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Heterogeneously catalyzed conversion combined with solvent extraction: An inventive approach for isolating dilute constituents

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Abstract

For successful combination of a heterogeneously catalyzed conversion combined with solvent extraction impeded in a continuous process, appropriate requirements to apparatus design for three-phase operation are necessary. The Taylor-Couette Disc Contactor (TCDC) is expected to meet the requirements of intensive three-phase contact. The construction principle of the TCDC does not provide dead zones for accumulation of solids and crud, and it offers excellent mixing properties for solid/liquid/liquid contact. The rotating shaft does induce formation of stapled toroidal vortices with a hydrodynamic shear gap in between. Solid catalysts of higher density compared to the continuous phase collect in this shear gap, providing acceleration of heterogeneously catalyzed reactions. Low density solvents are dispersed and trapped in the vortices and may contribute to intensification of conversion by collecting the products. To gain design rules and for modeling purposes the effect of the hydraulic load, rotational speed and phase ratio on residence time distribution were investigated in detail. Analysis of the residence time distribution of the continuous phase suggests application of the tank-in-series model.

Keywords: Taylor-Couette Disc Contactor, solvent extraction, reactive separation, residence time distribution

Introduction

Global and 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 constituents from the aqueous effluent 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 additional bulk byproducts of cellulose preparation [1]. Process optimization can be obtained by combining simple solvent extraction with properly chosen chemical conversion of acids by esterification, which has a significant impact on water solubility of the product and therefore separation properties. Esters have wide applicability in industry and consumer products. Consequently, esterification with phase transfer by liquid/liquid and consecutive isolation of esters by distillation definitely sustainably contributes to economically feasible whole-plant usage of renewable resources. Unfavorably, esterification reactions are slow chemical equilibrium reactions and catalytic acceleration is inalienable.
High water content of the reaction broth shifts the chemical equilibrium composition to the reactant side. Via solvent extraction, the carboxylic acids can be transferred into the solvent phase prior to or after esterification, and the limitation of conversion is avoided by shifting the equilibrium composition of the carrier phase. The byproduct water is transferred to the aqueous phase, due to the limited solubility in the solvent phase. For easy separation of the catalyst after esterification, heterogeneous catalysts are recommended whereby specific requirements to apparatus design arise, especially when implemented in a continuous process.

The Taylor-Couette Disc Contactor (TCDC), a continuously operating stirred liquid/liquid extraction column, is able to meet the requirements for three-phase contact due to formation of stapled toroidal vortices along the column. Experimentally validated CFD-simulations predict a geometric optimum for hydraulics (dynamic formation of stable stapled toroidal vortices) when, based on the design of Rotating Disc Contactors (RDC), the shaft diameter as well as rotor disc diameter d_R of the internals are increased [2]. The TCDC is able to operate without stator rings, as seen at RDC columns, whereby crud accumulation and fouling along the active mass transfer zone is avoided and thus harsh operation conditions as well as liquid/liquid/solid operations are feasible. To provide high hydraulic load, an optimum ratio of the shaft diameter to the column diameter of $D_{Sh}/D = 0.5$ is recommended. This design specification also prevents from formation of hydrodynamic dead zones along the area of the shaft and induces banded two-phase flow. Banded two-phase flow can also be observed in Taylor-Couette reactors (TCR), but the TCDC offers much higher hydraulic load beyond 30 $m^3\,m^{-2}\,h^{-1}$. The TCDC thus evolves from optimizing the Rotating Disc Contactor and the Taylor-Couette reactor, as shown in figure 1. [2-5]

For successful design and operation performance of the TCDC, comprehensive knowledge of hydraulics is needed since the design is not a straightforward process particularly in scale up. The present work summarizes the results of experimental analysis of the residence time distribution in 0.1 m and 0.3 m diameter scale of TCDC contactors [6].

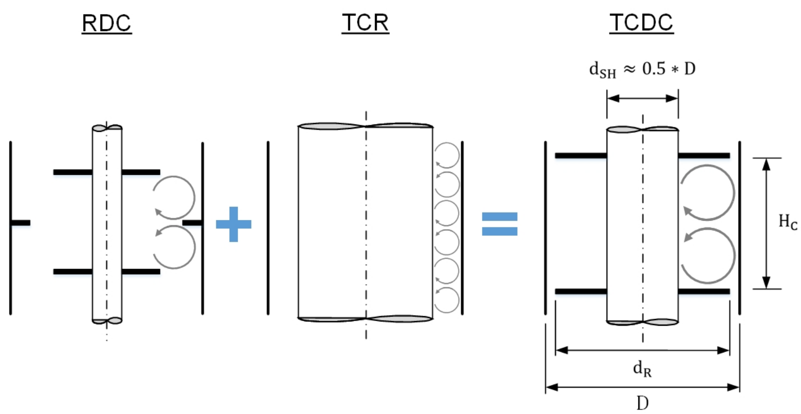

Figure 1: Schematic drawing of a Rotating Disc Contactor(RDC), Taylor-Couette Reactor(TCR) and Taylor-Couette Disc Contactor (TCDC)

Materials and methods

Materials

Hydraulics and operation performance of the TCDC were investigated in terms of determining the residence time distribution (RTD) in a pilot plant scale with 0.1 m tower diameter (TCDC100) and in pilot plant scale with 0.3 m tower diameter (TCDC300). The geometrical design specifications of the columns are listed in table 1 in which H_{active} is the active height of the mixing zone, D_R is the rotor disc diameter and H_C is the compartment height. RTD was measured in single phase as well as dual phase operation, with the test system ShellSol T (SST)/Water, with SST being the dispersed phase and water the continuous phase in counter-current operation. The key properties of the test system are summarized in table 2.

Table 1: Geometrics of the TCDC100 and the TCDC300 column

	H_{Active} [m]	D [m]	D_{SH} [m]	D_R [m]	H_C [m]	H_{Active}/D [-]	$N_{Compartment}$ [-]
TCDC 100	1	0.1	0.05	0.085	0.05	10	20
TCDC 300	1	0.3	0.15	0.255	0.15	3.33	6

Reference: Grafschafter et. al (2018)

Table 2: Physical properties of the test system

	Kinematic Viscosity [m² s⁻¹]	Density [kg m⁻³]
ShellSol T (dispersed)	$1.85*10^{-6}$	756.8
Deionized water (continuous)	$1.102*10^{-6}$	998.1

Equal power per volume (P/V) in both columns maintains comparability of operation conditions and energy input. The rate of rotation for the TCDC300 was calculated according to equation 1, based on the rate of rotation of the TCDC100 ($n_{TCDC100}$) and the rotor disc diameters ($D_{R,TCDC100}$, $D_{R,TCDC300}$).

$$n_{TCDC300} = n_{TCDC100} \left(\frac{D_{R_{TCDC100}}}{D_{R_{TCDC300}}}\right)^{\frac{2}{3}} \quad (1)$$

The volumetric flow rate of the dispersed and the continuous phase were adjusted to ensure same hydraulic load B $m^3\, m^{-2} h^{-1}$ (for the continuous and the dispersed phase) related to the free net cross-sectional area of the column.

Methods

Residence time distribution (RTD) was determined with a pulse signal by injecting 1.5-2 ml of saturated sodium chloride solution into the continuous phase (deionized water) at the top of the column. The electric conductivity was measured on four positions along the active column height via non-commercial probes [7, 8] with minimum invasive impact to avoid disruptions of the flow pattern. For this purpose, electrodes with tip sensors made of stainless steel wire (d_{Tip} = 0.6 mm) were used.

The results of the RTD were interpreted with the dispersion model as well as the tank-in-series model. For the evaluation with the dispersion model, open-open boundary conditions (large deviation from plug flow $D_{ax}/uL > 0.01$) [9] was applied:

$$E_{\theta,oo} = \frac{1}{2} \sqrt{\frac{\bar{t}}{\pi\, t*\left(\frac{Dax}{uL}\right)}}\ \exp\left[-\frac{\bar{t}\left(1-\frac{t}{\bar{t}}\right)^2}{4\, t*\left(\frac{Dax}{uL}\right)}\right] \quad (2)$$

In equation 2, t represents the time, $\bar{t}$ the mean residence time and D_{ax}/uL the vessel dispersion number with D_{ax} as axial dispersion coefficient. For comparison with the dispersion model, the number of corresponding vessels in series N was calculated via the maximum of the dimensionless exit age distribution $E_{\theta,\,max}$ according to Levenspiel [9]:

$$E_{\theta,max} = \frac{N*(N-1)^{N-1}}{(N-1)!} * e^{-(N-1)} \quad (3)$$

Results and discussion

Results

The residence time distribution (RTD) was investigated for different total hydraulic load B_{total}, different phase ratio w/o and varying rate of rotation in the TCDC100 and the TCDC300 extractor. The total hydraulic load B_{total} composed of the hydraulic load of the continuous phase B_c and the hydraulic load of the dispersed phase B_d based on the free net cross-section area of the column. The operation conditions are listed in table 3.

Table 3: Operation conditions for RTD experiments in the TCDC100 and TCDC300

	TCDC 100			TCDC 300		
	B_{total} [$m^3\,m^{-2}h^{-1}$]	n [rpm]	w/o [-]	B_{total} [$m^3\,m^{-2}h^{-1}$]	n [rpm]	w/o [-]
single phase	10 15 20	250 300 400 500 600	-	5 10 15	121 170 218 242	-
two phase	20 25 30 35	250 300 400 500 600	1	10 15 20 25	121 170 218 242	1
two phase	20 25	400	0.5 0.67 1 1.5 2	-	-	-

Reference: Grafschafter et. al (2018)

The exit age distribution E_θ for both column scales is exemplarily shown in figure 2. Tailing of the RTD in the TCDC300 is more distinct as compared to the TCDC100. The nonsymmetrical E_θ curves indicate large deviation from plug flow (D/uL > 0.01) in both columns, recommending application of the tank-in-series model for RTD analysis. For comparison, $D_{ax,c}$ was deduced from the exit age distribution too.

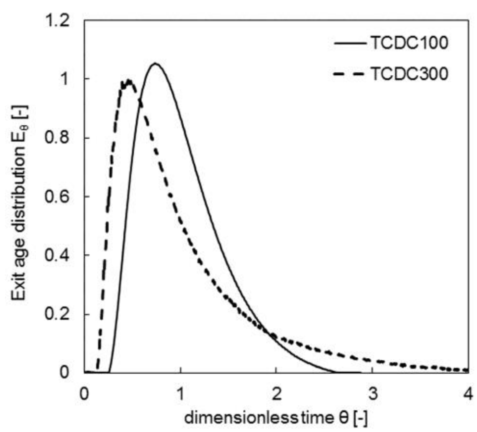

Figure 2: Exit age distribution E_θ for TCDC100 and TCDC300 at B = 20 $m^3\,m^{-2}\,h^{-1}$ and P/V = 240 $W\,m^{-3}$
Reference: Grafschafter et. al (2018)

On the left side of figure 3, the number of vessels *N* in series for single and two-phase operation mode is displayed. Plotting *N* over the rate of rotation and the hydraulic load of the continuous phase B_c provides comparability between single phase and two-phase operation mode. With increasing hydraulic load, the number of corresponding vessels *N* in series increases. Higher rate of rotation leads to decreasing *N* due to higher axial dispersion. Compared to single phase operation, two-phase operation engenders a higher number of vessels *N* and the effect of increasing hydraulic load is more pronounced. A maximum number of vessels *N* for single phase operation and two-phase operation is obtained at n = 250 rpm and $B_{.} = 40\ m^3\,m^{-2}\,h^{-1}$ ($B_{c.} = 20\ m^3\,m^{-2}\,h^{-1}$ in single phase operation).
The axial dispersion coefficient of the continuous phase $D_{ax,c}$ is shown on the right side of figure 3. $D_{ax,c}$ increases with rising rate of rotation. In single phase operation the effect of increasing hydraulic load on dispersion is negligible. Compared to single phase operation, two phase operation shows 2.5 times higher $D_{ax,c}$ values. In two phase operation $D_{ax,c}$ increases more distinct with increasing rate of rotation.

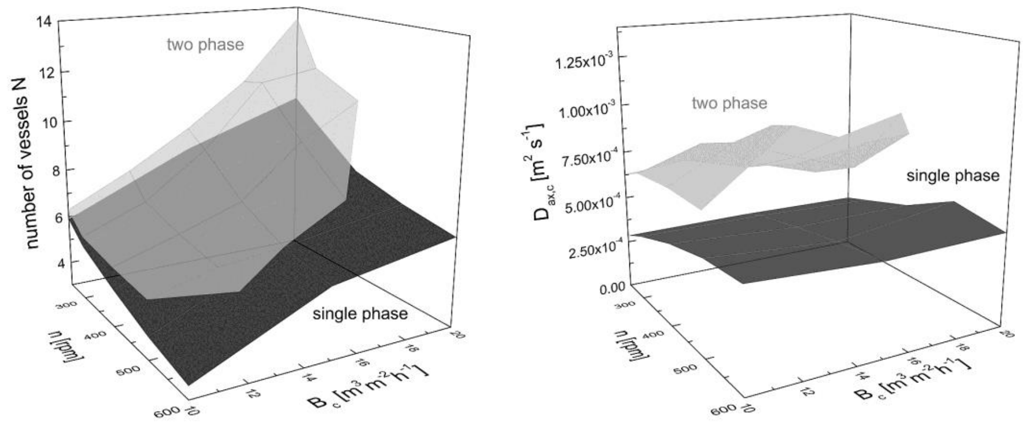

Figure 3: Results of single phase and two phase operation for varying hydraulic rate of rotation and hydraulic load; left side: number of corresponding vessels *N* in series, right side: axial dispersion coefficient of continuous phase $D_{ax,c}$

Reference: Grafschafter et. al (2018)

The effect of different phase ratio w/o on RTD was investigated for the total hydraulic load of B = 20 $m^3 m^{-2} h^{-1}$ and varying rate of rotation. The results are depicted in figure 4. High w/o values (w/o = 2) engender higher number of corresponding vessels *N* and lower $D_{ax,c}$ values. With decreasing w/o ratio the number of vessels *N* in series decreases and $D_{ax,c}$ values increase.

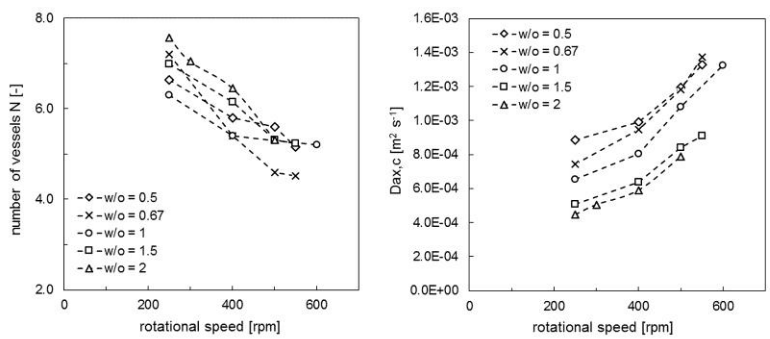

Figure 4: Effect of varying phase ratio w/o on RTD at a total hydraulic load of B = 20 m^3 m^{-2} h^{-1} and varying rate of rotation

Reference: Grafschafter et. al (2018)

Conclusion

The TCDC can handle three phase flow. It may be applied for heterogeneously catalyzed conversion with liquid/liquid extraction. For hydrodynamic characterization the effect of the hydraulic load, rate of rotation and w/o ratio was investigated. Analysis of the residence time distribution of the continuous phase suggests application of the tank-in-series model. For given rate of rotation, the number of corresponding vessels in series increases with increasing hydraulic load. A reversed trend was observed for fixed hydraulic load and varying rate of rotation. Increasing rate of rotation will cause a drop of the number of corresponding vessels N in series.

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