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Homogeneously catalyzed hydroamination in a Taylor–Couette reactor using a thermomorphic multicomponent solvent system

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ABSTRACT

In order to design an innovative continuous process for the conversion of the renewable β -myrcene, three methodical steps are shown in this paper to find a setup for the demanding homogeneously catalyzed hydroamination. First step is the theoretical and practical design of a suitable thermomorphic multicomponent solvent (TMS)-systems for recycling the catalyst system. The necessary phase equilibria were successfully investigated by modelling using the Perturbed Chain – Statistical Associating Fluid Theory (PC-SAFT) and measuring liquid–liquid equilibria of the ternary systems substrates/solvents mixtures at the separation temperature. In the next step the promising TMS-system was subsequently used to investigate the recycling of the catalyst in continuous operation. A Taylor–Couette reactor (TCR) was developed and modified for the application in homogeneous transition metal catalysis. The reactor was integrated in a miniplant setup and a continuous recycling of the catalyst phase as well as an efficient synthesis of the desired terpenyl amines is achieved in 3 complete cycles. The results show that the TCR is suitable for the hydroamination and generates high conversion and yields ($X_{Myr} = 82\%$, $Y_{HA} = 80\%$). Recycling experiments were conducted successfully in the miniplant setup to show the long-term operation in a period of 24 h.

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1. Introduction

The direct application of renewable resources in the chemical industry is currently in the focus of discussion, as renewable resources like sugars, fats and oils are one way to reduce the dependency from the oil market. An alternative class of renewable resources for the chemical industry are terpenes, which are unsaturated hydrocarbons (Behr and Johnen, 2009; Behr and Wintzer, 2014). β -Myrcene (myrcene) can easily be obtained from β -pinene, a main

component of turpentine oil, in high yields using pyrolysis. Due to the diene moiety myrcene is an interesting starting compound used in a variety of syntheses, mostly for the production of fragrances or flavours (Breitmaier, 2006).

A variety of functionalizations have already been demonstrated using myrcene as the starting compound (Behr and Johnen, 2009).

The hydroamination is an interesting atom economic reaction to obtain amines, which are interesting for e.g. surfactants

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Nomenclature

μ_D	dipole moment D
σ_i	segment diameter of component i , Å
\bar{t}	mean residence time (first momentum), s
a	parameter of the temperature dependent k_{ij} expression
A_1	initial value (logistic function)
A_2	final value (logistic function)
a	Helmholtz energy, mol
DMF	dimethylformamide
$E(t)$	residence time distribution, 1/s
$F(t)$	cumulative distribution function (sum function)
GC	gas chromatography
hc	hard chain
Index i	component i
Index j	Component j
k_B	Boltzmann constant, J/K
k_{ij}	binary interaction parameter of the dispersion energy between components i and j
LLE	liquid–liquid equilibrium
m_i	segment number
M_m	molar mass, kg/mol
myrcene	β -myrcene
N_A	Avogadro constant, mol ⁻¹
p	pressure, mbar
PC-SAFT	perturbed chain statistical associating fluid theory
Q	number of equivalent CSTR in series (cascade model)
res	residual
T_R	reaction temperature, °C
u_i	Dispersion energy J
w	mass fraction
X_{Myr}	myrcene conversion, %
Y_{Dim}	yield dimers, %
Y_{HA}	yield hydroamination products, %
Y_{Telo}	yield telomers, %
α	polarizability, Å ³
σ^2	variance (second momentum), s ²

(Behr et al., 2010a). This homogeneous catalysed reaction allows the synthesis of valuable products, e.g. terpenyl amines in case of terpenes, in a very efficient way without the formation of large quantities of by-products. However, the recycling of homogeneous catalysts, especially valuable noble and transition metal catalysts remains a big challenge and is a crucial factor for the feasibility of a process.

A wide variety of recycling concepts are currently being discussed for the recycling of homogeneous catalysts mostly trying to heterogenize the catalyst e.g. on solid supports either as a solid or in a second liquid phase (Behr and Neubert, 2012). Examples of a successful recycling of hydroamination catalyst are just rarely reported. The recycling system concept for the homogeneous catalyst used in this work is the application of thermomorphic multicomponent solvent (TMS)-systems. These TMS-systems consist of at least two solvents of different polarity and exhibit a strong temperature-dependant miscibility gap. The reaction in a TMS takes place in a homogeneous phase at elevated temperatures. After the desired reaction time the reaction mixture is cooled down and the

solvent-system splits into two liquid phases again. The catalyst phase can be recycled and used again, while the product phase can be further purified (Fig. 1). A detailed description of the design aspects of TMS systems has been done by Behr and Henze (Behr et al., 2008, 2013a).

This recycling concept has already been applied in a variety of homogeneously catalysed reactions, e.g. hydroformylation (Behr et al., 2005) or hydroesterification (Behr et al., 2013b).

From a thermodynamic point of view, the TMS-approach is based on a liquid–liquid equilibrium (LLE). The LLE formed by the solvents is usually considered for a selection as TMS e.g. by the UCST (upper critical solution temperature) and the densities. But other aspects are important for a comprehensive investigation. On one hand, the partitioning behaviour of the substrates is important for recycling and reuse of unconverted substrates to increase efficiency and therewith sustainability of a process. On the other hand, it is known that substrates and product can act as solubilizer and affect the LLE used for catalyst recycling (Brunsch and Behr, 2013). Recent research on phase equilibria of TMS composed of acetonitrile and n -alkanes with both substrates of the hydroamination as third component applied thermodynamic modelling for a comprehensive description (Riechert et al., 2015a,b; Schäfer and Sadowski, 2012).

Within this work, LLEs are modelled using an equation of state. As an advantage, a description of the vapor phase for the consideration of vapour–liquid equilibria (VLE) enables process optimization. Therewith, a description of both LLE and VLE with a consistent parameter set as in the above mentioned investigation of the acetonitrile-containing TMS (Riechert et al., 2015a,b; Schäfer and Sadowski, 2012) was aimed. Additionally, the application of an equation of state provides information on fluid densities during phase equilibria calculation for process design and a following up scale-up to industrial scale. The applied equation of state is the Perturbed Chain–Statistical Associating Fluid Theory (PC-SAFT, Gross and Sadowski, 2001). Hence, a comprehensive description of the phase equilibria is provided for process design and the application of the TMS concept.

In the course of a process design for a continuously operated system, a suitable reactor for the miniplant has to be designed. The choice of a suitable reactor concept is often a compromise, as the “standard” reactor types like “Continuous Stirred Tank Reactor” (CSTR) or “Plug Flow Reactor” (PFR) often cannot fulfil all the desired criteria, like intensive mixing, effective heat transfer or a high conversion. The “Taylor–Couette reactor” (TCR) offers the possibility to combine the specific advantages of CSTR and PFR reactors. The flow profile is similar to a PFR with low back-mixing, while the vortices are well mixed (Judat et al., 2004). In contrast to the plug-flow reactor, where the hydrodynamics are in most cases determined by the volumetric flow rate, the back-mixing can be precisely controlled in a TCR, as it is controlled by the shape and the rotational speed of the inner cylinder (Richter et al., 2008).

The specific advantages of the Taylor–Couette reactor correspond very well with the demands of homogeneous reactions, as they tend to be slower and more sensitive towards the reaction conditions in comparison to many heterogeneously catalysed reactions (Behr and Neubert, 2012).

The ongoing design of a TMS for the hydroamination of myrcene with morpholine by modelling and experimental validation is followed by the tailoring of a miniplant setup. The successful reactor development and process synthesis as well

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