



# Reaching steady state under cyclic operations with dispersion: The case of the reverse flow adsorber



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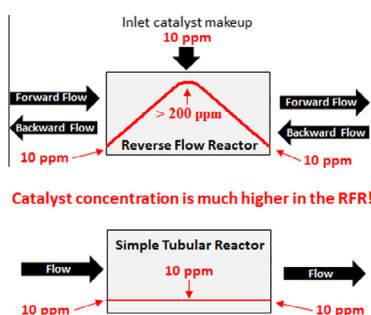
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## HIGHLIGHTS

- Using make-up of the adsorbate in the reactor, a cyclic steady-state is reached despite dispersive phenomena.
- The catalyst/adsorbate concentration inside the reactor is much higher than at the boundaries.
- Leaching of catalyst/adsorbate out of the reactor is compensated which is key for homogeneous catalysis.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The reverse flow adsorber (RFA) can be used as a catalytic reactor for homogeneous catalysis to avoid the issues of catalyst separation. The RFA combines the reverse flow circulation and the separation of the dissolved solute from the liquid homogeneous mixture. In this work, the RFA is modeled and simulated in order to evaluate its separation performances and its behavior. The studied adsorber is a single adsorption/desorption packed bed, and the reversal of flows is applied to keep the solute inside the bed as long as possible while minimizing its outlet concentration (leaching). The chosen one dimensional model accounts for the axial dispersion and the non-equilibrium effects (mass transfer resistances, etc). The numerical method of lines (MOL) is used to solve the partial differential algebraic model equations (PDAEs). Two cases are studied; the first one is the dynamic of the homogeneous solute concentration starting from a pre-loaded column and without solute addition. The second case considers operations with continuous solute side stream addition. In the first case, leaching persists until the initially pre-loaded adsorption column with solute is completely emptied thus demonstrating unsteady-state operations in contrast with previous works. To compensate leaching, solute makeup is added at the center of the column. This leads, after priming a number of cycles, to a stationary periodic state operation.

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## 1. Introduction

Many industrial processes use homogeneous molecular catalysts. In many cases the catalyst should be separated, recovered and, eventually, concentrated from the reaction mixture prior to

reuse, and/ or to meet product specifications. The downstream catalyst separation stage can use classical separation methods such as liquid-liquid extraction or distillation. These separation methods have some drawbacks e.g. thermal decomposition of the catalyst and/or high energy consumption. Thus, many strategies have been developed over more than 30 years to cope with the separation and recycling of molecular catalysts. This encompasses biphasic liquid-liquid catalysis as employed in the so called Rhone-Poulenc-Ruhr

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### Nomenclature

$C$	current concentration of the solute in the mobile phase $C(t, z)$ (mol/l)	$q$	concentration of the solute in the stationary phase in equilibrium with the mobile phase $q(t, z)$ (mol/l)
$C_{\text{adsorber}}$	average solute concentration in the adsorber (liquid and solid phase) (mol/l)	$q_s$	solid maximal adsorption capacity (mol/l)
$C_{\text{leach}}$	average leaching concentration (mol/l)	$t$	time (s)
$C_{\text{liquid}}$	average solute concentration in the liquid phases (mol/l)	$t_{1/2}$	cycle duration of a half cycle (s)
$C_{\text{makeup}}$	makeup concentration (mol/l)	$t_r$	residence time (s)
$C_0$	initial concentration (mol/l)	$u$	flow velocity (m/s)
$D_{\text{app}}$	apparent dispersion coefficient ( $\text{m}^2/\text{s}$ )	$z$	axial distance (m)
$L$	length of the adsorber (m)	<i>Greek letters</i>	
$N$	column efficiency	$\alpha$	adsorption constant (l/mol)
		$\delta$	indication of the flow direction
		$\varepsilon$	total porosity

Chemie hydroformylation process in which the organic phase containing the reagents and products is mixed with an aqueous phase containing the catalyst [1]. The use of fluorinated liquids and ionic liquids as the catalytic layer has also been reported [2–4]. More recently, the use of membrane technologies was proposed with success. Many other separation processes – thermotropic and supercritical  $\text{CO}_2$  to name a few – have been also proposed reflecting the enormous challenge of molecular catalysts separation and recycling. Although some of these proposals are actually in use in the industry, including at a large scale, they all present bottlenecks that have prevented their widespread use. For example, biphasic catalysis is limited by the reagents solubility in the catalytic phase. The use of membranes requires the specific design of catalysts to achieve molecular sizes compatible with the molecular weight cut-off of the membrane material [5,6]. Thus membrane technology drives to a trade-off between low productivities for simple catalysts and higher productivities with sophisticated catalysts. Moreover additional separation stages increase the investment costs.

A traditional approach that could address most of these issues is the use of heterogenized catalysts, some being commercially available (e.g. Evonik Polymer-bound chlorotris(triphenylphosphine) rhodium(I) on styrene-divinylbenzene copolymer). Traditional packed-bed reactors can be used. However, this methodology results often in lower catalyst performances, likely due to surface interactions, making the irreversible anchoring of molecular catalysts on a solid support with the same activity and selectivity still challenging.

Within this context, the reverse flow adsorption (RFA) technology can potentially achieve both reaction, separation and recycling of the homogeneous molecular catalyst in one single piece of equipment. Application of the RFA was illustrated for Heck coupling [7] and hydrosilylation [8]. However, these demonstrations were generally not successful since empirical design and operations were used that hampers to take the full advantage of this technology. In a RFA, the catalyst is reversibly adsorbed/desorbed and is located in both the liquid and the solid phases according to the sorption isotherm. The reaction occurs in the liquid homogeneous phase, which allows the homogeneous molecular catalysis to operate freely, while the catalyst is separated from the liquid by adsorption onto the solid adsorbent.

The reverse flow reactor belongs to the cyclic processes family. The flow changes direction from forward to backward and vice versa after each cycle period (Fig. 1). The catalyst migrates inside the column as in chromatography according to the flow direction but more slowly than the products due to adsorption. This allows the products to exit the reactor while the solute (catalyst) is trapped. The stationary regime of the reverse flow reactor is the

cyclic steady-state (CSS), in which all conditions (concentrations, etc) are identical from one cycle to another.

The reverse flow technology was first developed and studied to maintain the thermal wave captive to enhance the reactor efficiency as applied to  $\text{SO}_2/\text{SO}_3$  oxidation and then to VOC polluted air [9–12]. This principle was then extended and evaluated for various applications in gas-solid heterogeneous catalysis [13–15]. In the thermal reverse flow reactor, the cyclic steady state (CSS) is reached after a given operation time. The convective heat losses are compensated by the heat of the exothermic reaction in the reactor catalytic zone [16,17].

By heat-matter analogy, the reverse flow technology was extended to catalyst trapping and separation from the homogeneous reaction mixture. Dunnewijk et al. [18] modeled the separation of  $\text{CoCl}_2$  and  $\text{PdCl}_2$  by adsorption on a triphenylphosphine polymer adsorbent. According to the authors, a stationary regime is reached after 500 cycles and the total initial catalyst quantity inside the column is trapped without any leaching of metal. The same team reached similar conclusions for the adsorption of  $\text{CoCl}_2$  catalyst on functionalized silica adsorbents [19]. So, in both studies, the process reaches a cyclic steady state despite the incorporation of dispersive phenomena such as the axial dispersion and the mass transfer limitations in their model. However, in the reverse flow technology, any dispersive phenomenon would lead to concentration profile broadening, to metal leaching and to column discharging. The conclusion about a dispersive system reaching a steady-state regime prompts us to re-investigate the application of the reverse flow adsorption to molecular catalysts trapping.

In this work, the reverse flow adsorber that accounts for the dispersion phenomena is modeled and simulated in order to evaluate its separation performance. The aim of this modeling and numerical study is to have a better understanding of the adsorber

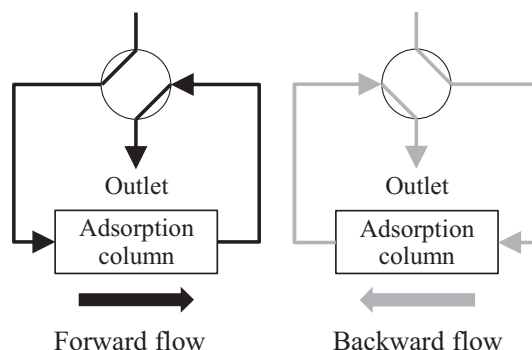


Fig. 1. Scheme of the reverse flow adsorber.

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