



A porous structured reactor for hydrogenation reactions



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ABSTRACT

A novel combination of catalyst carrier and reactor design was developed for intensified production of vitamin intermediates. The so called Design Porous Structured Reactor (*DPSR*) is a laser sintered porous 3D-structure that can be tailored to the desired reaction properties such as fluid conditions or heat removal and can also act simultaneously as catalyst support.

The selective hydrogenation of 2-methyl-3-butyn-2-ol (*MBY*) to 2-methyl-3-buten-2-ol (*MBE*) under solvent-free conditions was chosen as the reaction to evaluate the potential of *DPSRs* in comparison to conventional batch reactors. *DPSR* experiments were performed at varying temperatures and liquid flow rates.

DPSRs exceeded batch performance in terms of selectivity, yield and turnover frequency in the analyzed process parameter range. However, *DPSRs* showed some mass transfer effects. Selectivities and yields increased with higher liquid flow rate due to reduced system pressures and sharper residence time distributions.

Overall mass transfer coefficients for *DPSRs* were determined based on an isothermal non-ideal plug flow model applying heterogeneous Langmuir–Hinshelwood kinetics to account for the chemical conversion. The model showed sufficient accuracy to describe the occurring mass transfer processes.

DPSRs were found to be viable alternative for batch reactors, demonstrating the potential for process intensification with an inherent potential for further improvement.

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1. Introduction

Vitamins, especially lipophilic vitamins such as A (retinol) and E (tocopherol), are very important food supplements and are essential for healthy human and animal life. With production quantities that can exceed 10,000 tons per year [1,2], some vitamins could even be classified as bulk chemicals. Due to economies of scale, even small improvements in production efficiency can yield high benefits in terms of cost optimization. Vitamins are traditionally produced in (catalyzed) multi-step production procedures, either in batch or continuous mode. Fixed-bed or fluidized bed reactors are often used on an industrial scale as continuous reactors for such heterogeneously catalyzed processes. The specific choice for a certain type of equipment usually depends on operational conditions, type of catalysts, heat formation and integration, product yields, fluid dynamics, multiple economic considerations and many additional factors.

Cost efficiency plays an increasing role on fine chemicals. This led to an increased R&D effort on site to intensify production with the intention to vastly reduce production costs by various means, for example minimizing waste materials, increasing energy efficiency, use of improved catalysts, increasing component recycling or using novel processes.

Research and development started to focus on the implementation of innovative approaches to reach a substantial benefit in terms of quantity, safety and sustainability in various fields, summarized under the term “Process Intensification” [3]. Batch production enhancement, while not truly qualifying as process intensification in the sense of novelty and innovation, was often achieved by more traditional mechanical or chemical engineering means, i.e. improving fluid dynamics with different mixing elements or changing and improving the applied catalysts. Another approach focuses on replacing conventional stirrer blades with catalytically active parts. Leon et al. 2012 [4] presented study on a rotating solid metal foam stirrer reactor and found an increased gas–liquid and liquid–solid mass transfer compared to conventional slurry reactor. They found however a lower intrinsic activity of the catalyst compared to the slurry reactor due to inhomogeneous site distribution along active site distribution in the washcoat layer.

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Nomenclature

Abbreviations

<i>D, DIM</i>	C_{10} dimers
<i>DPSR</i>	Designed Porous Structured Reactor
H_2	hydrogen
<i>MBY</i>	2-methyl-3-butyn-2-ol
<i>MBE</i>	2-methyl-3-buten-2-ol
<i>MBA</i>	2-methyl-3-butan-2-ol
<i>SLS</i>	Selective Laser Sintering

Roman symbols

<i>c</i>	molar concentration [mol m^{-3}]
<i>CoV</i>	Coefficient of Variation [-]
D_{ax}	axial dispersion coefficient [$\text{m}^2 \text{s}^{-1}$]
d_p	<i>DSPR</i> pore diameter [m]
F_{gas}	gas flow rate [$L_n \text{ min}^{-1}$]
F_{liq}	liquid flow rate [kg h^{-1}]
$H_{A,H_2}(T)$	temperature dependent Henry's law constant [$\text{Pa m}^3 \text{ mol}^{-1}$]
<i>k</i>	reaction rate constant [$\text{m}^3 \text{ mol}^{-1} \text{ h}^{-1}$]
$k_{f,1}$	first Forchheimer parameter [bar s m^{-2}]
$k_{f,2}$	second Forchheimer parameter [$\text{bar s}^2 \text{ m}^{-3}$]
k_{HX}	heat transfer coefficient [$\text{kW m}^{-2} \text{ K}$]
k_{MT}	liquid–solid mass transfer coefficient [s^{-1}]
<i>K</i>	adsorption constant for Langmuir–Hinshelwood expression [$\text{m}^3 \text{ mol}^{-1}$]
L_R	equivalent reactor length [m]
L_n	gas norm liter [l]
m_{plant}	mass of reaction mixture in the plant [kg]
n_{pd}	palladium amount in reactor [mol]
<i>P</i>	reactor pressure [bar]
ΔP	reactor pressure drop [bar]
$\frac{\Delta P}{L}$	pressure drop [bar m^{-1}]
<i>r</i>	reaction rate [$\text{mol m}^{-3} \text{ h}^{-1}$]
<i>v</i>	interstitial flow velocity [m s^{-1}]
V_{liq}	liquid volume in reactor [m^3]
<i>S</i>	selectivity [-]
<i>T</i>	reactor temperature [$^{\circ}\text{C}$]
ΔT_{ad}	adiabatic temperature increase during reaction [K]
ToF	turnover frequency [$\text{mol MBY mol}^{-1} \text{ Pd s}^{-1}$]
t_p	process time [h]
t_R	reaction time [h]
<i>X</i>	conversion [-]
<i>Y</i>	yield [-]
<i>z</i>	reactor position [m]

Additional sub- and superscripts

<i>exp</i>	experimentally determined
<i>in</i>	reactor inlet
<i>mean</i>	mean values
<i>l</i>	liquid phase
<i>LH</i>	Langmuir–Hinshelwood
<i>s</i>	surface
<i>theoretical</i>	theoretically determined

Greek letters

η	reaction effectiveness [-]
μ_{mix}	viscosity of the reaction mixture [Pa s]
ρ_{mix}	density of the reaction mixture [kg m^{-3}]
σ	variance in concentration [mol m^{-3}]

In continuous systems, work has either focused on novel and innovative process equipment, e.g. combined heat-exchanger reactors or spinning disk reactors, or new production approaches, such as integrating multiple process steps in single devices (e.g. a distillation column filled with catalytically active packing by DeGarmo et al. [5]) or using alternative energy sources (e.g. ultrasound as a source of energy for chemical processing [6,7]).

A large variety of concepts for innovative continuous reaction devices have been proposed and used over the years for multi-phase reactions. Among many others, trickle bed and monolithic reactors [8–10], micro-reactors [11,12] and catalyst coated highly porous structures, like metal and ceramic foams [13–15], were studied and described in the literature.

An alternative to such systems, combining static mixing elements and catalyst carrier functions, are “Designed Porous Structure Reactors” (*DSPR*). *DSPR* are porous, stream-wise periodic structures with a catalyst coating intended for chemical reactions purposes. The original concept of these devices is based on porous foam-like structures to combine characteristics of highly porous structures, like mixing and pressure drop qualities, with the advantages of regularly shaped 3-D geometries, namely having good fabrication reproducibilities and being suitable for computationally demanding CFD simulations. The finally developed geometry of *DPSRs* is the negative pattern of tetrahedral overlapping spheres. Specific details about the structure's design and origin were reported previously (see Hutter et al., 2010 [16]).

To date, only hydrodynamic and thermal properties of *DPSRs* have been published in literature. Previous findings are reported in Tables 1 and 2 for mixing qualities, pressure drop and heat transfer in comparison to common process equipment applied in process engineering. In all respective categories, *DPSRs* demonstrate acceptable performances, which indicate an adequate potential as continuous reaction device from a hydrodynamic and thermal point of view.

Here we report our investigations of the chemical potential of *DPSRs* in the prospect of intensifying an industrially relevant reaction step in the production of vitamin intermediates.

The selective solvent-free hydrogenation of 2-methyl-3-butyn-2-ol (*MBY*) to 2-methyl-3-butyn-2-ol (*MBE*) was chosen as the test reaction, since selective hydrogenations, especially of C–C triple bonds, are often mentioned as important key steps in the production of vitamins [1]. The selective hydrogenation of *MBY* is known to deliver high conversions and yields in batch systems using Pd based catalysts and was previously studied by various authors, e.g. [26,27].

Fig. 1 and Eqs. (1)–(4) show the general reaction network. The reaction proceeds sequentially, the hydrogenation of *MBE* to *MBA* only becomes significant once all *MBY* is consumed. Small amounts of *MBA* could be formed directly from over-hydrogenation of *MBY* on the catalyst surface from not desorbed *MBE*. In addition, dimeric high-boiling C_{10} products (*D*) can be formed. The kinetic reaction behaviour is commonly described by simplified Langmuir–Hinshelwood expressions [26,27]. While reaction (3) might occur in reality in a two-step reaction on the catalyst surface, a simplified one-step conversion was assumed, as *MBA* is produced in very small amounts and contributes little to the overall kinetics.



The chemical potential of *DPSRs* in the prospect of intensifying the selected hydrogenation was compared to a batch reactor

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