



Evaluation of reactor concepts for the continuous production of fine chemicals using the selective hydrogenation of cinnamaldehyde over palladium catalysts



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ABSTRACT

Two reactor concepts based on the pellet string reactor (PSR) were evaluated using the continuous selective hydrogenation of cinnamaldehyde as a model reaction to characterize the suitability for the application in the production of fine chemicals or pharmaceuticals. Reaction studies were carried out in a single PSR and a scale-up concept consisting of 32 parallel channels (MPSR). The impact of liquid velocity, gas holdup and pressure on the conversion and selectivity were investigated for both reactors. It was found that the continuous reactors deliver a comparably high selectivity to a batch reactor when hydrodynamic conditions are chosen adequately to obtain plug flow. The results also indicate a comparable performance for both reactors in terms of reaction rate and selectivity. Thus, the concept seems to present a promising scale-up method based on single-channel experiments.

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1. Introduction

Over the past two decades, chemical and pharmaceutical industry aims to switch from batchwise mode of operation to a continuous production in order to intensify the reaction process in terms of increased product yield and quality, to improve process safety, to reduce the amount of catalyst or to simplify scale-up [1]. While most of the reactions of the so-called “flow-chemistry” contain only a liquid or gas phase, the integration of solid catalyst still presents a major challenge in reaction engineering during the realization of continuous three-phase reactions. Flow reactors containing parallel flow channels which are packed with catalyst particles, so called pellet string reactors, represent a promising concept [2]. In contrast to mini or micro fixed bed reactors, the catalyst particles are of the same dimension as the reactor diameter. Therefore the risk of fluid maldistribution in the catalyst bed is minimized.

The concept of the pellet string (PSR) reactor has been well-known for a long time and has been employed for measuring mass transfer coefficients, mostly in gas-phase reactions. Some examples are the publications of Scott et al. [3], Lee et al. [4], Sharma et al. [5], Solcova et al. [6,7] and Takacs et al. [8]. Works on gas–liquid–solid

applications are rarer. A pellet string of large particles (8.2 mm) was employed by Satterfield et al. [9] to investigate mass transfer limitations for the hydrogenation of alpha-methylstyrene to cumene. More recently, Kallinikos et al. [10,11] and Hipolito et al. [12] have published results on the application of a pellet string reactor for kinetic studies, e.g. for the hydrodesulphurization of heavy gasoil fractions. They also showed that it is possible to obtain a very close residence time distribution for two-phase flow in this type of reactor [10,12]. A detailed characterization of the mass transfer and hydrodynamic behavior for a three-phase reaction has been presented lately by Haase et al. [13] and Langsch et al. [14,15] based on the hydrogenation of alpha-methylstyrene.

Regarding the good performance of the PSR, in addition to the application in catalyst screening, the parallelization of multiple packed channels in the millimeter range as a channel array presents an interesting concept for the production of fine chemicals. For instance, monolith substrates can form the inert channel walls and are packed with spherical catalyst particles. A few examples of this integrated packing have been presented by Kapteijn et al. [16], Dautzenberg et al. [17] and Bauer et al. [2,13]. The latter has shown a high performance for the hydrogenation of alpha-methylstyrene. Different terms have been employed to describe this type of packing, including “structured trickle-bed reactor” [2,16], “composite structured packing” [17] and “composite minichannel reactor” [13]. In this work the term multi-channel pellet string reactor (MPSR) will be used. It represents a scale-up concept based on

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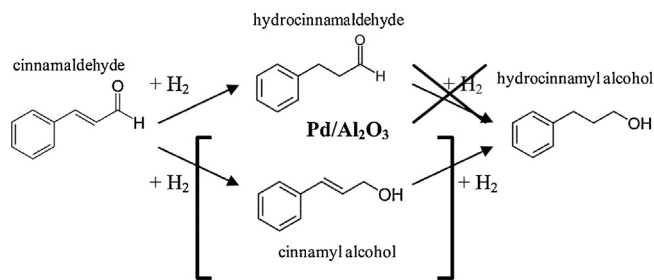


Fig. 1. Reaction network for the hydrogenation of cinnamaldehyde over palladium catalyst.

the numbering-up from one channel to several parallel channels of the same dimension. This approach is generally applied in mini and micro reactors to enlarge the production capacity while still preserving the benefits of the small dimensions [18].

Whereas reaction studies to characterize mass transfer have been carried out with different hydrogenation reactions, so far no investigations on the application of this reactor concept for a selective reaction have been published. This work will therefore focus on the investigation of a PSR for the selective hydrogenation of cinnamaldehyde (CAL) to hydrocinnamaldehyde (HCAL) as a model reaction to prove the beneficial reactor performance. The synthesis of a large number of fine chemicals, particularly in the field of flavor and fragrance chemistry and pharmaceuticals, involves the selective hydrogenation of unsaturated carbonyl intermediates as a critical step. The heterogeneously catalyzed hydrogenation of CAL over a palladium catalyst in the solvent toluene yields HCAL as main product and hydrocinnamyl alcohol (HCOL) as side product. In accordance with other publications, the intermediate cinnamyl alcohol (COL) cannot be detected [19–22]. As the unsaturated alcohol is the main desired product demanded from the industry, another catalyst, like platinum, should also be tested in the future. Kinetic studies with palladium catalysts have shown that HCOL is formed only via the COL route and not from HCAL. Thus, the reaction network is formed by two parallel reactions (Fig. 1).

In this contribution, results from first experimental studies in a single PSR will be presented. For comparison reaction kinetics will be determined in a batch reactor system. In all cases commercial egg-shell catalysts are employed (0.5% or 1.0% Pd/ γ -alumina). The scale-up to multiple channels (MPSR) will be carried out and first conclusions regarding the impact of the different process parameters are deduced.

2. Experimental

2.1. Chemicals and gases

Reaction studies were carried out with a solution of 50 kg/m³ (380 mol/m³) trans-cinnamaldehyde (C₉H₈O, 98%, abcr) in toluene (C₇H₈, >99.8%, Fisher Scientific). Two different commercial Pd/ γ -Al₂O₃ egg-shell catalysts were used (0.5% Pd/ γ -Al₂O₃, 3.0 mm (A); 1.0% Pd/ γ -Al₂O₃, 1.8–2.0 mm (B)). The main catalyst properties are given in Table 1. Prior to reaction the catalyst was reduced at 210 °C and 10 bar (a) for 4 h under flowing hydrogen. All chemicals and commercial catalyst particles were used as received. Gases used are of 5.0 purity (Air Liquide).

2.2. Reaction studies

Reaction studies were carried out isothermally at 353 K and a hydrogen pressure between 10 bar and 30 bar. The reaction conditions as well as characteristic dimensionless numbers regarding hydrodynamics are summarized in Table 2. Isothermal operation

Table 1
Main catalysts properties.

Catalyst	Pd/Al ₂ O ₃ (A)	Pd/Al ₂ O ₃ (B)
Metal content (by manufacturer) [wt.%]	0.5	1.0
Mean particle diameter [10 ⁻³ m]	3.0	1.9
Estimated thickness of active layer [10 ⁻⁶ m]	250	170
Total pore volume ^a [mm ³ /g]	291.27	270.03
Pore surface area ^a [m ² /g]	139.40	148.38
Modal pore diameter ^a [10 ⁻⁶ m]	0.0037	0.0037
Porosity ^a	42.97%	41.03%
Metal dispersion ^b	20.9%	25.9%
Metal particle size ^b [10 ⁻⁹ m]	5.4	4.3
Geometric specific surface area [m ² /m ³]	2000.0	3157.89

^a Determined by mercury porosimetry.

^b Determined by CO chemisorption.

was assured by monitoring the inlet and outlet temperature and regarding the moderate reaction enthalpy and low conversion. The following procedure was applied for all experiments. First the pressure was adjusted by feeding hydrogen into the system and adjusting the pressure controller. Then the reactor was flushed with liquid to ensure full wetting of the catalyst bed. Afterwards the desired liquid flow rate was set at the pump. Once the system temperature reached a stationary point, the hydrogen flow was set by the mass flow controllers. The system was allowed to reach a steady state, usually after 60 min. This was checked by analyzing liquid samples taken at the reactor outlet at several times during a run (every 10–20 min). Sample analysis was performed offline by an Agilent 6890N GC equipped with an HP-1 column and an FID detector. First reaction studies were carried out to evaluate the performance of the PSR. During the experiments the flow regime was observed so that a regular slug flow was maintained at all times. Studies on the influence of different process parameters were carried out, including the effect of liquid velocity, gas holdup and pressure. Superficial liquid velocity $u_{L,s}$ and gas velocity $u_{G,s}$ were calculated based on the reactor cross-sectional area S_R and the volumetric flow rate \dot{V} for the prevailing reaction temperature T_R and pressure p_R (Eqs. (1)–(3)) (STP – standard temperature T_{STP} and pressure p_{STP}).

Superficial liquid velocity:

$$u_{L,s} = \frac{\dot{V}_L}{S_R} \quad (1)$$

Superficial gas velocity:

$$u_{G,s} = \frac{\dot{V}_G}{S_R} = \frac{\dot{V}_{G,STP} p_{STP} \cdot T_R}{p_R \cdot T_{STP} S_R} \quad (2)$$

Gas holdup:

$$H_G = \frac{u_{G,s}}{u_{G,s} + u_{L,s}} \quad (3)$$

Table 2
Experimental conditions for both reactor concepts.

	PSR	MPSR
T_R [K]	353	353
p_R [bar]	10, 20, 30	10
$u_{L,s}$ [10 ⁻³ m/s]	10, 20, 40, 80	0.8, 1.6, 2.4
$u_{G,s}$ [10 ⁻³ m/s]	9 ... 68	0.7 ... 7.3
H_G	0.5, 0.65, 0.8	0.45, 0.6, 0.75
$c_{CAL,0}$ [mol/m ³]	380	380
$Re = u_{TP,S} \cdot \rho_L \cdot d / \eta_L$	131 ... 716	13 ... 82
$Re^* = u_{TP,S} \cdot \rho_L \cdot d / (\eta_L \cdot (1 - \epsilon_{bed}))$	301 ... 1652	29 ... 186
$Bo = \rho_L \cdot g \cdot d_h^2 / \sigma$	0.906	0.653
$Ca = u_{TP} \cdot \eta_L / \sigma$	4.05 · 10 ⁻⁴ ... 2.22 · 10 ⁻³	2.25 · 10 ⁻⁵ ... 1.46 · 10 ⁻⁴
$We_L = \rho_L \cdot u_L^2 \cdot d_p / \sigma$	5.43 · 10 ⁻³ ... 3.47 · 10 ⁻¹	6.09 · 10 ⁻⁵ ... 5.48 · 10 ⁻⁴
$d_h = d$	Krischer–Kast	
$\sqrt[3]{16\epsilon_{bed}^3 / (9\pi(1 - \epsilon_{bed})^2)}$	hydraulic diameter	

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