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High throughput screening of homogeneously catalyzed hydrogenations in a continuously perfused membrane reactor

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ABSTRACT

A new concept of a continuously working membrane reactor was developed and successfully used for hydrogenation screening reactions. Thus, an innovative concept intends the separation of the hydrogen source from the reaction medium. This method guarantees a constant pressure over the reaction time, but allows at the same time a rapid variation of the reaction conditions (reaction time, temperature, pressure of hydrogen), what can be carried out easily.

Investigations concerning the choice of membrane material, retention times of each run and phase separation of the sequences were conducted. Using toluene as reaction solvent and propylene carbonate and water as a wash solution, 1-octene, carvone and (-)- β -pinene were hydrogenated and the results compared to those yielded with a batch reactor.

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1. Introduction

Since its development more than 20 years ago, the high throughput screening (HTS) has been established as standard tool in catalysis (Schüth and Demuth, 2006). Due to an easy handling and the opportunity of a rapid variation of the reaction parameters it is most efficient in comparison to conventional screening and optimization reactions. However, the HTS enables a wide range of catalytic reactions at low costs and with much less effort and consequently brings nowadays great benefits in modern research (Satyanarayana and Kagan, 2005) and industrial applications (de Vries and Lefort, 2013; de Vries, 2014; Lefort et al., 2006).

Especially for the drug discovery and exploration as well as development of pharmaceuticals the HTS is most common (Hajare et al., 2014). One field is represented by the asymmetric organometallic catalysis (de Vries and de Vries, 2003), predominantly enantioselective hydrogenations (Lefort et al., 2010; Jiang et al., 2006; Tararov and Börner, 2005; Friedfeld et al., 2013; de Vries and Lefort, 2006; Wieland and Breit, 2010; Terrade et al., 2015). Thus, parameters influencing the stereoselectivity

of those reactions, e.g. the H_2 -pressure, the solvent and in particular the catalyst ("ligand screening"), can be examined in a very simple manner.

However, most of the high throughput screening devices for hydrogenations have in common not to be affordable for especially small and medium-sized companies, due to increased investment costs. Thus, several investigations for hydrogenations with focus on an economical application in HTS were undertaken in recent years: One concept, based on works of Battsengel et al. (2003, 2004), aims for the pre-saturation with reaction gas, what enables an easy handling of three-phase reactions (gas-liquid-solid). A two-phase reactor is utilized in which an already with hydrogen gas pre-saturated reaction solution is continuously carried over a packed-bed catalyst.

Researchers from the group of de Bellefon suggested a similar concept for homogeneously catalyzed hydrogenations using a plug-flow tube reactor with an upstream micro-mixer especially for a high throughput screening (de Bellefon et al., 2000, 2003, 2002; Abdallah et al., 2007; de Bellefon et al., 2005).

Asides from that, there is no indication for a simple HTS for hydrogenation reactions combined with membrane reactor. This kind of

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Nomenclature

Symbols

d_e or d_i	External or inner diameter [m]
$F(\theta)$	Sum function of the normalized retention time [-]
l	Length [m]
m_i^0	Starting mass of employed substance i [g]
m_i	Mass of substance i [g]
M_i	[g mol ⁻¹] Molar mass of substance i
n_i	Amount of substance i [mol]
n_i^0	Starting amount of employed substance i [mol]
p	Pressure [bar]
P	Permeability [cB]
t	Time [min]
T	Temperature [°C]
\dot{V}	Volume flow [mL min ⁻¹]
X	Conversion [%]
Y	Yield [%]
Z	Mass balance [%]
θ	Normalized retention time [-]
ω	Mass fraction [%]
ω_i^0	Starting mass fraction of employed substance i [%]

reactors find nowadays extensive application (Julbe et al., 2001) and is predominantly used for hydrogen-, biodiesel- and biogas production, methane reforming or dehydrogenation of alkanes to alkenes (Gallucci et al., 2011; Basile et al., 2015).

To the best of our knowledge, up to day, only O'Brien et al. (2011) conducted hydrogenation reactions in a membrane reactor via separation of the hydrogen source from the reaction solution. Homo- as well as heterogeneously catalyzed reactions of various alkenes were investigated, but without focusing on a HTS. A similar approach was succeeded by Greiner et al. (2007) with a discontinuously working batch reactor concerning a PTFE membrane. Additionally, in 2010 Islam et al., (2010) invented an apparatus using additionally scCO₂ in the membrane tube, what finally enables high overall-pressures up to 10 MPa.

The great demand in present-day research for a high throughput screening, what is simple in construction and inexpensive in purchase, has prompted us to undertake investigations on this field. Herein we present the development of a high throughput screening based on a plug-flow tube reactor for various hydrogenation reactions.

2. Experimental

The main concept for the membrane reactor in high throughput screening reactions consists of a combination of a flow reactor with an upstream micro-mixer (de Bellefon et al., 2000, 2003, 2002) and a plug-flow PTFE-membrane reactor. Based on the results of Greiner et al. (2003), dealing with a PTFE-

membrane reactor what takes up hydrogen gas through the external wall of the membrane by diffusion, a reactor concept was developed which works without any pre-saturation with hydrogen as illustrated in Fig. 1.

The membrane reactor works in principle as a plug-flow tube reactor, whose walls are permeable to hydrogen. A reaction solution, containing the substrate and the precatalyst, perfuses the reaction tube with a constant flow rate. Two reaction samples are separated from each other by using an inert wash solution what is immiscible with the reaction solvent. Hydrogen flows continuously through the membrane to the solution(s) and enables the start of the reaction. While passing through the reactor, the hydrogenation reaction proceeds with a constant pressure of H₂. Due to the continuous H₂-saturation of the gas atmosphere much lower pressures (<10 bar) for the reaction are necessary compared to those performed with pre-saturation. The reaction time depends on the length of the tube as well as on the flow rate of the solution. At the exit of the plug-flow reactor, the converted samples are collected and analyzed.

The process flow chart, based on this concept, is illustrated in Fig. 2.

In conclusion, there are three separate and independently working circuits of the entire miniplant: the cycle for the reaction and wash solutions (1), the cycle for the hydrogen supply (2) and the heating circuit (3).

2.1. Sample cycle (1)

The substrate solution, containing already the metal precursor and the ligand, is collected in storage tank T-01. The wash solution is stored in tank T-02 and both reservoirs are located in an ultrasonic bath. It ensures a complete solution of the substrate and precatalyst in the reaction medium. Furthermore, it enables an oxygen free operation with degassed solvents to prevent inactivation due to oxidation of the catalyst during the process.

With the peristaltic pump P-02 both solutions are pumped from T-01 and T-02, respectively, via a cross valve to the membrane reactor. By application of a pre-heater (HE-03), installed prior to the reactor, the samples are already warmed to reaction temperature before entering the reactor what consequently prevents a temperature gradient inside the reactor. After the reaction, the samples can be finally separated and collected in sample containers (T-03–T-07).

2.2. Hydrogen cycle (2)

Hydrogen flows from a gas cylinder through a mass flow detector (MFC-01) and then to the pre-heater (HE-01). Using a pressure regulator (PR-02), the desired gas pressure for the

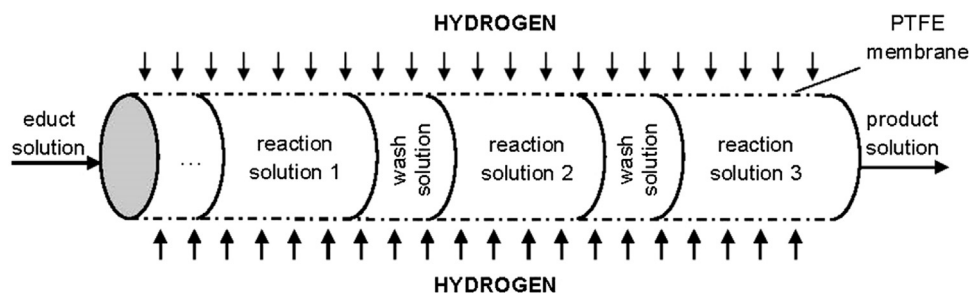


Fig. 1 – Simplified concept of the plug-flow tube reactor with a membrane for hydrogenation reactions.

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