | $3.19 \times 10^{-3}$ | $\text{m}^3/\text{mol}$      |
| $K_{water}$   | $1.23 \times 10^{-1}$ | $\text{m}^3/\text{mol}$      |

## THERMODYNAMICS

Water is the most volatile component of this system (Table 2). However, as cumene is present in a large excess, its vapour pressure is not negligible and, hence, cumene is stripped together with water. Since water also influences both conversion and selectivity (cf. equation 1), an accurate VLE description of the water-cumene system is particularly important, and hence, UNIQUAC was used together with the Redlich-Kwong equation for the vapour phase.

## HYDRODYNAMIC AND MASS TRANSFER CORRELATIONS

The liquid mass transfer coefficient correlation was determined for the physical absorption of oxygen in water (Schildhauer et al., 2005b). To take into account the difference in diffusion coefficients of the two systems, the mass transfer coefficient was adjusted based on the penetration theory. For stripping processes, the mass transfer resistance in the vapour phase can be neglected (Schildhauer et al., 2005c). The pressure drop over the column is very small and can be neglected, too.

## SIMULATIONS

### VALIDATION FOR CO- AND COUNTER-CURRENT OPERATION MODE

The developed model is validated for different monoliths (IFM and SQ) and operating modes (co-current and counter-current). The single pass conversion for the hexanoic acid is determined as:

$$X_{singlepass, acid} = \frac{X_{acid, inlet} - X_{acid, outlet}}{X_{acid, start}} \cdot 100\% \quad (2)$$

**Table 2.** Vapour pressures of pure components at 150°C

|                 |      |     |
|-----------------|------|-----|
| cumene          | 0.95 | bar |
| 1-octanol       | 0.24 | bar |
| acetic acid     | 0.15 | bar |
| octyl hexanoate | 0.02 | bar |
| water           | 4.75 | bar |
| dioctyl ether   | 0.01 | bar |

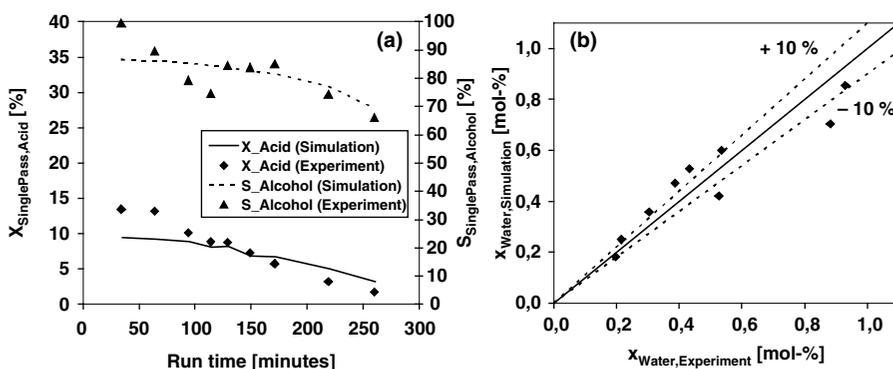
whereas the single pass selectivity of 1-octanol is:

$$S_{\text{singlepass, alcohol}} = \frac{x_{\text{ester, outlet}} - x_{\text{ester, inlet}}}{x_{\text{acid, inlet}} - x_{\text{acid, outlet}}} \cdot 100\% \quad (3)$$

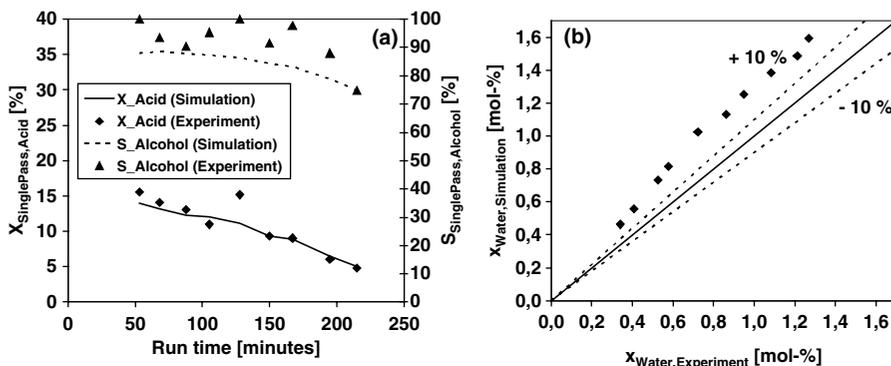
Figure 4a shows single pass conversion and selectivity for an experiment with the monolith IFM and counter-current flow. The acid conversion has an initial value around 15% and decreases below 5% towards the end of experiment. The single pass selectivity is between 70% and 90%. The agreement between measured and simulated conversion and selectivity is satisfactory. The deviations between simulated and measured conversion and selectivity can be explained by the measurements errors, because these characteristics are very sensitive in case of small concentration differences. In the considered example, these differences lie below 1.5 mol%. The comparison of the absolute values of simulated and measured concentrations shows a good agreement, with errors smaller than 2.5 mol%.

Along with the conversion and selectivity, water concentration in the monolith outlet represents an interesting characteristic, since it has a high volatility (cf. Table 2) and, thus, its concentration strongly depends on the interaction of both reaction and interfacial mass transfer. The parity plot (Figure 4b) demonstrates a good agreement between the simulation results and experimental measurements. Water concentration is quite low (<1 mol%) and decrease with the experimental run time.

For the monolith SQ, the co-current flow mode has been investigated. In Figure 5a, the measured and calculated conversion and selectivity are shown. For the co-current operation mode, high single-pass selectivities (above 90%) can be reached. The single-pass conversions of the acid are higher compared with the counter-current operation mode, too. The agreement between the measured and simulated conversion is good,



**Figure 4.** (a) Acid conversion and alcohol selectivity (IFM, counter-current mode); (b) parity plot for water outlet concentration (IFM, counter-current mode)



**Figure 5.** (a) Acid conversion and alcohol selectivity (SQ & co-current operation mode); (b) parity plot for water outlet concentration (SQ & co-current operation mode)

whereas the simulated selectivity is somewhat underestimated (because of too high calculated reaction rate of etherification).

Consequently, the simulated water concentration values are higher than experimentally determined (Figure 5b). Taking account of the low water concentrations (<1.5 mol%), the agreement between simulated and experimental water concentration can be estimated as satisfactory.

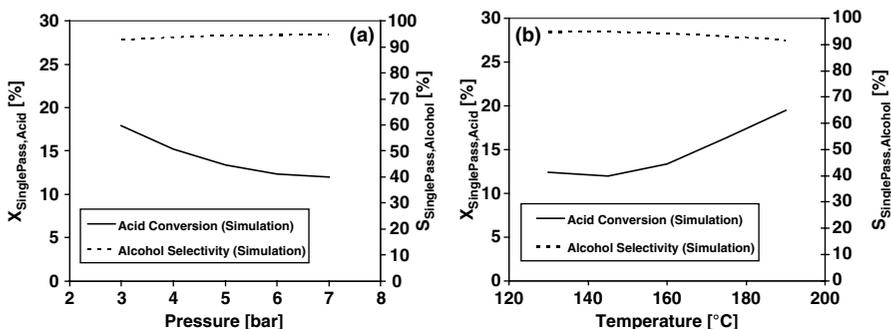
## PARAMETER STUDIES

The simulations are performed to study the influence of different process parameters. In this paper, the impact of the operating pressure and the liquid inlet temperature is demonstrated (Figure 6). The liquid inlet concentrations are kept constant at the experimental values achieved after 20 minutes.

To study the influence of operating pressure inside the monolith, the latter is varied between 3 and 6 bar. As shown in Figure 6a, the stripping efficiency with respect to water is reduced with increasing pressure. As the water removal shifts the chemical equilibrium toward reactant side, the acid conversion decreases significantly. On the contrary, the selectivity shows only small changes.

The temperature influence on process characteristics is shown in Figure 6b. Below 160°C the temperature has only minor effects on conversion and selectivity, but above 160°C the acid conversion increases considerably. The selectivity remains nearly constant again. These effects are caused by the enhanced stripping performance of water due to higher temperatures, which shifts the chemical equilibrium towards the product side.

Water stripping leads also to a higher undesirable stripping of the other components, e.g., cumene and 1-octanol. Thus, for an overall optimisation of this process, the efforts towards the recycling of these components from the stripping gas should be considered, too.



**Figure 6.** (a) Influence of pressure on conversion and selectivity (IFM, counter-current mode,  $T = 160^\circ\text{C}$ ); (b) influence of temperature on conversion and selectivity (IFM, counter-current mode,  $p = 5$  bar)

## CONCLUSIONS AND OUTLOOK

The concept of reactive stripping was successfully realised and experimentally studied for the esterification of 1-octanol with hexanoic acid. A rate-based model was developed and validated against experimental results obtained for two different monoliths and both different operation modes. For the most investigated parameters (including concentrations and conversion), good agreement could be achieved. It was shown that the choice of the operation mode (co-current or counter-current) hardly influences the acid conversion, but has a significant effect on the reaction selectivity. The parametric study of the system pressure and liquid temperature showed that they can be used to shift the reaction conversion favourably. The model proposed and validated in this work can be further used for the optimisation of reactive stripping processes.

## NOTATION

|                          |                                |  |
|--------------------------|--------------------------------|--|
| $A$                      | kinetics constant              | –  |
| $c_i$                    | concentration of component $i$ | $\text{mol}/\text{m}^3$                                |
| $K_i, k_i$               | kinetics constants             | $\text{m}^3/(\text{gcat s}), \text{m}^3/\text{mol}, -$ |
| $K_{eq}$                 | equilibrium constant           | –  |
| $m_{cat}$                | catalyst mass within monolith  | g  |
| $r$                      | reaction rate                  | $\text{mol}/\text{s}$                                  |
| $S_{\text{single pass}}$ | single pass selectivity        | –  |
| $X_{\text{single pass}}$ | single pass conversion         | –  |
| $x$                      | molar concentration            | $\text{mol}/\text{m}^3$                                |

## SUBSCRIPTS

|       |                 |
|-------|-----------------|
| ester | octyl hexanoate |
| ether | dioctyl ether   |

|        |                                       |
|--------|---------------------------------------|
| start  | concentration at $t = 0$ minutes      |
| inlet  | concentration of liquid inlet stream  |
| outlet | concentration of liquid outlet stream |

### ACKNOWLEDGMENTS

The support of the European Commission in the context of the 5th Framework Programme (INTINT, Contract No. G1RD-CT-1999-00048) is greatly acknowledged.

### REFERENCES

- R. Baur, A. P. Higler, R. Taylor & R. Krishna. "Comparison of equilibrium stage and nonequilibrium stage models for reactive distillation", *Chem. Eng., J.*, 76, 33–47 (2000).
- E.Y. Kenig, R. Schneider & A. Górak. "Reactive absorption: optimal process design via optimal modelling", *Chem. Eng. Sci.*, 56, 343–350 (2001).
- M. Klöker, E. Y. Kenig, A. Hoffmann, P. Kreis & A. Górak. "Rate-based modelling and simulation of reactive separations in gas/vapour-liquid systems", *Chem. Eng. Process.* 44, 617–629 (2005).
- T.A. Nijhuis, A.E.W. Beers, Th. Vergunst, I. Hoek, F. Kapteijn & J.A. Moulijn. "Preparation of monolithic catalysts", *Catal. Rev.-Sci. Eng.*, 43, 345–380 (2001).
- T. J. Schildhauer, F. Kapteijn & J. A. Moulijn. "Reactive stripping in pilot scale monolith reactors - application to esterification", *Chem. Eng. Process.* 44, 695–699 (2005a).
- T. J. Schildhauer, A. K. Hebel, A. Yawalkar, F. Kapteijn & J. A. Moulijn. "Reactive stripping in structured catalytic reactors – hydrodynamics and reaction performance", in: K. Sundmacher, A. Seidel-Morgenstern (Eds.) *Integrated Chemical Processes*, Wiley-VCH (2005b).
- T. J. Schildhauer, S. Tromp, I. Müller, A. Schilkin, E. Y. Kenig, F. Kapteijn & J. A. Moulijn. "Modelling of reactive stripping in monolith reactors", *Catal. Today* 105, 414–420 (2005c).
- T. J. Schildhauer, I. Hoek, F. Kapteijn & J. A. Moulijn. "Kinetics of zeolite BEA catalysed esterifications – a focus on side reactions and the role of water", submitted to *Appl. Catal., A* (2006).