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Scale and causes of catalyst activity loss in enzymatic catalyzed reactive distillation

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HIGHLIGHTS

- First systematic study of enzyme activity in enzymatic catalyzed reactive distillation process.
- Experimental verification of feasibility of stable reactant conversion for 320 operation hours.
- New mechanism for enzyme activity loss in reactive distillation identified.
- New ideas proposed for the improvement of design and operation of enzymatic catalyst reactive distillation processes.

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ABSTRACT

Continuous enzymatic catalyzed reactive distillation (eRD) is a new process that can reduce product inhibition and the need for additional purification steps. However, the enzymatic catalyst is exposed to markedly different conditions than in conventional processes. The enzyme stability, a crucial cost factor, has not been investigated for the application in an eRD and the underlying mechanisms for catalyst deactivation are still unknown. This article presents for the first time a comprehensive study on the scale and causes of enzyme activity reduction in eRD processes. Pilot plant experiments with the transesterification of butyl acetate with hexanol catalyzed by Novozyme 435 confirm the existence of a process window with high reaction rates and low activity loss. The remaining activity after 320 h of operation is investigated in each reactive packing, leading to a new found cause of activity reduction that has so far not been considered for enzymatic catalyzed reactive distillation. The results allow for a better design and operation of eRD processes and the development of enzyme immobilisates that cater to the specific needs of integrated operation.

1. Introduction

Enzymatic catalysts are increasingly applied in the chemical industry as they offer a very high selectivity and mild process conditions (Aehle, 2004). At present, the most commonly used production technique in which enzymatic catalysts are employed, is the batch stirred tank reactor followed by several purification steps. However, this process has two major drawbacks: product inhibition as well as limited production quantities. In order to overcome these problems the use of enzymes in a continuous process with an in-situ product removal is proposed: the continuous enzymatic catalyzed reactive distillation (eRD). Due to the continuous in-situ removal of reaction products the inhibition of the enzymatic catalyst is minimized compared to batch processes. Furthermore, employing a continuous process significantly increases the production quantity and reduces the necessity of frequent start-ups, increasing the process safety and ensuring constantly high product qualities.

Another advantage of the proposed process is the integrated nature of the RD. Process integration is known to provide efficient operation and high energy savings at the same time, which makes integrated processes attractive from the economic as well as the environmental point of view. In the industrial practice the employment of RD achieves energy savings between 15% and 45% (Harmsen, 2007). If more than two product streams are to be separated, the integration of a dividing wall into the reactive distillation column can further decrease the process' energy demand (Fig. 1). The resulting column containing a dividing wall and reactive as well as separation sections is called reactive dividing wall column (RDWC). Simulation studies in the literature demonstrate the RDWC's great cost saving potential and successful operation

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Nomenclature

P_{rel}	relative product quantity in activity test
T	temperature, K
V	volume, µl

Greek letters

Δp	pressure difference, Pa

Subscripts

BuAc	*n*-butyl acetate
HeOH	1-hexanol
rel	relative

Abbreviations

BuAc	*n*-butyl acetate
CAL B	*Candida antarctica* lipase B
DWC	dividing wall column
eRD	enzymatic catalyzed reactive distillation
eRDWC	enzymatic catalyzed reactive dividing wall column
HeOH	1-hexanol
P	packing element
PNPB	p-nitrophenyl butyrate
RD	reactive distillation
RDWC	reactive dividing wall column
S	column section

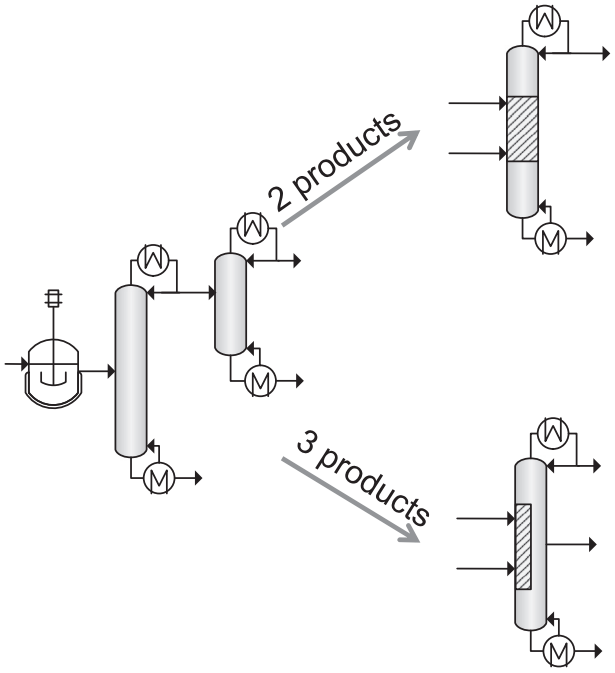

Fig. 1. Considered process alternatives: left: stirred tank reactor with column sequence; top: eRD; bottom: eRDWC.

(Schröder et al., 2016; Ryll, 2009; Müller, 2010; Ehlers et al., 2017; Egger and Fieg, 2017).

The feasibility of enzymatic catalyzed reactive distillation has already been shown for several reference systems in batch laboratory scale columns (Paiva et al., 2003; Au-Yeung et al., 2013; Heils et al., 2015). Recently, two studies demonstrated the stable continuous operation of pilot plant scale columns, for eRD (Wierschem et al., 2017) and eRDWC (Egger and Fieg, 2017). While the reaction in conventional RD processes can either be homogeneously or heterogeneously catalyzed, enzymatic catalyzed RD has only been heterogeneously catalyzed so far. The enzymes are typically immobilized on carrier pellets or, in one known case, coated on a structured packing (Heils et al., 2016). For reasons of simplicity the article uses the terms enzyme stability and enzyme activity as synonyms to the activity of the employed enzyme immobilisate.

A crucial aspect regarding the industrial implementation of these processes is the stability of the employed enzyme immobilisates, as a low stability leads to reduced conversion, more frequent catalyst changes and down times. Although there are lots of investigations on enzyme and immobilisate stability in non-integrated processes (Leipold, 2014; Gianfreda et al., 1985; Howell and Mangat, 1978; Kim et al., 1982; Arroyo et al., 1999; Aymard and Belarbi, 2000; Pal and Khanum, 2011; Mateo et al., 2007), little knowledge exists about the behavior of enzymatic catalysts in a RD column. The effects that act on the enzyme immobilisate in a RD column differ strongly from the conditions in a stirred tank reactor, for example. Therefore, it is not ensured that findings from these studies can be transferred to the operation of RD.

In the stated studies for continuous eRD and eRDWC, the pilot plants were operated for the relatively short time of 80 h and no reduction in the measured conversion was found (Egger and Fieg, 2017; Wierschem et al., 2017). In these studies it is not clear though, whether there was actually no enzyme activity loss or whether the conversion remained constant due to a big enough amount of catalyst so that deactivation would be of no consequence. To our best knowledge, no study has been published that gives detailed information about the actual remaining activity of the enzymes in an integrated eRD process and the causes of activity reduction. However, this knowledge is required for a proper design of eRDs and the development of enzymatic catalysts specifically for integrated processes.

This paper presents an integrated approach of experimental work and simulation studies to investigate the eRD process' conversion stability quantify the enzyme immobilisate activity reduction and identify the causes of deactivation. Furthermore, the article shows key elements for a successful design and operation of eRD processes. For the study a well measured reference system is employed, the transesterification of butyl acetate with hexanol, catalyzed by the immobilized lipase Novozyme 435 (Eq. (1)).

$$\text{butyl acetate} + \text{hexanol} \rightleftharpoons \text{hexyl acetate} + \text{butanol} \quad (1)$$

For this system an eRDWC is employed to recover excess educts in the third external stream. In the present manuscript the focus lays clearly on the reactive prefractionator that is equivalent to an eRD. A validated simulation tool (Egger and Fieg, 2017) is used for the column design of the employed eRDWC pilot plant and the selection of operating points. A two-step approach was chosen to quantify the enzyme immobilisate's stability. First, the evaluation of the overall conversion for over 320 h, approximated two weeks, operating time assesses the long term enzyme immobilisate stability. Second, the specific determination of remaining enzyme activity for each of the 20 reactive packing elements in the pilot plant allows determining the underlying causes of activity reduction. Finally, it is shown how the results can lead to a better design and operation of eRD processes and the development of enzyme immobilisates that cater to the specific needs in integrated operation.