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Feasibility studies and dynamics of catalytic liquid phase esterification reactions in a micro plant

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Abstract

We present a new micro reactor concept which is suitable for investigations of heterogeneously catalyzed liquid phase reactions. In the set-up two reactants are mixed in a commercially available interdigital micro mixer. The outlet of the micro mixer is connected to a modular micro reactor that consists of stacked plates. Each plate contains a milled meandering channel filled with catalyst beads. By using a variable number of plates the residence time can be manipulated and thus adjusted for a specific task. The synthesis of butyl acetate is considered as a model reaction since it has been investigated in detail in conventional reaction systems. In a first step, some experimental results of the heterogeneously catalyzed reaction are presented. In the second part, the set-up is operated as a chromatographic reactor. Dynamic behaviour is investigated applying the frontal analysis mode and the elution chromatography mode.

Keywords: Modular micro reactor; Heterogeneous catalysis; Chromatographic reactor; Integrated process

1. Introduction

The application of micro reactors has received strongly growing interest during the last years [1–3]. In particular, precise temperature control of very exothermic reactions is beneficial with respect to process safety and to avoid byproducts [4–6]. Other important applications are portable production facilities, especially for highly toxic gases to relieve safety precautions [7]. Moreover, syntheses inside explosive regions can be performed safely [8].

Most studies so far were devoted to heterogeneously catalyzed gas phase reactions or homogeneously catalyzed liquid phase reactions. Micro fixed bed reactors for heterogeneously catalyzed gas phase and gas liquid phase reactions have been successfully applied [9,10]. Comparatively few reports deal with heterogeneously catalyzed liquid phase reactions, although reactions with high potential for chemical synthesis have been performed successfully [11,12]. Esterification reactions are very important reactions which are usually accelerated by acidic catalysts. Strong mineral or organic acids have been used as effective homogeneous catalysts. To facilitate the separation of the catalyst from the products, the application of heterogeneous catalysts like acidic ion exchange resins has also been tested successfully [13,14]. In this study we focus on the heterogeneously catalyzed synthesis of butyl acetate in a micro system as a model reaction. Since butyl acetate is an important chemical substance for industrial applications a lot of data about the kinetics of this reaction are available from studies using conventional equipment [15–17]. The study of the homogeneously catalyzed butyl acetate synthesis in a micro reactor has already been discussed in previous work [18].

Since the esterification of *n*-butanol represents an equilibrium-limited reaction, it appears attractive to perform it within an integrated (multifunctional) process. In such processes reaction and product separation are carried out simultaneously, which allows to overcome limited reaction equilibria. With respect to the model reaction studied here, some attempts towards reactive distillation and reactive extraction have been reported. However, they partly suffered from the formation of side products or from poor performance due to temperature limitations [19]. In this context, the application of a chromatographic reactor might be an interesting alternative.

The paper is arranged as follows. First we discuss the set-up used for the heterogeneously catalyzed reaction and present typical experimental results. In the second part, some first

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Nomenclature

a	activity of component i in the liquid phase
a'_i	product of the adsorption constant and the activity for component i
$k_{\mathrm{f,Het}}$	forward reaction rate constant for the heterogeneously catalyzed reaction [kmol/(kg s)]
K_{Het}	equilibrium constant for the heterogeneously catalyzed reaction
$K_{\mathrm{S},i}$	adsorption constant of component i
m_{cat}	mass of the catalyst [kg]
n	molar hold-up [kmol]
r_i	reaction rate for component i [kmol/s]
t	time [s]
x_i	mole fraction of component i

Greek letters

α	constant in the modified Langmuir–Hinshelwood model
ν_i	stoichiometric factor

results of dynamic experiments are presented. Due to the different adsorptivity of the involved compounds, not only reaction effects but also separation effects come into play, i.e., the system can be interpreted as an integrated process involving reaction and separation and is operated as a chromatographic reactor.

2. Experimental

2.1. Chemicals

All chemicals used are of synthesis grade (99.5% acetic acid, *n*-butanol, butyl acetate, all from Merck). The purity of the chemicals was also checked by GC-analysis. Amberlyst-15 (Rohm & Haas Deutschland, Arnsberg, Germany) served as heterogeneous catalyst and a fraction with a particle size of 500 μm was sieved out. The supplier reports the ion exchange capacity to be 4.75 mequiv/g of the dry resin and the inner surface to be 30×10^3 m^2/kg. The dry catalyst was washed several times with distilled water (specific conductivity $<10\,\mu\mathrm{S\,cm^{-1}}$) at 60 °C until the raffinate was colorless. Finally it was dried for 18 h in vacuum.

2.2. Set-up

Fig. 1 shows the experimental set-up. The reactants are supplied by HPLC pumps (Knauer, Berlin, Germany) at the desired feed ratio. The two feed streams are mixed by an interdigital micro mixer (SIMM-V2, IMM, Mainz, Germany) made of Hastelloy. The outlet of the micro mixer is connected to the inlet port of the micro fixed bed reactor (μFBR). The μFBR (Fig. 2) was designed and fabricated in-house at the Max Planck Institute Magdeburg using classical micro machining. It consists of a variable number of interconnected plates (60 mm × 40 mm) made of stainless steel (SS316) which are clamped between a top and a bottom plate and are sealed by o-rings. On each plate (thickness 3 mm, top and bottom plate 8 mm each) a rectangular meandering channel (width = 1.0 mm, depth = 1.5 mm) is milled (Fig. 2B). Changing the number of plates (channel length 0.4315 m per plate) allows for simultaneous adjustment of the optimal residence time and the feed flow rate. Fig. 2C shows channels filled with wet catalyst particles. The amount of catalyst is measured and is in the range of 1.26–1.42 g in dry condition. The outlet of each channel is provided with a circular piece of fine mesh (200 mesh size) in order to retain the catalyst particles on the plate. The complete μFBR is shown in Fig. 2D in comparison with a one Euro coin. The whole set-up is immersed in a thermostat (Lauda, Lauda-Königshofen, Germany) for isothermal operation. The presented experimental results are obtained at 80 °C.

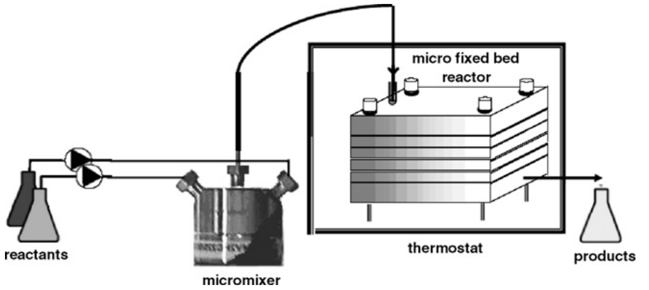

Fig. 1. Experimental set-up for the continuous heterogeneously catalyzed esterification.

2.3. Analysis

Samples for the steady state experiments were collected at the outlet of the reaction tube up to 8–9 times the dimensionless operating time τ ($\tau = tu/L$, where t [s] is the sampling time, u [m/s] the flow velocity and L [m] is the reactor length). Several test runs were made to assure that the steady state outlet compositions were reached.

The samples were analyzed using a gas chromatograph (HP 6890, HP Innowax column, length = 30 m, diameter = 250 μm) equipped with TCD and FID detectors.

3. Operation of the micro system as a continuous fixed bed reactor

Steady state compositions were evaluated for different residence times which were adjusted by changing the flow rate. A 50:50 mass feed of *n*-butanol and acetic acid was supplied. Fig. 3 shows the mass fractions (w/w) of all four components versus residence time. The mass fractions of butyl acetate and water are increasing and the mass fractions of *n*-butanol and acetic acid are decreasing with increasing residence time approaching thermodynamic equilibrium. At residence times above 1500 s the mass fractions remain rather constant. Models with different rate expressions were applied in order to find a suitable interpretation of the experiments. The best fit was obtained using a modified Langmuir–Hinshelwood model [18] (Fig. 3).

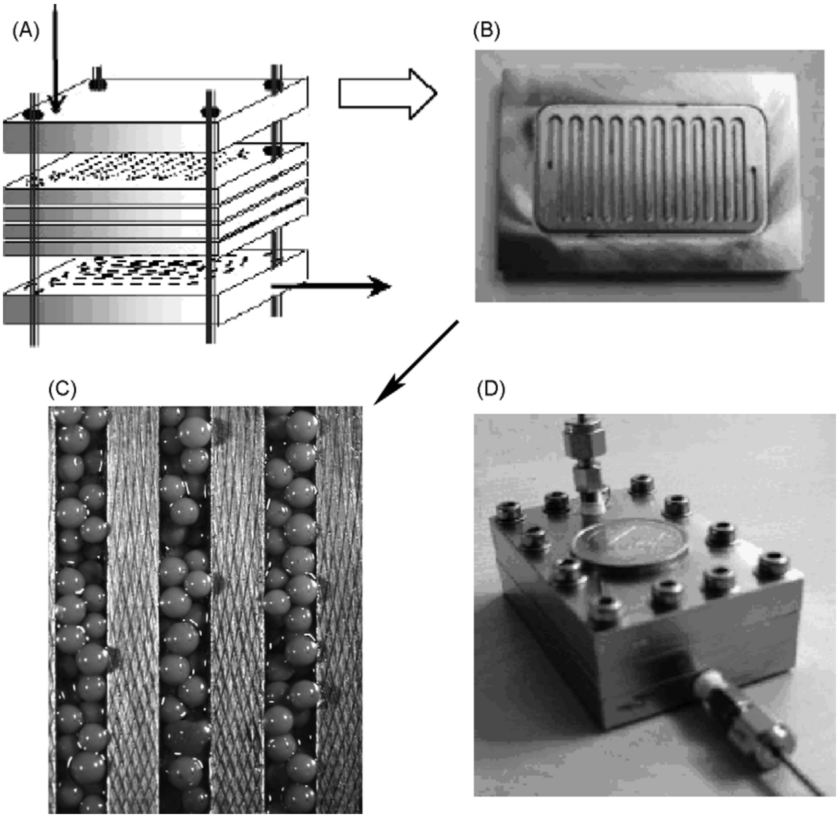

Fig. 2. (A) Schematic view of the micro fixed bed reactor. (B) Channel structure on a plate. (C) Channels filled with wet catalyst particles. (D) Assembled micro fixed bed reactor with four plates.

The rate expression of the modified Langmuir–Hinshelwood model reads [19]

$$r_i = n\frac{\mathrm{d}x_i}{\mathrm{d}t} = \nu_i m_{\mathrm{cat}} k_{\mathrm{f,Het}} K_{\mathrm{S},3} K_{\mathrm{S},2} \frac{a_3 a_2 - (1/K_{\mathrm{Het}}) a_1^{\alpha} a_4}{(1 + a_3' + a_2' + a_4' + K_{\mathrm{S},1}\alpha_1^{\alpha})^2}. \quad (1)$$

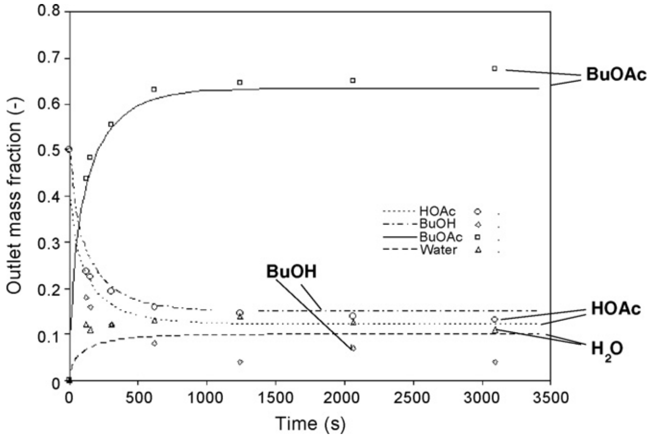

Fig. 3. Mass fraction of water (H_2O), *n*-butanol (BuOH), acetic acid (HOAc), and butyl acetate (BuOAc) versus residence time. A 50:50 mass feed of *n*-butanol and acetic acid was applied. $T = 80\,^{\circ}\mathrm{C}$. The experiments are indicated by symbols. The relative error was estimated to be below 2%. The simulations (lines) are based on the modified Langmuir–Hinshelwood model [18,19]. Best results were found with $\alpha = 1.98$. α corresponds to the extent of distribution of water on the active surface of the catalyst [20].

r_i is the reaction rate for component i and the subscript numbers correspond to water (1), *n*-butanol (2), acetic acid (3), and butyl acetate (4). α is an empirical parameter that describes the adsorption of water into the gel-phase of the ion-exchange resin [20]. The symbols of Eq. (1) are explained in Nomenclature. The parameters for the simulation were taken from [19]. Activity coefficients for the individual components have been calculated by the UNIQUAC method. These rate expressions were used under the following assumptions: (i) isothermal operation and plug flow condition, (ii) uniform distribution of the catalyst and of the active sites throughout the bed, (iii) each catalyst particle behaves identically, (iv) the rate constants can be expressed in Arrhenius form, (v) the overall conversion is not limited by solid–liquid interfacial transport, (vi) the liquid phase is homogeneous, and (vii) the activity based approach as discussed in the literature is valid for the reaction in the miniaturized system.

The above steady state compositions were obtained from “regular” fixed bed experiments. However, there is also the possibility to operate the set-up in a non-steady state mode. In this case, the transient behaviour of the system is of major interest. Fig. 4 shows the results of a typical experiment, where the reactor was first equilibrated with *n*-butanol and then a 50:50 volume feed of *n*-butanol and acetic acid was supplied. From the concentration–time profile, the following decreasing order of adsorptivities can be deduced: water/acetic acid, butyl acetate. The complete order was determined by batch-equilibrium experiments (not shown) to be water, *n*-butanol, acetic acid, and butyl acetate in accordance with similar systems described in litera-

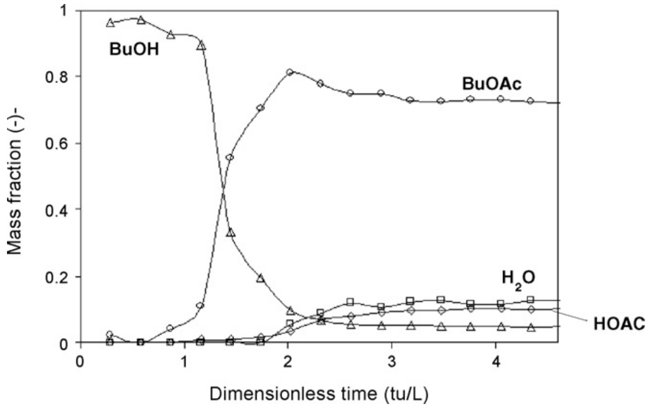

Fig. 4. Typical transient behaviour. Reactor initially equilibrated with *n*-butanol. A 50:50 volume feed of *n*-butanol and acetic acid was applied at a flow rate of 0.05 ml/min. $T = 80\,^{\circ}\mathrm{C}$.

ture [21–23]. It can be explained by the fact that Amberlyst-15 is a strongly acidic cation exchange resin that contains polar $–SO_3H$ groups.

The figure also indicates that at the outlet, pure *n*-butanol is followed by a fraction of only butyl acetate and *n*-butanol, before the effluent also contains acetic acid and water. Furthermore, it is noteworthy that the butyl acetate concentration is temporarily higher than in steady state. This effect is due to the selective adsorption of the components and can be purposefully exploited by operating the unit as a chromatographic reactor, which will be discussed in the next section.

4. Operation of the micro system as a chromatographic reactor

4.1. Background and fundamentals

A chromatographic reactor is an integrated process in which chemical reaction and chromatographic separation of products and educts are carried out simultaneously. Such concept comprises mainly two possible benefits. (i) Due to the different adsorptivities of the components involved, product(s) and educt(s) can be locally separated and, thus, equilibrium limited reactions can be driven towards completion. (ii) The separation effect might be exploited to produce pure or enriched products, which obviously decreases necessary efforts for downstream separations. For more details, see [24–26].

The concept of the chromatographic reactor has received considerable attention and was investigated, for example, for esterifications, transesterifications [24], hydrolyses, hydrogenations [27], dehydrogenations, and enzymatic isomerizations [28]. In the current system, since the desired product (butyl acetate) has lowest and the second product (water) has highest adsorptivity, the application of a chromatographic reactor is regarded promising. Furthermore, such integrated process appears a particularly innovative concept in the area of micro reaction engineering since there are only limited options available with respect to separations.

There are different types of chromatographic reactors, i.e., fixed bed units for discontinuous and simulated moving bed (SMB) units for continuous operation, respectively. With respect to fixed bed reactors, different operating modes might be defined, e.g., elution and frontal operation. Below the applicability of the micro fixed bed unit as a chromatographic reactor for these two modes is investigated experimentally.

4.2. Experimental results

4.2.1. Frontal operation

In frontal operating mode, a step input of a reactive mixture is applied to a reactor initially equilibrated with a pure reactant. While here focus is set on the transient start-up behaviour, this type of experiment obviously corresponds to the steady state investigations described above (see Fig. 4).

In the experiments, equilibration was performed with pure *n*-butanol for 40 min at a flow rate of 0.1 ml/min. Then the feed composition was switched to a mixture of *n*-butanol and acetic acid. The effect of changing the composition of this feed mixture was investigated. The resulting outlet concentrations versus time are shown in Fig. 5.

The results shown in Figs. 4 and 5 can be interpreted as follows. During transport and reaction, water is strongly retained

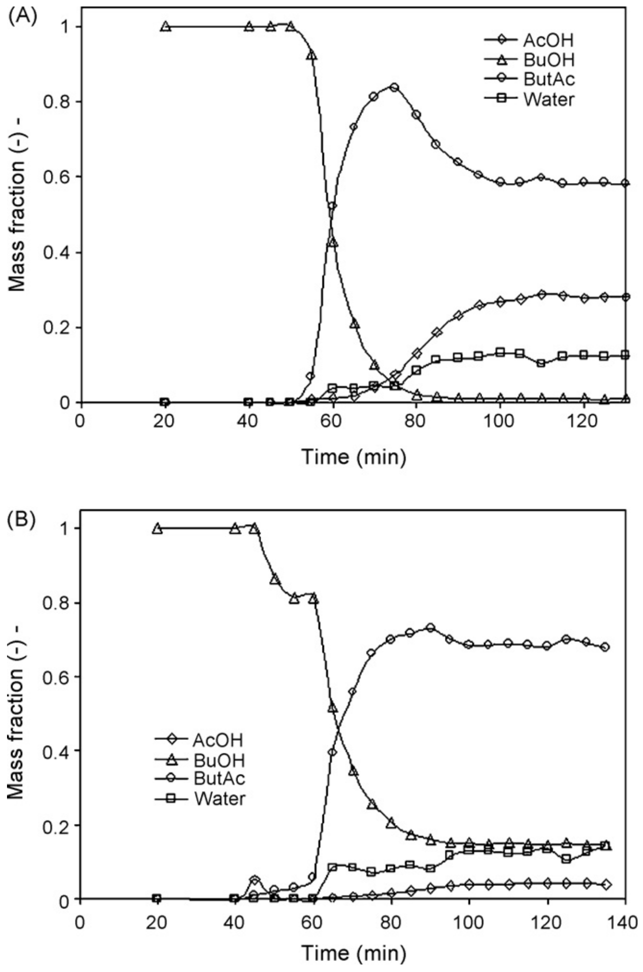

Fig. 5. Dynamic behaviour of the chromatographic reactor for frontal operation. $T = 80\,^{\circ}\mathrm{C}$. Inlet feed ratio of *n*-butanol/acetic acid (A) 30:70 (v/v) and (B) 70:30 (v/v).

by the resin, whereas butyl acetate is desorbed easily and carried faster by the fluid. This corresponds to selectively removing water from the reaction zone, and thereby shifting the esterification equilibrium locally towards the side of products—at maximum until complete consumption of the limiting reactant. However, after this transient effect, all compositions approach their steady state values.

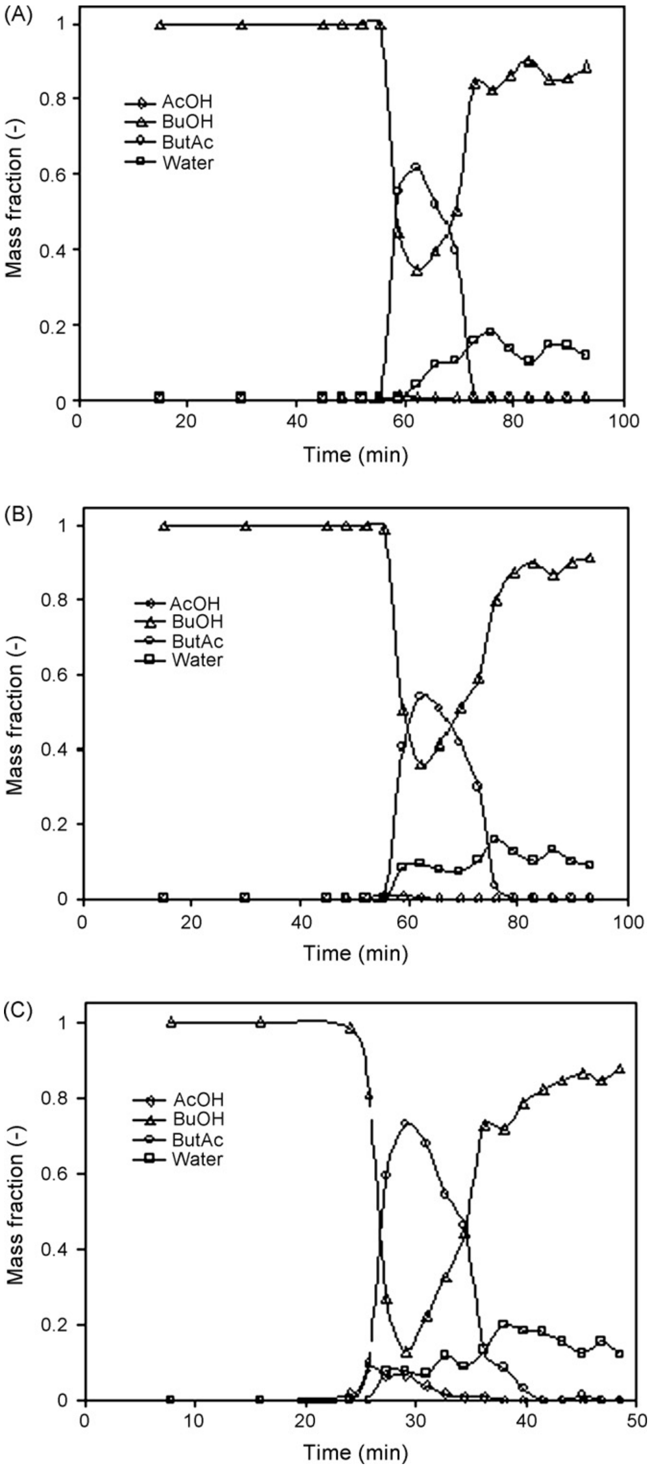

Fig. 6. Typical mass fraction profiles obtained with the micro fixed bed reaction using the elution mode. $T = 80\,^{\circ}\mathrm{C}$. Parameters (flow rate in ml/min, pulse flow rate in ml/min, pulse time in s): A (0.1, 2.0 ,5), B (0.1, 8.0, 5), C (0.2, 8.0, 5).

The feed composition has a strong influence on process performance. For example, in the case of a volumetric ratio for *n*-butanol/acetic acid of 70:30 (Fig. 5B), a complex elution behaviour of water can be observed. This is due to the interplay of nonlinear adsorption, chemical reaction, and almost complete consumption of acetic acid. The highest steady state mass fractions for butyl acetate were achieved for volumetric feed ratios of 50:50 and 70:30. However, the maximum transient value of this mass fraction was obtained at $t \approx 70$ min for a ratio of 30:70 (Fig. 5A).

These results indicate that a pulsed operation mode might be useful in order to maximize purity and concentration of the butyl acetate fraction. In this context, the feed composition should be regarded a as a free variable, since it strongly influences the achievable transient compositions.

4.2.2. *Elution (pulsed) operation*

In elution or pulsed operation, the reactor is equilibrated with a pure reactant. Limited amounts of reactive mixture are then injected into this stream.

In the experiments *n*-butanol was used for equilibration (at least 40 min) and pulses of pure acetic acid were injected. Several parameters were studied by variation of the flow rate of *n*-butanol, the flow rate during the pulse, as well as pulse duration. Selected results are given in Fig. 6. It can be seen that both amount and purity of the butyl acetate depend mainly on the injected amounts of acetic acid.

An advantage of the approach is given by the strongly enhanced purity of the butyl acetate fraction in comparison to the steady state compositions presented above. Although the achieved mass fractions are not higher than in steady state, preliminary model calculations indicate that this limitation might be overcome by injecting mixtures of *n*-butanol and acetic acid. Besides the composition of the injected pulse, also the duration of the pulse and regeneration should be included in the optimization of a chromatographic reactor.

5. Summary and outlook

In the first part of this study a self-designed micro fixed bed reactor is described. This reactor offers the well known advantages of microsystems such as effective thermostating due to low thermal inertia and good heat transfer properties. It is worth noting that the reactor concept represents a rather simple and inexpensive approach, since the apparatus can be fabricated using classical mechanical engineering; no demanding technique like etching, LIGA, etc. is necessary. However, it also offers a certain flexibility with respect to the adjustment of residence times (i.e., by simply changing the number of platelets) and the type of packing that can be used (i.e., particulate solids, monoliths, coatings, gel-type materials). Bed lengths up to several meters can be adjusted in a compact manner. Due to the structure of stacked plates the reactor can be disassembled very easily which facilitates catalyst exchange and maintenance. The micro fixed bed reactor can be used for heterogeneous catalysts where no appropriate coating technique is available. Furthermore, the structured design allows for simple inclusion of side streams; for example, for distributed feed addition and product removal, or for quenching purposes and implementation of in-line analysis. All in all the presented micro fixed bed reactor was found to be a flexible tool for screening of heterogeneous catalysts and reactions with low amounts of chemical substances.

The heterogeneously catalyzed synthesis of butyl acetate is used as a test system. This system has the advantage that butyl acetate is an important substance in chemical industry and that, therefore, the kinetics have been studied in detail on conventional scale.

First the successful performance of this reaction in a micro fixed bed reactor was shown. Furthermore, it was demonstrated that a dynamic operation of the set-up might be beneficial because the two products water and butyl acetate are having highest and lowest adsorptivity to the catalyst, respectively. In this case the micro fixed bed reactor not only serves as a reactor but also as a chromatographic separation unit. That means that reaction and separation are integrated in one unit, i.e., the system can be regarded as a chromatographic reactor. It should be noted that thermal effects are also important for weakly exothermic reactions in chromatographic reactors since thermal waves develop that significantly affect the process dynamics [29]. Therefore, good temperature control is also desirable for this process. It was demonstrated that with respect to the esterification of *n*-butanol, the given order of adsorptivity allows not only for the integrated (partial) purification of the products, but also to overcome the limited chemical reaction equilibrium within a certain time interval. The experimental observations emphasize the potential of this approach, but also indicate the inherent complexity of the process.

A mathematical process model is therefore indispensable in order to optimize the performance of a chromatographic reactor, because it comprises a number of free variables and multiple objectives have to be considered (e.g., purity, recovery yield, productivity). Current work focuses on parameter and model validation in order to facilitate this non-trivial task. As soon as an optimal dynamic operation procedure is found it can be repeated periodically to achieve attractive throughputs.

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