Esterification of Acetic Acid with Methanol and Simultaneous Product Isolation by Liquid-Liquid Extraction in a Taylor-Couette Disc Contactor

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Isolation of carboxylic acids from dilute aqueous effluents can be achieved by the combination of liquid-phase catalyzed reaction with liquid-liquid extraction. Exemplarily the heterogeneously catalyzed esterification of acetic acid with methanol, accelerated with a cation-exchange resin and simultaneous transfer of the product methyl acetate into the solvent ShellSol T, was successfully performed in a Taylor-Couette disc contactor (TCDC) in batch operation mode. Stable three-phase flow (liquid-liquid-solid) was confirmed in lab scale. The conversion of acetic acid in a TCDC operated in batch mode compares well with conversion in a batch reactor.

1 Introduction

Sustainable implementation of biobased raw materials has become a high priority task. Unfortunately, downstream processing in the biobased industry often faces highly dilute multicomponent mixtures, making product isolation a challenge. For instance, black liquor condensate from pulping contains carboxylic acids at low concentration. Isolation of these low-value constituents from aqueous effluents fails because state-of-the-art downstream processes like distillation cannot achieve economic feasibility. Hence, nearly 50 % of the processed wood is finally used for steam production, with a significant loss of carboxylic acids as for example shown in Fig. 1 [1, 2].

In dealing with highly dilute carboxylic acids, process optimization can be obtained by chemical conversion of acids by esterification combined with solvent extraction. Esters are important fine chemicals and have wide applicability in the industry and consumer applications [4–8]. Berthelot and St. Gilles [9] already studied esterification reactions in the year 1862 and found that in general esterification is an equilibrium reaction [7]. Theoretically, yields of 100 % can be achieved when the product ester is removed from the reaction broth as fast as it is formed [7]. A possible way to remove the ester is shown in Fig. 2. Separation of the ester from the heterogeneous reaction mixture is performed by liquid-liquid extraction.

For continuous operation of the presented process approach (Fig. 2), an appropriate apparatus design is needed. Polyakova et al. [10] compares different liquid-liquid extraction devices. The Taylor-Couette disc contactor (TCDC) has a high tolerance for solid particle load. Continuous solid-liquid-liquid operation for chemical reaction combined with liquid-liquid extraction in a TCDC column has been confirmed by Painer et al. [11].

This study focuses on the validation of stable continuous three-phase flow in the TCDC and its applicability for combining heterogeneously catalyzed esterification of acetic acid (HAc) with methanol (MeOH) and simultaneous solvent extraction of methyl acetate (MeAc) with ShellSol T in a lab scale TCDC column. The process concept was first investigated in batch experiments. HAc was esterified with methanol and ethanol (EtOH) at different temperatures (65 °C and 80 °C). Solvent extraction of MeAc and EtAc (ethyl acetate) was performed with ShellSol T and Biodiesel. Analysis of batch experiments confirmed applicability of the operation mode of ester separation into ShellSol T from the reaction broth of HAc, MeOH and the catalyst, although liquid-liquid partition of methyl acetate between water and ShellSol T is rather poor. The system was then chosen for continuous esterification in the TCDC in batch operation mode. Before performing the esterification experiments the hydraulic performance of the TCDC was investigated to

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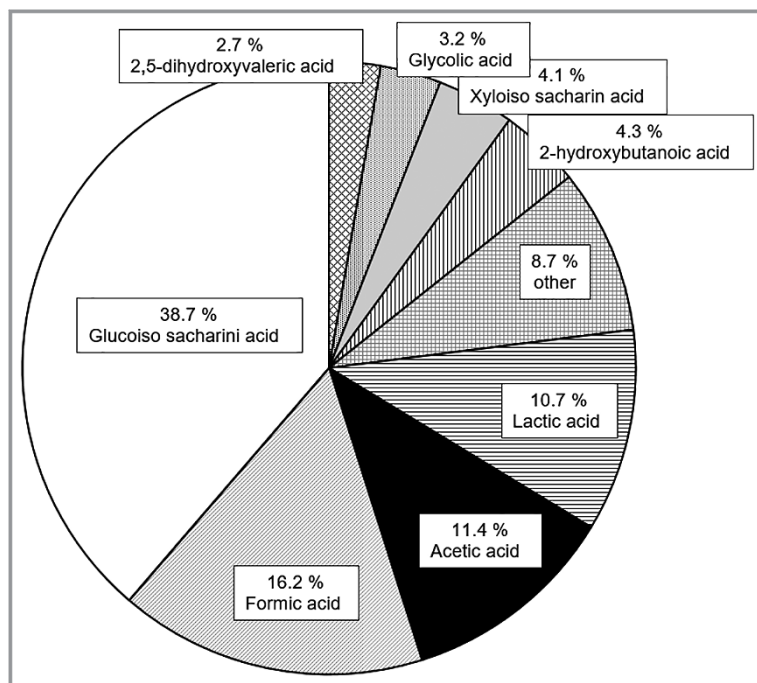
Figure 1. Exemplary composition of black liquor in wt % beside lignin from pine, Kraft-Process. Total amount of black liquor based on the mass of wood is 17 % [3].
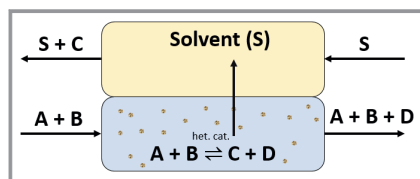

Figure 2. Operation principle of heterogeneously catalyzed esterification with liquid-liquid extraction. Acid (A) and alcohol (B) are mixed with a heterogeneous catalyst (het. cat.). The ester (C) is extracted to the solvent phase (S) to shift the equilibrium on the product side.

collect data for modelling multiphase flow. Detailed research of liquid-liquid phase contact in a TCDC column was already performed by Grafschafter et al. [12–14]. The operation window for liquid-liquid (LL) phase contact, including determination of dispersed phase holdup and residence time distribution (RTD), was investigated. After detailed investigation of LL hydraulics, solid phase holdup measurements were performed. Finally, the dispersed phase holdup and solid phase holdup, as well as the on-set of appropriate liquid-liquid-solid (LLS) operation were investigated for different rate of rotation, hydraulic load and mass flow rate of the solid phase. To validate the concept of chemical conversion with product separation by liquid-liquid extraction, several esterification experiments with simultaneous liquid-liquid extraction were then performed in the TCDC in batch operation mode (by short-circuiting both flow lines with the corresponding storage vessel). The experimental results were compared to esterification with-

out solvent extraction. As mentioned, liquid-liquid partition of methyl acetate between Shell-Sol T and water is poor. However, simultaneous extraction of MeAc from the reaction broth in the TCDC increases the overall HAc conversion from 20 % to 30 %. Based on the outcome of experiments in batch operation mode continuous concurrent chemical conversion with liquid-liquid extraction was then modelled with the CSTR (continuous stirred tank reactor) cascade model.

2 Kinetics of Heterogeneously Catalyzed Esterification

The heterogeneously catalyzed esterification of acetic acid with methanol in a dilute aqueous system is modeled by a homogeneous second order reversible reaction, according to the general rate law (Eq. (1))

$$-r_{HAc} = -\frac{dc_{HAc}}{dt} = k_1 c_{HAc} c_{MeOH} - k_2 c_{MeAc} c_{H2O} \quad (1)$$

with following boundary conditions:
– equimolar start concentration of MeOH and HAc
– in dilute systems the concentration of water is nearly constant and incorporated to the apparent backward reaction rate constant k_2' ($k_2' = k_2 c_{H2O}$).

The relative conversion of acetic acid is defined as Eq. (2).

$$X_{HAc} = X = \frac{c_{HAc,0} - c_{HAc}}{c_{HAc,0}} \quad (2)$$

With the boundary conditions and the relative conversion, the rate law (Eq. (1)) can be rearranged to Eq. (3).

$$\frac{dX}{dt} = k_1 c_{HAc,0}(1 - X)^2 - k_2' X \quad (3)$$

At equilibrium conditions $dX/dt = 0$, k_2' can be written as Eq. (4).

$$k_2' = \frac{k_1 c_{HAc,0}(1 - X_{equ})^2}{X_{equ}} \quad (4)$$

After reinserting Eq. (4) into the rate law (Eq. (3)) and integration from 0 to X and from $t = 0$ to t the relative conversion at time t can be expressed according to Eq. (5).

$$X(t) = \frac{X_{equ}\left[\exp\left(\frac{c_{HAc,0}k_1 t}{X_{equ}}\right) - \exp\left(X_{equ}c_{HAc,0}k_1 t\right)\right]}{\exp\left(\frac{c_{HAc,0}k_1 t}{X_{equ}}\right) - X_{equ}^2 \exp\left(X_{equ}c_{HAc,0}k_1 t\right)} \quad (5)$$

The reaction equilibrium constant K_{equ} is defined as Eq. (6).

$$K_{eq} = \frac{k_1}{k_2'} \qquad (6)$$

3 Hydraulics

3.1 Dispersed Phase Holdup

The dispersed phase holdup φ is defined as ratio of the volume of dispersed organic phase (V_o) to the total volume of the active height of the reactor ($V_o + V_a$).

$$\varphi_o = \frac{V_o}{V_o + V_a} \qquad (7)$$

The solvent phase holdup can be calculated from the differential pressure measured at steady-state operation.

$$\varphi_o = \frac{\Delta P}{gh(\rho_a - \rho_o)} \cdot 100 \qquad (8)$$

The static pressure equilibrium ΔP shows the measured pressure difference between bypass line filled with continuous phase and the column filled with continuous and dispersed phase. Fig. 3 illustrates the connection ports of the differential pressure transducer (PDT).

The holdup of the solid catalyst is determined by Eq. (9)

$$\varphi_{cat} = \left(\frac{r^2 \pi \Delta h_{cat} 0.74}{V_{reactor}}\right) \cdot 100 \qquad (9)$$

Δh_{cat} is the height in the catalyst sedimentation vessel (B3) between the first solid particle entering the column and steady-state operation. The radius r is the inner radius of the catalyst sedimentation vessel (25.8 mm). The factor 0.74 corresponds to dense packing of the catalyst particles in the sedimentation vessel [15].

3.2 Residence Time Distribution

Deviation from ideal flow behavior in a TCDC can be modelled with a CSTR cascade [14]. The residence time distribution is measured with a pulse signal after injection of 1 mL saturated sodium chloride solution into the aqueous phase. The change of conductivity over time is recorded. The data is then normalized to generate E_Θ vs Θ curves. According to Levenspiel the number of corresponding vessels
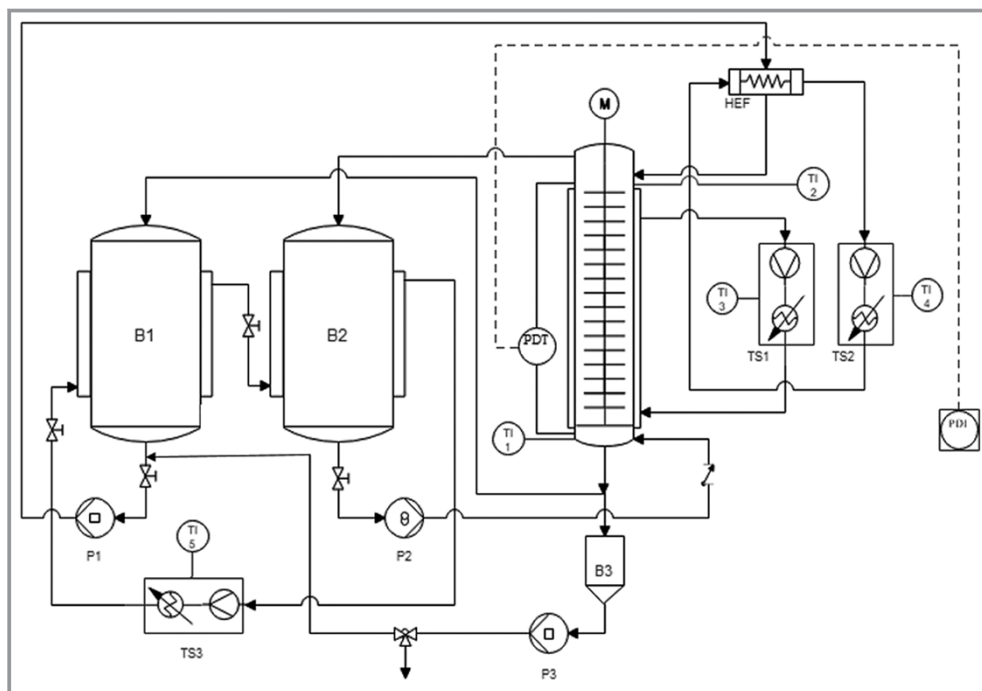

Figure 3. Process flow scheme of the three-phase flow TCDC setup (B1 – storage tank aqueous phase; B2 – storage tank organic phase; B3 – catalyst sedimentation vessel; HEF – heat exchange feed, PDT – differential pressure sensor; PDI – online pressure readout with laptop; P1 – aqueous phase pump; P2 – solvent phase pump; P3 – catalyst slurry pump; TI1 – temperature indicator bottom; TI2 – temperature indicator head; TI3 – temperature indicator thermostat reactor double jacket; TI4 – temperature indicator thermostat feed heater; TI5 – temperature indicator thermostat storage tanks double jacket; TS1 – thermostat reactor double jacket; TS2 – thermostat feed heater; TS3 – thermostat storage tanks double jacket; SP1 – sample port aqueous phase inlet; SP2 – sample port organic phase inlet; SP3 – sample port aqueous phase outlet).

N for the tank in series model can be calculated from $E_{\Theta,\max}$ [16].

$$E_{\theta,\max} = \frac{N(N-1)^{N-1}}{(N-1)!}\exp(-(N-1)) \qquad (10)$$

From the residence time distribution data, the number of corresponding vessels and the mean residence time is calculated.

3.3 Chemicals and Analytics

The chemicals were technical grade. The physical properties are summarized in Tab. 1. The physical properties of the cation-exchange resin Amberlyst 15 are shown in Tab. 2.

All solvent samples and all aqueous phase samples were analyzed by gas chromatography in a Shimadzu GC-2010 Plus equipped with an auto injector (AOC-20i). To avoid post process reaction of the aqueous samples, the samples were quenched in a glass beaker filled with ice directly after being taken. The samples were transferred to a 1.5-mL crimp vial and stored in the cooled auto sampler at 5 °C to avoid further reactions. 0.3 µL of the sample were injected to a ZB-WAX plus column and analyzed with a FID detector.

3.4 Experimental Setup

Esterification reactions are slow reactions, and catalytic acceleration is necessary. Homogeneous acid catalysts are not recommended, because of several disadvantages as for instance corrosion problems and loss of catalyst. Major drawback for using homogeneous catalysts is the huge energy consumption needed for separating the catalyst from the reaction broth [17]. Acceleration of esterification reactions with heterogeneous catalysts has found increasing interest especially for continuous operation. They are easy to separate from the reaction broth via sedimentation [7, 9–10]. Therefore, the cation-exchange resin Amberlyst 15 was used

Table 2. Physical properties of the cation-exchange resin Amberlyst 15.

Name	Amberlyst 15
Type	Macroporous
Acid sites	4.7 eq kg^{-1}
Moisture holding capacity	52–57 % (H$^+$ form)
Harmonic mean size	0.6–0.85 mm
Surface area	53 m^{2}g^{-1}

for heterogeneous catalysis of acetic acid esterification. Batch experiments were performed to investigate the behavior of two different solvents. The solvents Biodiesel (FAME) and ShellSol T were compared. Esterification of acetic acid was performed with methanol and ethanol at different temperatures (65 °C and 80 °C) and phase ratios P (aqueous to solvent). In a first series batch experiments were performed in a reaction vessel. In a second series acetic acid was esterified with methanol at 65 °C and simultaneous product extraction with ShellSol T in the TCDC setup in batch operation mode.

3.5 Batch experiments

The batch esterification experiments were performed in a 3-L glass reactor. A water cooled reflux condenser was installed on top of the reactor to avoid evaporation of volatile components. The temperature of the reaction mixture was set to 65 °C or 80 °C by using a Lauda RE206 thermostat. Deionized water was used as heat transfer medium and pumped through the double jacket of the reactor. The reaction temperature was recorded with a digital thermometer (MGW Lauda R40/2; ±0.1 °C). The sensor was installed directly inside the reaction mixture. Water with 2 mol L^{-1} of acetic acid, the solvent and the heterogeneous catalyst Amberlyst 15 (10 wt % related to the aqueous phase, hydrogen form) were heated to the desired reaction temperature. An equimolar amount of preheated alcohol (methanol or

Table 1. Chemicals used for esterification experiments.

	Manufacturer	CAS	M [g mol^{-1}]	ρ at 20 °C [kg m^{-3}]	ν
ShellSol T	Donau Chemie	64741-65-7	172	756.8	1.85 (20 °C) mm^{2}s^{-1}
Biodiesel	BioEnergy International	–	295	875	2.76 (65 °C), 7.5 (20 °C) mm^{2}s^{-1}
Amberlyst 15	Sigma Aldrich	39389-20-3	314	1100–1400	solid
Methanol	Carl Roth	67-56-1	32	792	0.59 (20 °C) mPas
Ethanol	AustroAlco	64-17-5	46	789	1.44 (20 °C) mPas
Acetic Acid	Carl Roth	64-19-7	60	1005	1.17 (20 °C) mm^{2}s^{-1}
Deionized water	In-house source	–	18	998	1.00 (20 °C) mPas

ethanol) was then added to the reactor. The reaction mixture was constantly stirred with a blade stirrer connected to a laboratory motor drive (Hei-TORQUE Precision 200). For sampling 2×0.5 mL of the aqueous phase were taken with a syringe and analyzed by gas chromatography. All experiments were performed over 6 h to reach equilibrium conversion. The experiments were compared to esterification experiments without simultaneous product extraction and ranked according to the maximum relative conversion.

3.6 Continuous Experiments in the TCDC in Batch Operation Mode

Continuous multiphase flow (liquid-liquid-solid) requires adequate process and apparatus design. When focusing on column type extraction devices, the TCDC [18] satisfies the requirements of appropriate multiphase contact and simple phase separation. The TCDC is a stirred multiphase contactor. The design of internals does avoid formation of hydrodynamic dead zones for accumulation of solids and/or crud. The TCDC provides excellent mixing properties for liquid-liquid-solid (LLS) phase contact. The TCDC design is similar to the design of the rotating disc contactor (RDC), but with increased shaft and rotor disc diameter and without stator rings. The rotor discs separate the column into compartments, offering sufficient space for formation of two counter rotating toroidal vortexes of the dispersed phase in the single compartment. The vorticity of the toroidal vortexes depends on the rate of rotation of the shaft. The shaft and rotor discs of the TCDC induce stable three-phase flow with appropriate mixing of the liquid phases and the solid catalyst phase to provide sufficient residence time for the solid catalyst and the dispersed solvent phase in the single compartment. The continuous esterification experiments were performed in a lab-size Taylor-Couette Disc Contactor with 50 mm inner diameter and 600 mm active mixing height. The geometric data of the TCDC is shown in Tab. 3.

Table 3. Geometric data of the used TCDC column.

TCDC DN50	
Active length [mm]	600
Reactor diameter [mm]	50
Shaft diameter [mm]	25
Number of compartments [–]	24
Compartment height [mm]	25
Volume [L]	0.88
Rotor disc diameter [mm]	43

Fig. 3 illustrates the flowchart of the TCDC setup. The continuous phase (reaction mixture of water, methanol and acetic acid) was stored in feed tank B1. At the outlet of B1 the solid catalyst was fed to the continuous phase from the catalyst sedimentation vessel B3. A peristaltic pump P3 (Ismatec Ecoline VC-280) was used to pump the solid catalyst. An additional peristaltic pump P1 (Ismatec Ecoline VC-280) was used to transport the slurry of solid catalyst and aqueous reaction mixture to the top of the column. Before the slurry entered the column, it passed a water filled heat exchanger (HEF connected to Corio CD-200F, 2.0 kW) to ensure the desired reaction temperature. The dispersed solvent phase was stored in the feed tank B2. A gear pump P2 (Ismatec Ecoline VC-280) was used to feed the solvent phase to the TCDC at the bottom of the column. Both feed tanks (B1, B2) were temperature controlled with a water filled double jacket connected to a Thermostat (Corio CP-601F, 2.0 kW). The active height of the column was temperature controlled with a water filled double jacket connected to a thermostat (K20 Lauda, 2.2 kW) to provide constant temperature over the entire column. All tubes and glass parts, not equipped with a double jacket, were insulated with conventional pipe insulations. The reaction temperature was recorded on top of the column (T2 MGW Lauda R43/2) and at the bottom (T1 MGW Lauda R 40/20). A differential pressure transducer (PDT) was used to monitor the actual dispersed phase holdup inside the active column part. This differential pressure transducer was connected to a bypass tube filled with the continuous phase. Sampling ports for the aqueous reaction mixture were located at the inlet (SP1) and at the outlet (SP3). Samples of the dispersed solvent phase were taken at the inlet (SP2) and at the outlet. The solvent phase outlet samples were taken with a syringe on top of the column near the phase interface. The entire column and feed tanks were sealed to avoid evaporation of volatile components. The TCDC rotor was stirred with a laboratory motor drive (Hei-TORQUE Precision 200). In batch operation mode the outlet ports for the solvent phase and aqueous phase were connected to their feed tanks.

For the preparation of the aqueous reaction mixture 480 g of acetic acid and 256 g of methanol were diluted with deionized water to a volume of 4 L, resulting in a solution with mass concentrations of $120\,\mathrm{g\,L^{-1}}$ acetic acid and $64\,\mathrm{g\,L^{-1}}$ methanol, corresponding to an equimolar amount of $2\,\mathrm{mol\,L^{-1}}$ for both compounds. Directly after preparation of the feed mixture, a sample was taken. All samples were taken with single use syringes, transferred into 1.5-mL crimp vials, which were capped and instantly cooled in an ice bath. The feed solution was then transferred into the storage tank B1 and aqueous phase circulation was started and the rotor drive was switched on. The solvent phase tank B2 was filled with ShellSol T. The amount of solvent corresponds to the phase ratio of the experiment. The aqueous phase was fed first to the column. After reaching the desired reaction temperature of 65 °C the solvent phase pump P2 was activated. The first set of samples was taken when stable liquid-liquid flow in the column was reached. Then the catalyst pump P3 was activated. Stable liquid-liquid-solid flow

was reached about 10 min after starting the slurry pump. At this operation state the second set of samples was collected. In the first 3 h samples were taken every 30 min, and after 3 h in intervals of 1 h. Each sampling procedure resulted in 4 samples of outgoing and ingoing streams of the aqueous and the solvent phase. Volumetric flow rates were adjusted according to pump calibration curves and checked in regular intervals. Fig. 4 shows the operation status of the TCDC after activating liquid-liquid contact and after activating the catalyst feed. For comparison the operation state of solid-liquid flow is shown too.

3.7 Results

3.7.1 Batch Experiments

Esterification of acetic acid (HAc) with methanol (MeOH) or ethanol (EtOH) with simultaneous transfer of the product ester into the solvents ShellSol T and Biodiesel was investigated at 65 °C and 80 °C. The equimolar initial concentration of the reactants HAc and alcohol was 2 mol L^{-1}. The mass fraction of the catalyst related to the total mass of the mixture was 10 wt %. The phase ratio P of aqueous to solvent phase was varied between 0.5 and 2. Fig. 5 presents the overall HAc transfer at temperatures of 65 °C and at 80 °C with and without extraction for esterification of HAc with MeOH or EtOH. By simultaneous extraction of the product, the overall yield of HAc with MeOH can be increased from 17 % to 29 % at the same reaction temperature of 65 °C for ShellSol T at a phase ratio of 0.5. Several investigations of HAc esterification with methanol confirm that higher temperature is favorable due to acceleration of the forward reaction [4, 17, 19, 20]. The experiments shown in Fig. 5 confirm the temperature dependency for both solvents. Increasing amount of solvent ($P = 0.5$) increases the overall

Figure 5. Comparison of maximum relative HAc conversion under variation of phase ratio (*P*), temperature and alcohol (MeOH, EtOH).

conversion. For comparison, esterification of HAc with EtOH was performed too. The kinetics of HAc esterification with MeOH and EtOH is well investigated and can be found in literature [8, 17, 21, 22]. Kinetics with ion-exchange resin catalysts is reported in [4, 20, 22].

Based on the outcome of the batch experiments HAc esterification with MeOH and extraction with ShellSol T at $T = 65$ °C and $P = 0.5$ was chosen for performing experiments in the TCDC. The forward reaction rate constant was determined from MeOH esterification batch experiments at 65 °C without extraction. For these experiments the reaction rate constants were determined to be $k_1 = 0.075$ L mol^{-1}h^{-1} and $k_2' = 0.51$ h^{-1}.

3.7.2 Continuous Experiments

The experiments were performed in the TCDC setup in batch operation mode as shown in Fig. 3. The experiments were performed over 10 h and repeated for validation. The mean values were used for data interpretation. The phase ratio P was varied from 0.5 to 2. High phase ratios were chosen for testing the hydraulic stability of the TCDC. Thermodynamics of HAc esterification with MeOH rather recommends very low phase ratio because of the excellent water solubility of methyl acetate. The temperature was kept constant at 65 °C. The amount of solid catalyst was kept constant. Tab. 4 summarizes the experimental parameters. Fig. 6 compares the equilibrium conversion for varying phase ratio.
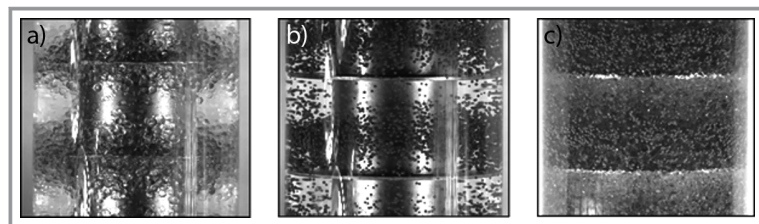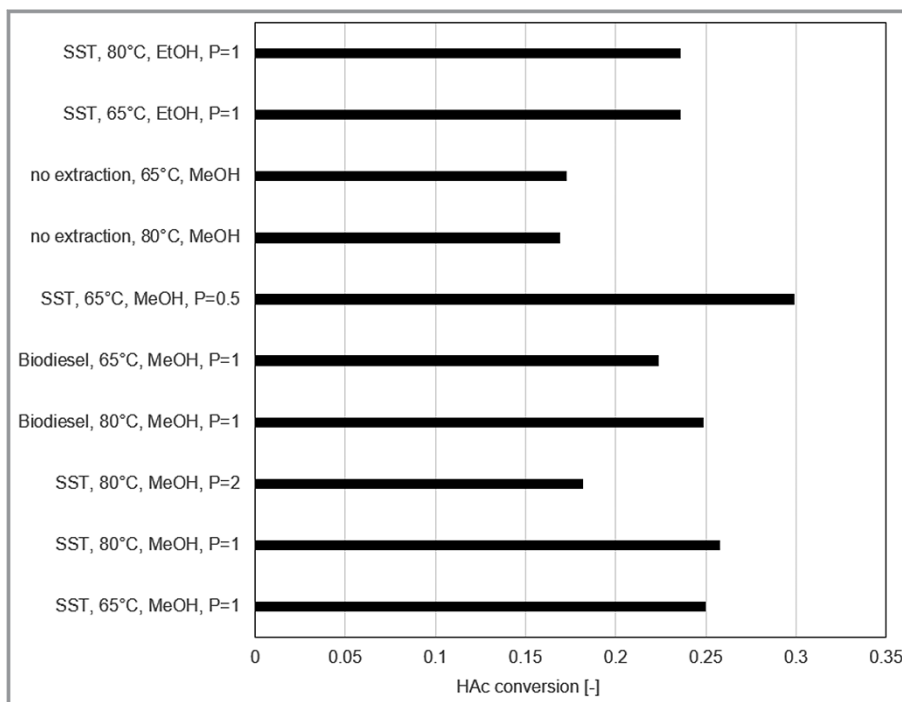
Figure 4. Flow pattern in a single compartment of the TCDC for a) liquid-liquid; b) solid-liquid; c) liquid-liquid-solid flow at 800 rpm and a hydraulic load of $B = 6$ m^{3}m^{-2}h^{-1}.

Table 4. Experimental parameters for the TCDC experiments.

Symbol	Unit	Exp. 1	Exp. 2	Exp. 3	Exp. 4
P	[–]	0.5	1	2	without extraction
$\dot{V}_o$	[L min^{-1}]	0.11	0.1	0.05	–
$\dot{V}_a$	[L min^{-1}]	0.06	0.11	0.1	0.6
φ	[vol %]	11	7	3.5	–
φ_{cat}	[vol %]	7.5	7.5	7.5	7.5
B	[m^{3}m^{-2}h^{-1}]	7	8.5	6	2.5
T	[°C]	65	65	65	65
rpm	[min^{-1}]	600	500	500	600
k_1	[L mol^{-1}h^{-1}]	0.075	0.075	0.075	0.075
k_2'	[h^{-1}]	0.226	0.281	0.38	0.423
X_{eq}	[%]	30	26.8	22	21
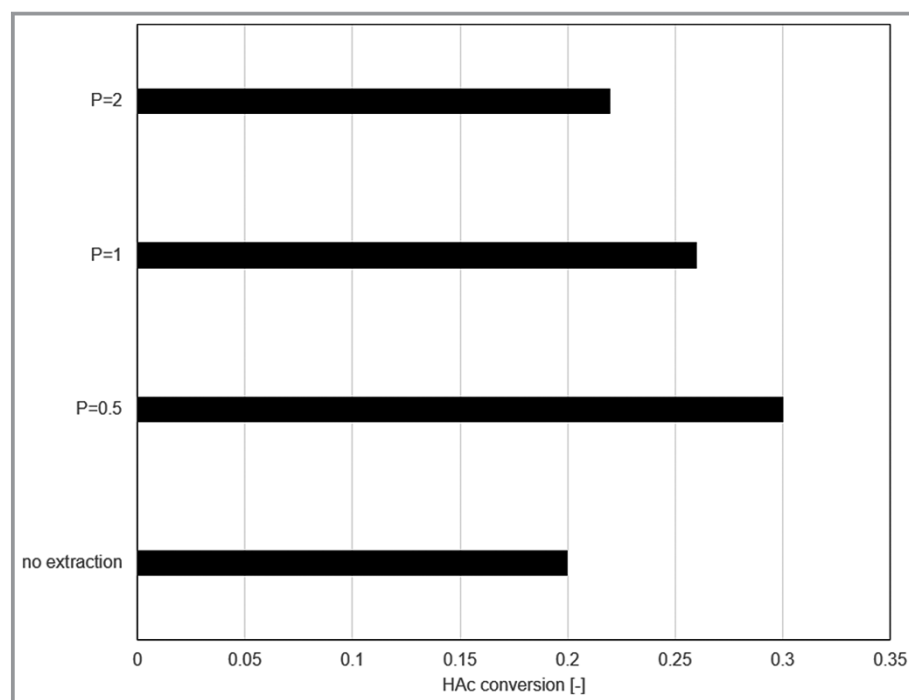
Figure 6. Comparison of HAc conversion with MeOH at equilibrium after 10 h of continuous operation in the TCDC in batch operation mode. The phase ratio P was varied. The operation settings for each experiment are summarized in Tab. 4.

Kinetic data from batch experiments without simultaneous product extraction was used for the determination of the forward reaction rate constant of $k_1 = 0.075$ L mol^{-1}h^{-1}. The forward reaction rate constant is assumed to be constant even when the reaction is performed with simultaneous product extraction. Extraction of MeAc changes the concentration of MeAc in the reaction mixture. According to Eq. (1) this influences the backward reaction expressed in terms of the apparent backward reaction rate constant k_2'. Fig. 7 shows the measured relative conversion of acetic acid compared to the modelled one at constant forward reaction rate constant k_1. The chosen kinetic model compares well with the experimental data.

4 Residence Time Distribution

The concentration profile in a TCDC column is well approached by a CSTR cascade [12]. From the normalized residence time distribution, the number of corresponding vessels can be calculated according to Eq. (10). The number of vessels for experiment 1 is 4 with a mean residence time of 1650 s. Fig. 8 illustrates the measured exit age function (solid) and the model for $N = 4$ (dotted line) and $N = 5$ (dash dotted line). The model for $N = 4$ sufficiently describes the measured RTD. The data from the residence time distribution is used for modelling the MeAc concentration in the reactor outlet for experiment 1.

The number of vessels and mean residence time are combined with the rate law for chemical conversion in Eq. (11). This equation is solved for every single tank in accordance to the inlet concentration of HAc. In Eq. (11) the subscript i indicates the actual tank with the constant forward reaction rate constant k_1 and the apparent backward reaction rate constant k_2' for experiment 1. The parameters of all experiments are summarized in Tab. 4. As expected k_2' correlates
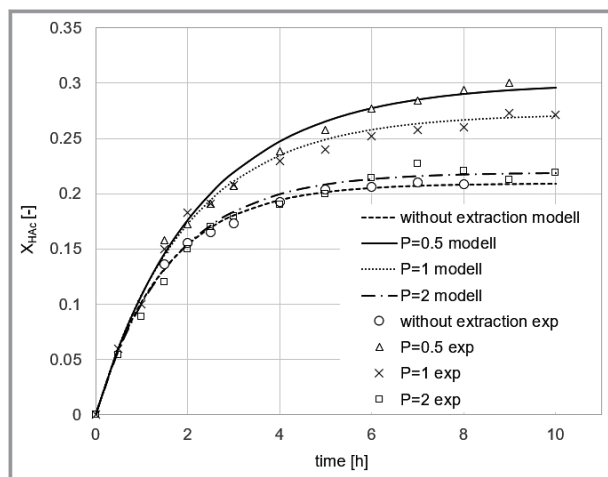
Figure 7. Relative conversion of acetic acid for experiment 1 (*P* = 0.5), experiment 2 (*P* = 1), experiment 3 (*P* = 2) and experiment 4 without solvent extraction; modelled relative acetic acid conversion of experiment 1 to 4. The used rate constants are shown in Tab. 4.
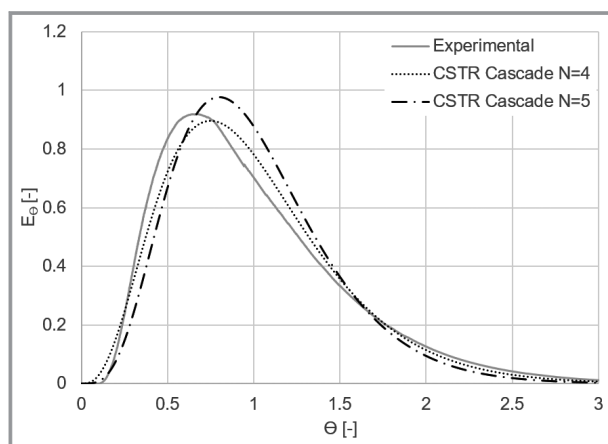

Figure 8. Normalized exit age distribution for experiment Nr. 1 with phase ratio *P* = 0.5 (solid line) and modelled exit age distribution for *N* = 4 (dotted line) and *N* = 5 (dash dotted line).

linearly with *P*. Fig. 9 shows the modelled outlet concentration of acetic acid for experiment 1 for four and five vessels in series. The experimental data compare well with the findings from RTD determination. Four vessels better approach the outlet concentration of HAc than five vessels.

$$\tau_i = \frac{\tau}{N} = \frac{c_{HAc,in(t)}(X_i - X_{i-1})}{-r_i} \qquad (11)$$

5 Reactor Modelling

With the assumption that the reaction only occurs in the aqueous phase the distribution of the reaction product MeAc has to be considered according to the phase ratio *P*
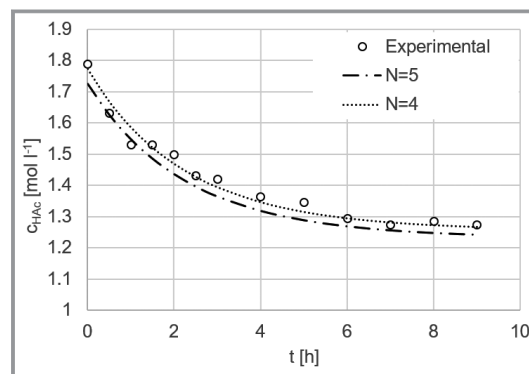

Figure 9. Modelled outlet concentration of HAc for experiment 1. The dotted line indicates the outlet concentration with 4 vessels. The dash dotted line shows the outlet concentration for 5 vessels in series.

and the partition coefficient *K*. The general MeAc balance is expressed by Eq. (12). The partition coefficient of MeAc between the solvent phase and the reaction mixture was experimentally determined to be *K* = 1.1 at *T* = 65 °C.

$$c_{Hac,0}X(t)\dot{V}_a = c_{MeAc,a}\dot{V}_a + c_{MeAc,o}\dot{V}_o \qquad (12)$$

The partition coefficient of MeAc is defined as *K* (Eq. (13)).

$$K = \frac{c_{MeAc}^o}{c_{MeAc}^a} \qquad (13)$$

The phase ratio *P* is defined as ratio of the volumetric flow of the reaction mixture (a) to volumetric flow of the solvent phase (o).

$$P = \frac{\dot{V}_a}{\dot{V}_o} \qquad (14)$$

The remaining MeAc concentration in the aqueous phase after extraction can be expressed as following

$$c_{MeAc}^a = \frac{c_{HAc,0}X(t)P}{K+P} \qquad (15)$$

The constant dispersed solvent phase holdup along the reactor height allows assumption of constant volume for each continuous stirred tank reactor along the height. Equilibrium partition of MeAc is assumed constant for every single reactor. Evaluation of the residence time distribution show that 0.6 m active reactor height equals four continuous stirred tanks. Combined with the residence time in one single reactor the relative conversion of acetic acid can be calculated. Partition of the reaction product MeAc is calculated according to Eq. (15). For the operation parameters of experiment 1 the concentration of HAc in the aqueous phase and the concentration of MeAc in the solvent phase and the aqueous phase is shown in Fig. 10. In concurrent esterification of HAc with MeOH in a DN 50 TCDC column equilibrium conversion would need a total height of 30 m.
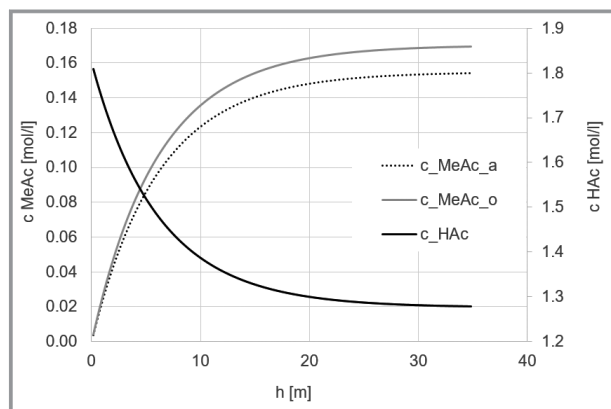
Figure 10. Modelled concentration profiles of HAc (solid black line) and MeAc (dotted line) in the aqueous phase for experiment 1. The solid grey line indicates the corresponding MeAc concentration in the solvent phase.

6 Summary

The outcome of this study confirms that the TCDC is able to continuously operate three phases (liquid-liquid-solid). The three-phase flow regime is stable and stationary. Exemplarily the esterification of acetic acid with methanol, accelerated by heterogeneous catalysis with a cation-exchange resin, with simultaneous transfer of the product methyl acetate into the solvent ShellSol T was successfully performed in a lab-size TCDC in batch operation mode at $T = 65\,°C$. The experimental data from TCDC experiments compare well with batch reactor experiments. The applied second order reversible reaction kinetics sufficiently model the esterification reaction. Extraction of the reaction product is considered in the apparent backward reaction rate constant k_2'. The forward reaction rate constant k_1 was kept constant as the same start concentration of reactants, same temperature and catalyst loading was used for all experiments. The overall conversion of acetic acid was increased from 20 % without extraction up to 30 % with simultaneous product extraction. The process performance is limited by the huge water solubility of MeAc and the small partition coefficient of $K = 1.1$. The esterification process in a TCDC can be modelled as continuous stirred tank reactor cascade. From residence time distribution measurements, the number of vessels for given rotational speed and volumetric flow rates was determined. In dependence of the hydraulic parameters the concentration of reactants over the reactor height was modelled. Modelled data and experimental results compare well.

Symbols used

ΔP	[Pa]	pressure difference
B	[m³m⁻²h⁻¹]	total hydraulic load
c	[mol L⁻¹]	concentration
E_Θ	[–]	normalized exit age distribution
g	[m s⁻²]	gravitational constant
h	[m]	height
K	[–]	partition coefficient
k_1	[L mol⁻¹h⁻¹]	forward reaction rate constant
k_2	[L mol⁻¹h⁻¹]	backward reaction rate constant
k_2'	[h⁻¹]	apparent backward reaction rate constant
K_{equ}	[L mol⁻¹]	reaction equilibrium constant
M	[g mol⁻¹]	molecular weight
N	[–]	number of vessels
P	[–]	phase ratio (aqueous to organic)
r	[mol L⁻¹h⁻¹]	reaction rate
t	[h]	time
V	[m³]	volume
$\dot{V}$	[L min⁻¹]	volumetric flow rate
X	[–]	relative conversion

Greek symbols

Θ	[–]	normalized time
ν	[mm²s⁻¹]	kinematic viscosity
ρ	[kg m⁻³]	density
τ	[s]	mean residence time
φ	[–]	holdup

Subscripts

0	initial
a	aqueous phase
cat	catalyst
equ	equilibrium
i	vessel i
o	organic phase

Abbreviations

CSTR	continuous stirred tank reactor
EtOH	ethanol
GC	gas chromatography
HAc	acetic acid
LL	liquid-liquid
LLS	liquid-liquid-solid
MeAc	methyl acetate
MeOH	methanol
RDC	rotating disc contactor
RTD	residence time distribution
SST	ShellSol T
TCDC	Taylor-Couette disc contactor

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