

Application of a Taylor-Couette Reactor in Homogeneous Catalysis

Arno Behr*, Tobias Färber

TU Dortmund University, Department of Biochemical and Chemical Engineering, Laboratory of Technical Chemistry, Emil-Figge-Strasse 66, 44227 Dortmund, Germany
arno.behr@bci.tu-dortmund.de

New developments of synthesis routes in homogeneous catalysis often require a precise control of the reaction conditions in order to achieve optimal results. A precise control of the flow- and reactor behaviour can improve the performance of a catalytic system, e.g. by suppressing side- and consecutive reactions. The Taylor-Couette reactor (TCR) allows a precise control of the flow conditions combining the benefits of continuously stirred tank reactors (CSTR) and plug-flow reactors (PFR). A ribbed Taylor Couette reactor for the application in homogeneous catalysis was developed and tested in the continuous hydroamination of the renewable β -myrcene in miniplant-scale. The application of the atom-efficient hydroamination to terpenes allows the continuous production of terpenyl amines based on renewable resources. Catalyst recycling of the homogeneous transition metal catalyst was achieved by means of Thermomorphic Multicomponent Solvent (TMS)-systems. TMS-systems enable the realisation of the reaction under homogeneous conditions at elevated temperatures, but also allow a biphasic phase separation after the reaction. This way the homogeneous catalyst can be separated from the product phase and used again. Yields of the desired terpenyl amines of up to 87 % could be generated in a homogeneous toluene solution on a laboratory scale.

The application of the TMS-system acetonitrile/*n*-heptane yielded 86 %, the TMS-system *N,N*-dimethylformamide/*n*-heptane generated 45 % of the desired hydroamination products. Both systems were then transferred into a continuously operated miniplant and realised using a Taylor-Couette reactor. The reactor performance was then validated and compared to the laboratory batch experiments. In the continuous miniplant experiments, the Taylor-Couette reactor could reproduce and even surpass the results of the batch experiments.

1. Introduction

1.1 Hydroamination reaction and catalytic system

The hydroamination is an atom-efficient method for the addition of an amine to an alkene or alkyne forming a new C-N bond. A variety of catalysts can be used for the hydroamination, ranging from acid/base catalysts over alkali and rare earth metal catalysts to late transition metal catalysts. A number of reviews show the scope of catalysts for hydroamination, amongst others by Müller et al. (Müller et al., 2008) and Müller and Beller (Müller and Beller, 1998).

In the present work the reactor performance was evaluated using the hydroamination as a test reaction and β -myrcene in combination with morpholine as the model substrates. Myrcene has been selected as a model compound, as it allows the production of the desired terpenyl amines based on renewable resources. Myrcene can be derived from β -pinene, a side product of the paper production, by pyrolysis with high yields (Kolicieski et al., 2007). Today terpenes are in most cases only used energetically or as solvents (turpentine oil) and have limited application in chemistry, although they are readily available. The unsaturated carbon backbone without functional groups makes them an interesting starting material for further functionalisation.

Behr and Johnen developed a catalytic system for the hydroamination of β -myrcene consisting of a homogeneous palladium precursor and a diphosphine ligand (Behr et al., 2010), which has been modified and used in this work (Figure 1). This catalytic system features high conversion to the desired hydroamination products. The telomerisation can be observed as the main side reaction, as it is catalysed by the same

catalytic system as the hydroamination. This way terpenyl amines with a longer carbon-backbone are formed. The selectivity between both reactions can be influenced by the reaction conditions. In most cases the hydroamination is favoured by high catalyst:substrate ratios as well as high phosphor:metal ratios.

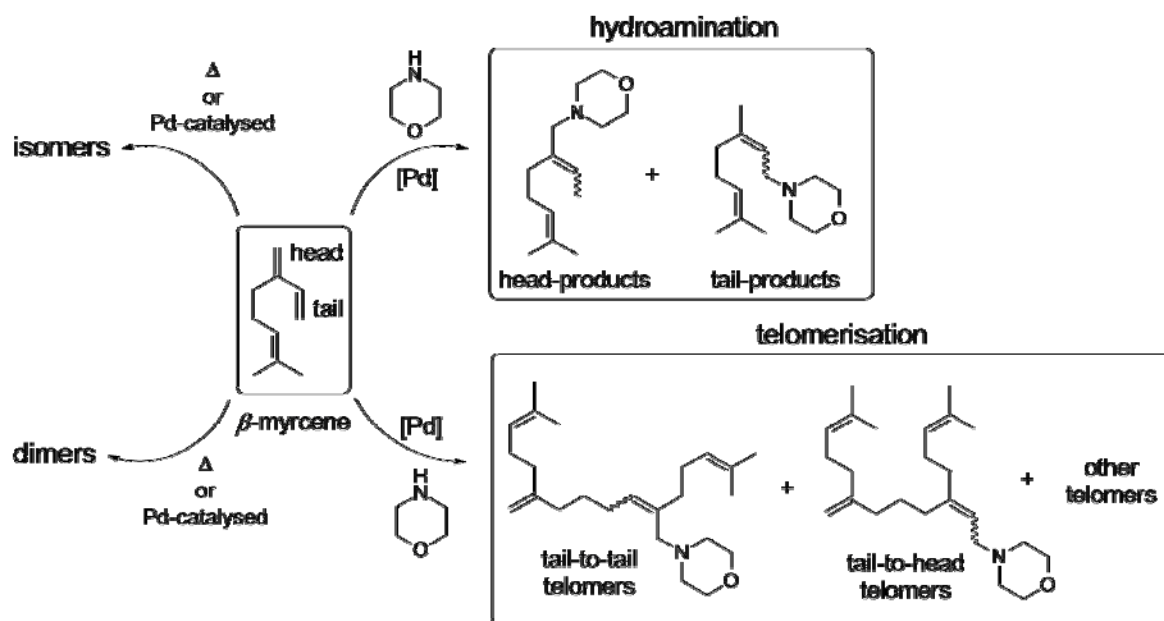


Figure 1: Hydroamination and telomerisation of β -myrcene

1.2 Catalyst recycling

One of the biggest challenges of homogeneous catalysis lies in the catalyst recycling, as the catalyst and the substrates/products reside in the same phase as the catalyst. In this work Thermomorphic Multicomponent Solvent (TMS)-systems have been used for the efficient recycling of the valuable palladium catalyst. TMS-systems consist of a mixture of at least two solvents of different polarity that feature a strongly temperature dependent miscibility gap. This allows the reaction to take place under homogeneous conditions at elevated temperatures, as well as the catalyst recycling after the reaction media has been cooled down yielding a biphasic system (Figure 2).

Although a variety of 'standard' TMS-systems exist, in general the selection of a suitable system has to be made specifically for the demands of the desired reaction and the catalytic system. The scope of TMS-systems can in most cases be narrowed down by looking at parameters like the upper critical solution temperature (UCST) and the Hansen solubility parameters (Behr et al., 2008). The UCST represents the temperature where the system is homogeneous independent of its composition and the Hansen solubility parameters allow an estimation of the polarity and phase behaviour of the solvents.

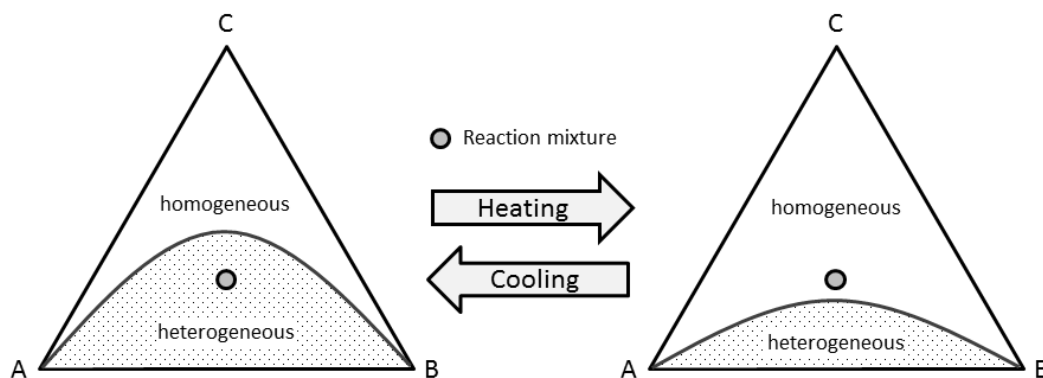


Figure 2: Principle of Thermomorphic Multicomponent Solvent (TMS)-systems (A,B,C = solvents or reactants)

1.3 Taylor-Couette reactor (TCR)

The Taylor-Couette reactor in its basic form consists of two concentric cylinders, which rotate in relation to each other. The rotation causes vortices to form in the annular gap between the cylinders. These counter-rotating vortices feature only limited mass transfer between each other, but are well mixed. The flow regimes inside the annular gap can be controlled by the rotational speed, so the hydrodynamic properties can be influenced independently from the feed flow. This limited mass transfer leads to a residence time distribution similar to a plug-flow reactor, but with intense mixing within each vortex. This behaviour leads to a wide application spectrum for the TCR, as it features good heat dissipation and low hydrodynamic shear rates in the liquid phase. The Taylor-Couette reactor has already been proposed among others for the application in polymer synthesis (Liu et al., 2013) as well as photochemical (Sczechowski et al., 1995), enzymatic (Giordano et al., 2000) and electrochemical reactions (Coeuret and Legrand, 1981). Furthermore the intense mixing in the vortices allows the application of heterogeneous catalysts (Giordano et al., 2000).

For special demands the inner cylinder can be modified in its profile. Sorg et al. showed that a lobed cylinder drastically reduces the shear rates for the application in biotechnology (Sorg et al., 2011). Richter et al. developed a ribbed rotor, which further reduces the mass transfer between the vortices resulting in an even narrower residence time distribution (Richter et al., 2008).

2. Experimental

All chemicals in this work were used as received from Acros Organics without further purification. Batch reactions were carried out in a 300 mL Parr steel autoclave with an overhead stirrer. The Taylor-Couette reactor was manufactured at the mechanical workshop of the Department of Biochemical and Chemical Engineering at TU Dortmund. The autoclave and the Taylor-Couette reactor were inerted prior to all experiments. All measurements in this work were carried out using a Hewlett Packard 6890 gas chromatograph with an Agilent HP-5 capillary column, FID detector and an internal standard.

3. Results and Discussion

After the selection of suitable solvents for the hydroamination in a TMS-system, the catalytic performance of these systems was tested in the hydroamination and telomerisation of myrcene, as the solvents can have a big impact on the catalytic performance. The results of the variation of the polar solvent are shown in Table 1.

Table 1: Influence of polar solvent on the hydroamination (TMS-system polar solvent/*n*-heptane)

| Polar solvent | Conversion (myrcene) [%] | Yield (hydroamination products) [%] | Yield (telomers) [%] | UCST with <i>n</i> -heptane [°C] |
|--------------------------------|--------------------------|-------------------------------------|----------------------|----------------------------------|
| Acetonitrile | 85 | 79 | 0 | 78 |
| Methanol | 57 | 50 | 0 | 54 |
| <i>N,N</i> -Dimethylformamide | 37 | 30 | 1 | 67 |
| <i>N</i> -Methyl-2-pyrrolidone | 11 | 0 | 0 | 55 |
| 3-Methoxypropionitrile | 15 | 1 | 6 | 99 |

Reaction conditions: $c(\text{Pd}(\text{CF}_3\text{CO}_2)_2) = 0.4 \text{ mol}\%$, 1,4-Bis(diphenylphosphino)butane, M:P = 1:8, $t = 3 \text{ h}$, $p(\text{Argon}) = 5 \text{ bar}$, $T = 100 \text{ }^\circ\text{C}$, $c(\text{substrates}) = 0.1667 \text{ mol/L}$, $n(\text{polar solvent}):n(\textit{n}\text{-heptane}) = 40:60$

After these preliminary tests acetonitrile and *N,N*-dimethylformamide have been selected for further testing on a continuous scale, as they showed high selectivity towards the hydroamination. The comparison of the solvents shows the impact the solvent has on the catalytic performance. Differences between product yield and myrcene conversion are a result of unwanted isomer and dimer formation. Acetonitrile as a solvent shows high conversion and selectively yields the hydroamination products, whereas in *N,N*-Dimethylformamide the conversion is lower and some telomerisation products are formed. Although methanol showed good performance in the hydroamination, it was neglected from further testing, as the deactivation of the palladium catalyst and formation of palladium black could be observed.

3.1 Reactor construction

Based on the works of Richter et al. we developed a Taylor-Couette reactor for the application in homogeneous catalysis (Figure 3). Sealing of the liquid phase is achieved by two graphite-filled Teflon seals. The TCR features a ribbed rotor enclosing 44 reaction chambers and has a total liquid volume of 440 mL. Furthermore it can be pressurised for reactions with gaseous substrates or inert gases. The ribbed rotor enables a plug-flow profile, even at low flow rates and long reaction times, which makes it suitable for homogeneous catalysis. The bearing of the inner cylinder is achieved by a fixed/floating bearing combination

at the top of the reactor to absorb the radial and axial forces. Furthermore the reactor is designed in a modular way, so the rotor as well as the inner and outer piping can be replaced by removing the flange at the bottom of the reactor. Sealing between the piping and the top and bottom flange is achieved by Teflon seals and tension rods. The liquid reaction media is fed at the bottom of the reactor and leaves below the second flange. The rotor is driven by a magnetic drive coupled with an electric motor. For the precise control of the reaction conditions, the reactor is fitted with four temperature sensors to ensure an even temperature distribution.

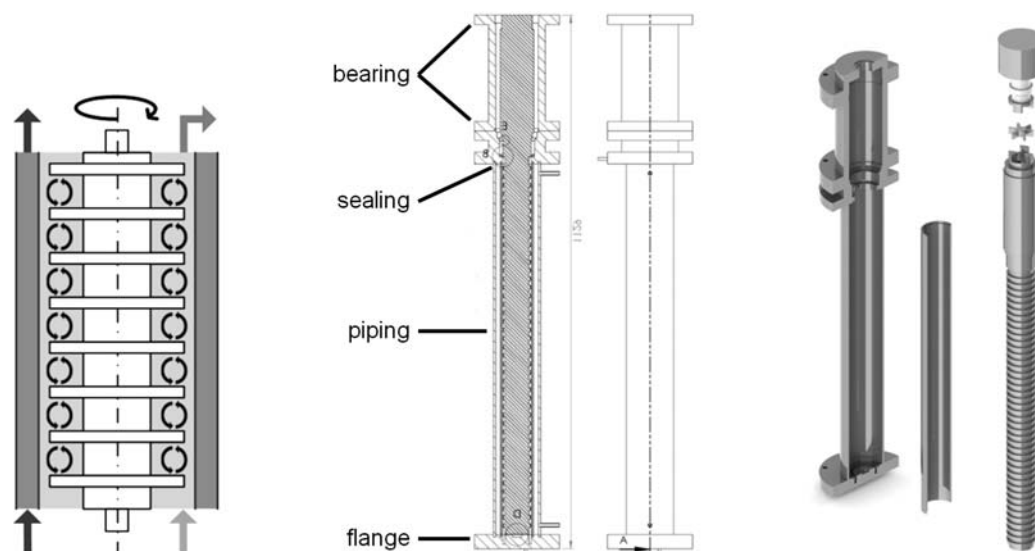


Figure 3: Taylor-Couette reactor (operating principle, engineering detail drawing and exploded view)

3.2 Miniplant integration

After the assembly, the Taylor-Couette reactor was integrated into the miniplant and equipped with process control equipment. A simplified flow chart and the final miniplant construction are shown in Figure 4.

Liquid dosing is achieved by two precise HPLC pumps and a diaphragm pump for the solvent. The substrates and the catalyst phase are fed into the mixer, homogenised and then flow into the TCR. After the reaction has taken place, the reaction media flows gravity-driven into the phase separator, where the TMS-system splits into two phases. The catalyst phase is recycled and the product phase is excluded from the system and collected for further purification. The process parameters (temperature, pressure, mass flow) are monitored and controlled by National Instruments CompactRIO and Labview.

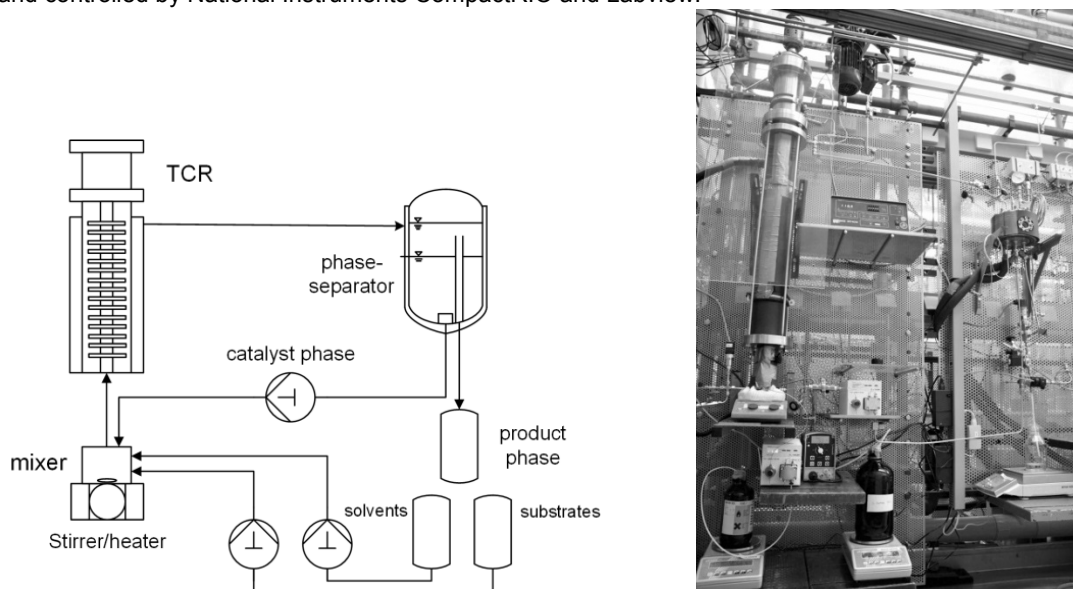


Figure 4: Simplified process flow diagram (left) and constructed miniplant with Taylor-Couette reactor (right)

After the integration of the reactor into the miniplant, the TCR was tested in the homogeneous hydroamination of β -myrcene with morpholine. The reaction was performed in a homogeneous toluene solution and compared to the laboratory batch experiments (Table 2). All experiments were performed with a liquid feed of 120 mL/h with equivalent concentrations and ratios to the batch experiments. The temperature was increased in comparison to the batch experiments (100°C) as a slightly higher conversion and selectivity can be achieved. A further increase in temperature (120°C) leads to catalyst deactivation and the formation of elementary palladium. As a result 110°C was selected as the temperature for the continuous experiments. In this experiment the catalyst was not recycled. Samples were collected directly after the reactor and analysed using gas chromatography.

In comparison to the batch experiments, the reactor shows comparable results in the hydroamination product yield, while generating a slightly higher conversion. In this experiment the mean residence time of the liquid phase in the TCR was set slightly higher than the batch reaction time to accommodate for back-mixing effects during continuous operation. The necessary residence time has been determined by previous residence time distribution experiments under equivalent flow conditions.

Table 2: Comparison of batch and continuous hydroamination (solvent toluene)

| | Conversion (myrcene) [%] | Yield (hydroamination products) [%] | Yield (telomers) [%] |
|-------|--------------------------|-------------------------------------|----------------------|
| Batch | 94 | 87 | 0 |
| TCR | 97 | 88 | 0 |

Reaction conditions: toluene, Pd(CF₃CO₂)₂, 1,4-Bis(diphenylphosphino)butane, c(cat.) = 0.4 mol%, M:P = 1:8, p(argon) = 5 bar, T = 110 °C, c(substrates) = 0.1667 mol/L; a) TCR: 100 rpm, τ = 4 h; b) batch: 450 rpm, t = 3 h

After the reactor performance was verified in the hydroamination, the reactor and the miniplant were tested using two different TMS-systems with continuous recycling of the homogeneous catalyst. The miniplant was first evacuated, then the phase separator was charged with the catalyst phase and pressurised with inert gas. The dosing of the catalyst and substrate phase was started at the same time and both streams were fed into the reactor. The results of the continuous experiments during the first recycle of the catalyst phase are shown in Table 3. A total of five recycles of the catalyst phase could be achieved in these TMS-systems.

Table 3: Comparison of batch and continuous hydroamination (TMS-systems)

| TMS-system | | Conversion (myrcene) [%] | Yield (hydroamination products) [%] | Yield (telomers) [%] |
|---|-------|--------------------------|-------------------------------------|----------------------|
| Acetonitrile/ <i>n</i> -heptane | Batch | 88 | 86 | 0 |
| | TCR | 55 | 23 | 32 |
| <i>N,N</i> -dimethylformamide/ <i>n</i> -heptane | Batch | 83 | 45 | 38 |
| | TCR | 86 | 70 | 16 |

Reaction conditions: Pd(CF₃CO₂)₂, 1,4-Bis(diphenylphosphino)butane, c(cat.) = 0.4 mol%, M:P = 1:8, p(argon) = 5 bar, T = 110 °C, c(substrates) = 0.1667 mol/L, n(polar solvent):n(*n*-heptane) = 40:60; a) TCR: 100 rpm, τ = 4 h; b) batch: 450 rpm, t = 3 h

The results of the TMS-system acetonitrile/*n*-heptane differ both in conversion and product spectrum from the laboratory results. The overall conversion of myrcene is lower and the reaction is shifted towards the telomerisation. This is a result of the ligand precipitation that could be observed during the miniplant operation in the phase separator at low temperatures. Johnen already showed that a decrease in ligand concentration can shift the reaction system towards the telomerisation (Behr et al., 2010). As a result of the insufficient solubility of the ligand in the solvent acetonitrile, *N,N*-Dimethylformamide (DMF) was selected as the polar solvent, as it showed increased solubility of the catalytic system, even at low temperatures. The shift towards the telomerisation in the DMF batch-experiments is partly a result of the increased temperature, but has to be investigated further. With this TMS-system, the myrcene conversion from the laboratory experiments can be reproduced, however, the product distribution differs. This is a result of the slightly higher morpholine concentration during miniplant operation, as morpholine mostly resides in the polar catalyst phase and is recycled together with the catalyst phase. To prevent this accumulation, further experiments have to be carried out at lower morpholine concentrations. The catalyst leaching into the non-polar product phase was below 1 % for palladium and below 0.8 % for phosphor respectively. Catalyst leaching was determined by means of ICP-OES.

4. Conclusions

In this work we described the construction of a Taylor-Couette reactor for the application in homogeneous catalysis. The reactor was tested in the continuous hydroamination of β -myrcene yielding the desired terpenyl amines. The TCR enables the efficient conversion of the renewable substrate β -myrcene to the desired products, with low back-mixing even at low flow rates. The recycling of the homogeneous catalyst was achieved using Thermomorphic Multicomponent Solvent (TMS)-systems. Two TMS-systems were tested in batch and miniplant-scale using the Taylor-Couette reactor. The TMS-system *N,N*-Dimethylformamide showed the best results with a myrcene conversion of 86 % and a hydroamination product yield of 70 %.

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References

- Behr A., Henze G., Johnen L., Awungacha C., 2008, Advances in thermomorphic liquid/liquid recycling of homogeneous transition metal catalysts, *Journal of Molecular Catalysis A: Chemical*, 285, 20–28.
- Behr A., Johnen L., Rentmeister N., 2010, Novel Palladium-Catalysed Hydroamination of Myrcene and Catalyst Separation by Thermomorphic Solvent Systems, *Advanced Synthesis & Catalysis*, 352, 2062–2072.
- Coeuret F., Legrand J., 1981, Mass transfer at the electrodes of concentric cylindrical reactors combining axial flow and rotation of the inner cylinder, *Electrochimica Acta*, 26, 865–872.
- Giordano R.L.C., Giordano R.C., Cooney C.L., 2000, Performance of a continuous Taylor–Couette–Poiseuille vortex flow enzymatic reactor with suspended particles, *Process Biochemistry*, 35, 1093–1101.
- Kolicheski M.B., Cocco L.C., Mitchell D.A., Kaminski M., 2007, Synthesis of myrcene by pyrolysis of β -pinene: Analysis of decomposition reactions, *Journal of Analytical and Applied Pyrolysis*, 80, 92–100.
- Liu Z., Jin T., Kind M., 2013, Continuous polymerization of methyl methacrylate in a Taylor-couette reactor. I. Influence of fluid dynamics on monomer conversion, *Polymer Engineering & Science*, 53, 96–104.
- Müller T.E., Beller M., 1998, Metal-Initiated Amination of Alkenes and Alkynes, *Chemical Reviews*, 98, 675–704.
- Müller T.E., Hultsch K.C., Yus M., Foubelo F., Tada M., 2008, Hydroamination: Direct Addition of Amines to Alkenes and Alkynes, *Chemical Reviews*, 108, 3795–3892.
- Richter O., Hoffmann H., Kraushaar-Czarnetzki B., 2008, Effect of the rotor shape on the mixing characteristics of a continuous flow Taylor-vortex reactor, *Chemical Engineering Science*, 63, 3504–3513.
- Sczechowski J.G., Koval C.A., Noble R.D., 1995, A Taylor vortex reactor for heterogeneous photocatalysis, *Chemical Engineering Science*, 50, 3163–3173.
- Sorg R., Tanzeglock T., Soos M., Morbidelli M., Périlleux A., Solacroup T., Broly H., 2011, Minimizing hydrodynamic stress in mammalian cell culture through the lobed Taylor-Couette bioreactor, *Biotechnology Journal*, 6, 1504–1515.