Simultaneous local determination of mass transfer and residence time distributions in organic multiphase systems

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HIGHLIGHTS

- Simultaneous local determination of mass transfer and residence time.
- Significant differences in mass transfer over height of column.
- Determination of residence time distribution using ATR FTIR.

ARTICLE INFO

ABSTRACT

A new method for simultaneous local determination of mass transfer coefficients and residence time distributions in continuously operated bubble columns has been developed. Since for organic liquids not many experimental data sets are available in respect to mass transfer, measurements were carried out with the organic gas/liquid multiphase system consisting of cumene (1-methylethylbenzene) and carbon dioxide. The concentration of carbon dioxide in the gas phase was adjusted by mixing with nitrogen. To measure concentrations of compounds in the liquid phase, attenuated total reflectance Fourier transform infrared spectroscopy (ATR FTIR) was applied: five ATR probes integrating silver-halide optical fibers with a length of 1.5 m were integrated in a bubble column of 128.5 cm height and a diameter of 10 cm. The probes were distributed over the height of the reactor and could be shifted within the reactor to measure radial profiles of the mass transfer coefficients in steady state operation mode at different positions. The superficial liquid velocity of the system was adjusted in the range of 0.7–1.4 cm s^{-1}. The used superficial gas velocities were between 1.5 cm s^{-1} and 2.1 cm s^{-1} to ensure a homogeneous flow regime. Furthermore, tracer experiments with benzaldehyde for the investigation of the residence time distributions were performed. From the FTIR spectral data, CO_2 and benzaldehyde tracer concentration data were determined simultaneously by conducting multivariate chemometric models. The corresponding mass transfer coefficients were calculated using a compartmental method for stationary flow. The residence time distributions were calculated from the benzoic aldehyde concentration data. Both parameters could be determined successfully. For the mass transfer coefficient of carbon dioxide into cumene, an interesting profile could be observed, which arose from several influences like areas of different bubble densities, caused by bubble breakage and coalescence, superficial velocities of gas and liquid as well as the applied type of sparger.

1. Introduction

Since for 99% of all chemical reactions more than one phase is needed, the importance of multiphase reactors becomes clear [1].

Focussing on reactions integrating a gas as well as a liquid phase, bubble columns are important reactors, which are widely used in chemical, pharmaceutical as well as in biological and wastewater treatment processes [2–5]. In fermentation processes using bubble columns the mass transfer is an important factor determining the reactor efficiency [6]. One advantage of this system is the low energy input because a mechanical stirrer for dispersing the phases

is not required. Compared to the trickle bed reactor, faster reaction rates could be observed, especially for high viscous media [7]. Slurry bubble columns are preferred nowadays over the use of trickle bed reactors in industry, e.g. for the Fischer-Tropsch synthesis [8]. In many chemical reactions, the limiting factor in view of efficiency is the mass transfer between two phases [9]. Bubble column reactors are easy in view of construction and also very large reaction volumes are possible, however the design and scale up of these systems is rather difficult [10].

The mass transfer performance is usually determined with the volumetric mass transfer coefficient $k_L a$ depending on many factors, like the physical properties of the liquid and gaseous phase, the hydrodynamic conditions as well as the gaseous phase holdup. For a more detailed characterization, the volumetric mass transfer coefficient can be separated into the mass transfer coefficient k_L and the specific interfacial area 'a' that is taking into account the bubble surface per volume. Several studies have been performed to characterize gas/aqueous liquid two phase systems since the 60's of the last century [11] but data for organic liquids used in bubble column reactors are very rare. Therefore, most equations for the design and scale up are based on empirical correlations [12,13]. Öztürk et al. [14] showed, that correlations for aqueous systems are only valid for some of these organic liquids. Also in these experiments only one overall mass transfer coefficient was determined describing the whole column, no local coefficients were regarded. The usage of these correlations for scale up of a bubble column reactor has to be done with caution, since parameters determined in lab scale could heavily change while scaling up [15]. Deckwer further states that bubble columns show such a complex behavior, especially at high mass transfer rates, that it is hard to describe them by simple models. The mass transfer coefficients change greatly over the column hight and also higher values in the region of the sparger were observed [16]. In the last couple of years computational models have been further developed to improve simulations concerning the determination of mass transfer effects in multiphasic systems [17,18].

Besides mass transfer, the residence time distribution is an important tool to describe flow and mixing behavior for reactor design. For the determination, common methods like colorimetry or conductometry are used [19]. However, these methods are time consuming in view of calibration. To overcome this, Laske et al. [20] suggested to use NIR to determine the residence time distribution of polymers in an extruder. Also radiotracer experiments are common for the determination of such plots in industry [21].

For efficient upscaling, it is necessary to understand the complex interactions between mass, energy and momentum transfer, which results in multi-scale transport kinetic interactions [22]. Some techniques are described to analyze parameters at local positions, however they mostly focus on flow characteristics and not on the mass transfer. Sharaf et al. [23] were utilizing wire mesh sensors to obtain information about flow regimes comparing different gas distributors. Bothe et al. [24] reported about local endoscopic measurements determining bubble size and velocity distributions. State of the art in this field of chemical engineering is the use of empirical data and correlations. However, recently the application of computational methods become more and more prominent [25,26]. Suitable computational models have to be further developed to characterize multiphase reactors and to enable a reliable scale up of these systems [27]. To reach this, a dependable system is needed to determine local mass transfer coefficients and residence time distributions to characterize multiphase systems and validate scale independent models, particularly in respect to a more efficient use of energy and resources, resulting in a reduction of carbon dioxide emissions [28].

FTIR has been improved over the last decades and became an established tool in chemical industry. Also the use of ATR probes

gave this powerful method more flexibility in process development and improvement [7]. Another big advantage of ATR FTIR is that, the signal is not disturbed by bubbles in multiphase systems and so the measurement of heterogeneous mixtures is possible [29]. Additionally, by integrating ATR technology as a fast, inline measurement without the need for workup of samples is enabled [30]. Besides real-time measurements, it is possible to determine concentrations of different compounds simultaneously [31]. ATR FTIR could be integrated into the process control of production plants to supervise reactions and monitor process parameters [4], enabling industry 4.0 [32].

The aim of this study is to develop an experimental setup for efficient measuring of local volumetric mass transfer coefficients over radial and axial variation as well as a residence time distribution in a bubble column operated with organic liquids by ATR FTIR.

2. Materials and methods

2.1. Experimental setup

The column used for the experiments was made of glass (borosilicate, inner diameter 100 mm, height 1285 mm). In Fig. 1 the overall flow scheme is shown. For aeration a perforated plate, made of PTFE, with a diameter of 5.9 cm and 30 holes arranged in a hexagonal pattern was inserted at the bottom of the column. The diameter of the holes was 1 mm and the distance between two holes was 10 mm. Cumene was chosen as organic liquid and carbon dioxide as gas phase, or alternatively a defined mixture of carbon dioxide and nitrogen. Cumene was purchased at DOMO Caproleuna with a purity of min. 99.9 wt% (Leuna, Germany), benzaldehyde at Sigma Aldrich with purity of min. 99 wt% (St. Louis, USA) and all gases at Linde (Munich, Germany). Carbon dioxide shows a high solubility in cumene [33] and therefore susceptible results were to be expected. The operation was carried out in co-current flow; both liquid and gas were introduced at the bottom of the column.

At the side of the column 5 ATR FT-IR (Bruker IN 350-T) silver-halide fiber probes with a diamond anvil tip have been installed at different heights h/H (height of probe/height of column), which could be shifted within the column to carry out radial profiled measurements. From $r/R = 0$ (radial position of the probe/column radius) until $r/R = 1$, in the experiments steps of 0.25 were investigated. The probes were connected with an infrared spectrometer (Bruker Matrix-MF; Bruker, Billerica, USA) equipped with a liquid nitrogen cooled MCT detector (mercury cadmium telluride). To remove water vapor and atmospheric CO_2 the spectrometer was constantly purged with pure nitrogen. All spectra were collected in the range from 4000 to 850 cm^{-1} with a resolution of 4 cm^{-1}. To reduce noise, 64 scans were accumulated for one spectrum. OPUS and OPUS Process software (Bruker Optics, Ettlingen, Germany) were used to operate the spectrometer with automated multiprobe measurements. During the experiments, the measured spectra were processed using PEAXACT Application Server (S-PACT GmbH, Aachen, Germany), which was embedded with VBScript in OPUS Process as a predictor to calculate the parameters from the spectra. The data were sent via OPC protocol to the client (Data Service; Delphin Technology AG, Bergisch Gladbach, Germany) and then visualized with ProfiSignalKlicks (Delphin Technology AG, Bergisch Gladbach, Germany), which is the graphical user interface (GUI), where the data were plotted and saved. Dissolved carbon dioxide was measured at a wavenumber of 2336 cm^{-1} in contrast to wavenumber of 2342.9 cm^{-1} as observed by Falk [34], where the asymmetric stretch vibration of CO_2 in water is present. In cumene the maximum of this peak was shifted. Fig. 2 shows FTIR