Multicomponent dosing in membrane reactors with internal reactant recycling

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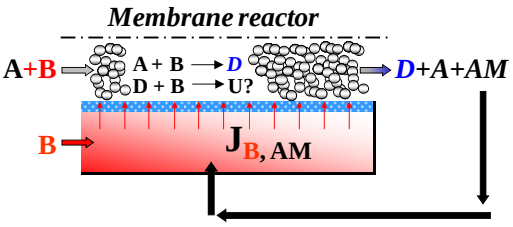
Currently, intensive research activities in chemical process engineering focus on simultaneous parallel-series reactions in order to maximize the selectivity and yield of desired but kinetically limited intermediate products. In particular for selective oxidations of short-chain hydrocarbons the yield of the precious activated olefins is limited. A process intensification of selective oxidation reactions can be realized based on an optimal local distributed feeding of oxygen in the catalyst bed via discrete and continuous dosing concepts applying dense or porous membranes [1]. An additional innovative option and up to now not considered possibility of increasing yields is the dosing of multi-component mixtures in membrane reactors including an internal recycling. The potential of such a kind of dosing and the influence on concentration of various components can be illustrated by means of the differential selectivity of a simple series reaction.

$$A + B \rightarrow D \quad r_1 = k_1 \cdot c_A \cdot c_B^{\beta_1}$$
$$D + B \rightarrow U \quad r_2 = k_1 \cdot c_D \cdot c_B^{\beta_2}$$
$$S_D = \frac{r_1 - r_2}{r_1} = 1 - \frac{k_2}{k_1} \cdot \frac{c_D}{c_A} \cdot c_B^{\beta_2 - \beta_1}$$

$S_D \uparrow$ if $c_B \downarrow$ **B = O_2**
$S_D \uparrow$ if $c_A \uparrow$ **A = HC**

Thus, for a given quantity of the reaction orders ($\beta_1 < \beta_2$) the selectivity of the desired intermediate product D can be enhanced by axial distribution and therefore a lowering of the local concentration of B (e.g. oxygen) [2]. If additionally to component B, A is dosed simultaneously as well into the tube and distributed via membrane, the decreasing concentration profile of A due to the reaction can be compensated. Consequently a higher selectivity of D and a higher reaction rate r_1 (conversion) can be expected, respectively. The process is efficient only



if the amount of A dosed through membrane additionally (AM) can be separated at the reactor outlet and fed again via a circular flow. For this background, the from the industrial point of view, interesting oxidative dehydrogenation of propane to propylene (limited intermediate) was analyzed. Therefore a reduced reactor model (isotherm, isobaric, plug flow) was utilized to evaluate the potential of a multi-component dosing, i.e. oxygen (only via membrane, B) and propane (tube side as well as distributed via membrane, AM), and to appreciate suitable experimental conditions. In contrast to the single-component dosing via membrane (only O_2) a binary-component mixture of oxygen and propane and an internal recycling of AM revealed an increase of the propylene selectivity from 14% to 27%, propane conversion from 41% to 65% and an enhance of the propylene yield from 6% to 17% for the conditions applied. Thus, the process could be significantly intensified. On the other hand, without recycling (AM=0) only a propane conversion of 22% and a propylene yield of 6% could be realized. For an experimental evaluation of the trends obtained in the simulation studies asymmetric ceramic membranes in a pilot scale (length = 104 mm, di = 21 mm, 10 nm γ-Al_2O_3-final layer , total flux < 1500 l/h, catalyst particles 1mm 1.4% V) are used. A practical realization of the recycling of propane fed additionally via membrane (AM) at the reactor outlet was

realized by a simple thermal separation. The experiments obtained a maximal propylene yield of 20% at 550°C and short residence times. The catalyst was stable over 400 h. No soot formation was obtained compared to the well established thermal dehydrogenation processes like CATOFIN® or Oleflex®.

[1] A. Seidel-Morgenstern, Membrane Reactors, Wiley-VCH, ISBN-13: 978-3527320394, 2010
[2] Y. Lu, A. G. Dixon, W. R. Moser, Y. H. Ma, CES, 52, 1349, 1997