Dynamic Simulation of Equilibrium Reactions in Discontinuously and Continuously Processed Membrane Reactors

(A. Rolf **, V. Jordan *, R. Korff *, H. Züchner **)

Continuously processed equilibrium reactions are frequently accomplished in reactive rectification processes. These can be very complex for special mixtures [1,2]. With this complexity problems arise with the operation of these reaction processes, as for example the phenomenon of the multiple-stationary operating conditions [3], which especially plays a large role in context with the automation of the process. An interesting alternative to the process of the reactive rectification is the reaction with simultaneous separation of one reaction component using a membrane [4]. Usually the separation is performed by means of pervaporation or vapor permeation [4,5]. By the development of new membrane materials with high selectivities and flux, the profitability of membrane reactors will increase [6]. An example for this are new membrane materials with high alcohol selectivity. The combination of a membrane process with heterogeneously catalyzed reactions offers additional potential to increase the economy of the process. The membrane adopts on this combination the additional task to keep back the catalyst. The main advantage is the simplified product processing following the reaction, whereby the power requirement and the quantity of waste can be reduced.

Theory

The modeling of the separation characteristics took place according to the solution diffusion model:

$$J_i = -\frac{D_{im}}{L_m}\frac{\overline{r}_m}{\overline{M}_m\,\overline{g}_{im}}(a_{imf} - a_{imp})$$

As a result of combining the material-specific variables in front of the bracket to an integral permeation coefficient and under acceptance of a temperature dependence according to the Arrhenius equation the following expression results:

$$J_i = A_i \times e^{\frac{B_i}{T}} \times (a_{imf} - a_{imp})$$

For the experimental determination of the constants of A_i and B_i pervaporation experiments with a water-selective ceramic membrane of the Netherlands Energy Research Foundation ECN were carried out (fig. 1) [7]. The permeate pressure adjusted itself with p_P = 7 mbar, the composition of the feed was w_{EtOH} = 0,96.

With a temperature rise the water as well as the ethanol flux increases, whereas the water flux increases faster than the ethanol flux. From this results a change of the separation characteristic of the membrane (fig. 2), whereby the water selectivity increases with increasing temperature.
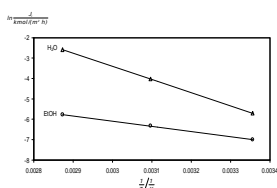

Fig. 1:   Ethanol- and water flux of a water-selective ceramic membrane at p_P = 7 mbar
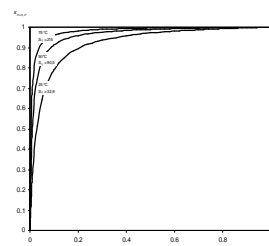

Fig. 2:   Separation characteristic of the membrane

Simulation Model

For the process simulation software ChemCAD a unit operation was programmed, which describes the separation characteristics of the membrane according to the solution diffusion model. For the application of the simulation in ChemCAD a loop membrane reactor was modeled (fig. 3). The represented arrangement offers the possibility to run continuous as well as discontinuous dynamic simulations.
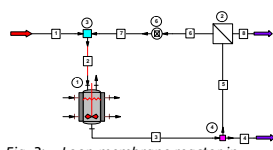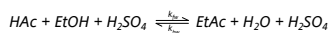

Fig. 3:   Loop membrane reactor in ChemCAD

As an example of a simple equilibrium reaction the acid-catalyzed esterification of acetic acid with ethanol was considered:

$$HAc + EtOH + H_2SO_4 \underset{k_{bw}}{\overset{k_{fw}}{\rightleftharpoons}} EtAc + H_2O + H_2SO_4$$

The data for the reaction rate and their temperature dependence were taken from the literature [8]:

$$k_{fw} = \left(4{,}195 \times \frac{c(H_2SO_4)}{mol/m^3} + 0{,}08815\right) \times e^{\frac{6500{,}1}{T/K}} \quad m^3/(mol\ s)$$

$$k_{bw} = \frac{k_{fw}}{K_C} \quad with \quad K_C = 7{,}558 - 0{,}015\ T/K$$

In order to take the nonideal behavior of the different components into account, the activity coefficient model UNIFAC was applied for the calculations.

Discussion

In the figures 4 and 5 the time-dependent trend of the conversion and the water mass fraction in the reactor is represented at different temperatures and membrane surfaces.

Due to the initially high reaction rate the water produced by the reaction cannot be removed fast enough by means of the membrane. After the reaction slows down the flux across the membrane is high enough to remove more water than is produced by the reaction system. The decreasing amount of water in the reaction mixture causes the shift of the equilibrium to the product side, whereby with increasing membrane surface this will occur more rapidly. Since the initial mixture was equimolar for the simulation and a small part of ethanol also diffuses through the membrane, a final conversion of 100% is not achieved. However, this is possible with a small ethanol excess.

The figures 6 and 7 show the conversion after two hours of reaction time. For a continuously operating reactor the optimal membrane surface can be estimated from this.
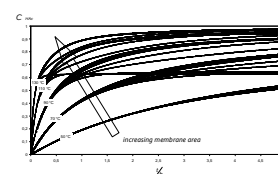

Fig. 4:   Time-dependent trend of the conversion
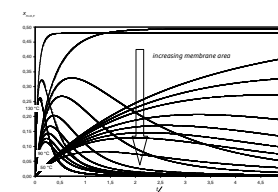

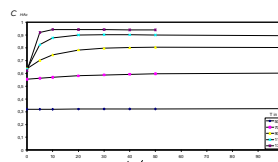Fig. 5:   Time-dependent trend of the water mass fraction

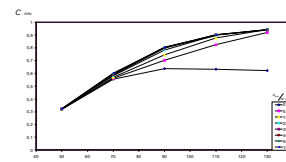Fig. 6:   Dependence of the conversion on the membrane area

Fig. 7:   Dependence of the conversion on the temperature

References

[1] Gmehling, J.; Brehm, A.: „Grundoperationen - Lehrbuch der Technischen Chemie", Band 2, Thieme Verlag, 1996, 236 - 238

[2] Pöpken, T.; Geisler, R. ; Götze, L.; Brehm, A.; Moritz, P.; Gmehling, J.: „Reaktionskinetik in der Reaktivrektifikation - Zur Übertragbarkeit von kinetischen Daten aus einer Rührzelle auf einen Rieselbettreaktor", CIT 71 (1999) 1+2 , 96 - 100

[3] Sundmacher, K.; Hoffmann, U.; Rapmund, P., Mohl, K.-D.; Kienle, A.; Gilles, E.D.: „Nachweis mehrfach stationärer Betriebszustände einer gepackten Reaktivdestillationskolonne für die Herstellung der Kraftstoffkomponente tert.-Amyl-methylether (TAME)", CIT 70 (1998) 9, 1099

[4] Schirg, P.; Waldburger, R.M.; Widmer, F.: „Entwicklung membranunterstützter Reaktionsprozesse", CIT 68 (1996), 1264 - 1271

[5] Dams, A.; Krug, J.: „Pervaporation Aided Esterification – Alternatives In Plant Extension For An Existing Chemical Process", 5th INTERNATIONAL Conference on Pervaporation Processes in the Chemical Industry, Heidelberg 1991, 338 - 348

[6] Waldburger, R.; Widmer, F.; Heinzelmann, W.: „Kombination von Veresterung und Pervaporation in einem kontinuierlichen Membranreaktor", CIT 66 (1994) 6, 850-854

[7] Y.C. van Delft, H.M. van Veen, C.W.R. Engelen, M.J. den Exter, P.P.A.C. Pex: „Dewatering of Organics by Pervaporation with Silica Membranes", Netherlands Energy Research Foundation ECN, Niederlande 1999

[8] Alejski, K.; Duprat, F.: „Dynamic Simulation of the Multicomponent Reactive Distillation", Chem. Engng Sci., Vol. 51, No. 18, 4237 - 4252, 1996

Fachhochschule Münster
University of Applied Sciences

*   Fachhochschule Münster
    University of Applied Sciences
    Stegerwaldstraße 39
    D-48565 Steinfurt
    Germany

** University Münster
    Institute of Physical Chemistry
    Schlossplatz 4/7
    D-48149 Münster
    Germany

Westfälische Wilhelms-Universität Münster