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ReDrop – A general method for solving drop-population balances with an arbitrary number of property variables

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Abstract

The simulation of liquid-liquid extraction columns has been of high interest for the last four decades. The well-known procedure is to solve drop-population balances. This approach reaches its limits if the additional influences like reactions shall be included in the simulation and can be solved only with extremely high mathematical effort. ReDrop (*Re*presentative *Drop*s) is an alternative way to model extraction columns. The idea is to follow the path of a discrete number of individual drops along their way in a column and to change their attributes according to undergoing hydrodynamics, mass transfer, breakage and coalescence. The ReDrop algorithm was successfully applied to simulate the behavior of pulsed pilot-plant columns for EFCE standard test systems and also for technical systems. It has also been extended to reactive extraction.

Keywords

Extraction, Reactive Extraction, Drop-Population Balances, Modelling

1. Introduction

Liquid-liquid extraction is like rectification and absorption a classical thermal unit operation. Mixer-settlers and columns are widely used as equipment. Although the design of a mixer-settler for a given problem can be performed with sufficient accuracy, the design of technical columns still requires scaling-

up pilot-plant columns which are time-, material- and manpower-consuming. Simulations of pilot-plant columns could minimize or even replace pilot-plant experiments. The well-known approach in the literature is to solve the drop-population balances [1] which are a set of non-linear integro-differential equations. If these balances are to be solved explicitly for every property of a drop, distributions have to be defined which are usually divided into classes. In general, classes with respect to drop size, concentration of transfer component and height position in the column have to be taken into account. If a new property of a drop e.g. drop age needs to be considered, a new distribution with respect to this property has to be included, consequently increasing the dimensionality of the simulation problem. Hence, predicting the behavior of a column for a slightly more complex situation results in a high numerical effort. For the general case of reactive extraction, each droplet has to be specified in regard to more than one component to determine the reaction kinetics. As an example, the reactive standard test system zinc + D2EHPA [2] should be shortly presented so that problems with directly solving drop-population balances with regard to reactive extraction become apparent. Zinc is solved in water and reacts with the organic D2EHPA by means of an interfacial reaction to an organic complex which is only soluble in the organic phase:

$$Zn^{2+} + 1.5\overline{R_2H_2} \Leftrightarrow \overline{ZnR_2(RH)} + 2H^+ \tag{1}$$

A bar indicates a component in the organic phase. The kinetic law in terms of activities can be written as follows:

$$-\frac{d[Zn^{2+}]}{dt} = \frac{\kappa_v[\overline{R_2H_2}]^{1.5}[Zn^{2+}] - \kappa_r[H^+]^2[\overline{ZnR_2(RH)}]}{[\overline{R_2H_2}]^{1.5} + C_1[H^+]^2}\left(\frac{\sqrt{[\overline{R_2H_2}]}}{C_2 + \sqrt{[\overline{R_2H_2}]}}\right)^2 \tag{2}$$

The values for the parameters κ_v, κ_r, C_1 and C_2 of this model can be found in [2]. In contrast to physical extraction the extracted amount of zinc is depending not only of the concentration of the extracted species, but also from other reacting components. In reality, in the continuous phase there are more components which are not found in Eq. (1) but which have to be considered for modelling mass transfer, e.g. sulphuric acid is often used to adjust pH. Simplifications like a constant concentration of some components along the entire column do not hold due to strong concentration changes. Therefore classes with regarding to all chemical components which can influence the chemical kinetics must be defined, if a reactive-extraction problem shall be solved with drop-population balances. The number of equations to be solved increases dramatically as well. It can not be guaranteed that there is an appropriate numerical method to solve the drop-population balances for such a complex task like reactive extraction in reasonable time.

A not principally, but mathematical completely different approach is represented by the ReDrop model which is mathematically more manageable.

The idea is to consider a discrete number of droplets. This approach avoids the numerical discretisation of the continuous distributions. The ReDrop model can also be viewed as a Monte-Carlo method to solve the drop-population balances. This paper shall describe the principles of ReDrop and show simulation results for pulsed columns.

2. ReDrop

2.1. Concept of ReDrop

The approach behind the ReDrop algorithm is to explicitly simulate the behavior of individual drops during their total life time in an extraction column. Each drop has its own properties e.g. drop diameter, age and concentration. Adding a new variable to describe the droplets means to add a single value for each drop. Hence, the dimensionality of the simulation problem remains unchanged. This kind of approach seems to be well suited for reactive extraction where each droplet must be specified with concentrations of a variety of components. For any drop in any position of the column, the exact composition can be known. The ReDrop algorithm is schematically illustrated in Fig. 1.
Before the calculation, the user has to supply the model with input data like mass flows, initial concentrations and model parameters. The column is divided into height elements. The drop feeding depends on the liquid load of the column, the drop-size distribution of the disperser and the chosen time step. In the inner drop loop, all effects acting on the droplets are calculated. For each single droplet, sedimentation velocity and the mass flux of the transfer component is determined. The influence of swarm behavior and that of the internals are taken into account by appropriate models. Besides, models are used for evaluating the probability of each droplet to coalesce or to break up. The decision if two drops coalesce or one drop is split, depends on the comparison of the corresponding probability modelled with appropriate expressions with a random number. If e.g. drop splitting will take place in a next step, the drop is marked and the number of drops into which the mother drop will split is determined as well as their drop-size distribution. It must be stressed that calculations of sedimentation, mass transfer, coalescence and breakage are not carried out for classes of droplets, but for every single droplet. After the drop loop, coalescence or splitting of the marked drops is carried out. Backmixing in the continuous phase is included to calculate the concentrations in the height element. After this step, the simulation continues with the drop feeding.

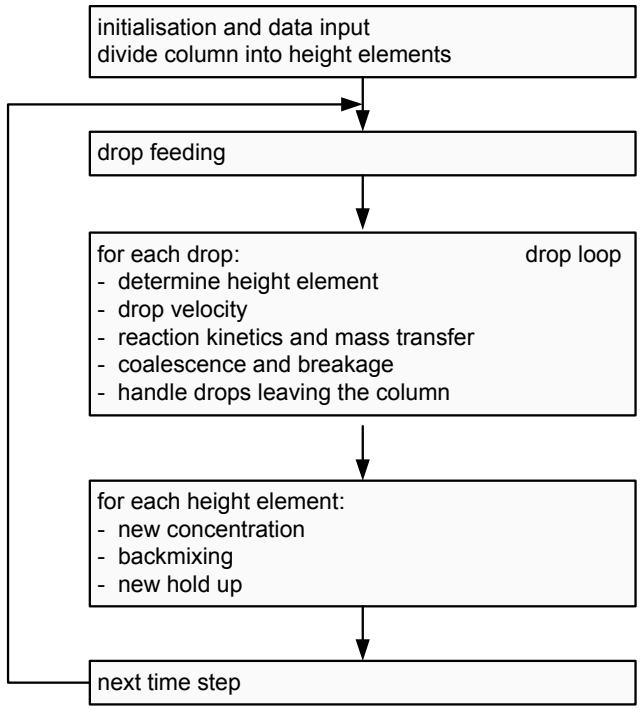

Fig. 1: Schematic illustration of the ReDrop model

The effects acting on a single droplet are predicted with engineering models. The parameters of these models have to be determined in single droplet lab-cells with small amounts of substance [3]. The details of these experiments are described in the next section.

2.2. Single-Drop Lab-Cells

Two cells for measuring the sedimentation velocity and mass transfer rate are shown in the Fig. 2. On the left side, the arrangement for sedimentation measurements can be seen. Droplets of the dispersed phase are formed by a nozzle and rise in the stagnant continuous phase. A video camera is used for recording and analyzing data. On the right, the mass-transfer cell equipped with a sieve-tray is shown [4]. The height of the mass transfer cell is approximately 30 cm. A second cell, which is larger by a factor of roughly 2.5, can be used for experiments with packings as internals. A drop of the dispersed phase with known volume is inserted in the cell with a computer driven syringe. Immediately after the production of the droplet, the continuous phase begins to

flow from the top to the bottom of cell, as indicated in the figure. The droplet rises in the conical part of the cell until its sedimentation velocity matches the counter flow of the continuous phase. The droplet levitates at that position till the continuous flow is switched off. The droplet can then rise further to the collecting funnel where it is withdrawn. The analysis of the composition of the withdrawn droplets with the initial composition gives quantitative information on the dependency of mass transfer from contact time, drop diameter and concentration gradients. Appropriate models are fitted to the results of these single-drop experiments to determine the unknown parameters which are needed by ReDrop to calculate the basic effects acting on a drop as described in the previous section.

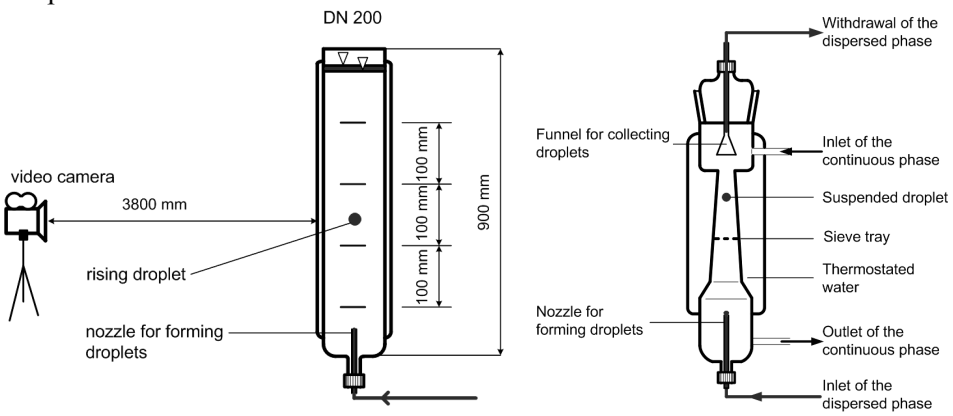

Fig. 2: Lab-cells for measuring sedimentation velocity and mass-transfer rates of drops.

2.3. Applications

The ReDrop algorithm was first developed for pulsed sieve-tray columns [3]. It has been extended for the simulation of columns with regular or random packings. The simulation results have been validated for a variety of systems, mostly EFCE standard test systems, but also for technical systems [3, 5, 6]. The concentration profiles as well as the flooding points agreed to 10% with the experimental values. Thus, ReDrop simulations do not only allow the prediction of steady-state column behaviour but can also anticipate the transient behavior of a column and so tell the design engineer precious information like the onset of flooding. For a given system, the behavior of a column can be fully characterized.

First simulations with simplified models for mass transfer have been run for the reactive standard test system zinc + D2EHPA. The results have shown the principal possibility of ReDrop to predict column behavior for reactive extraction.

3. Conclusions

ReDrop can take into account a variety of drop attributes without increasing the numerical dimensionality of the simulation problem, namely the drop diameter, concentration of transfer component in the drop, vertical position of the drop in the column and the life time of the drop. The advantage of ReDrop is the possible accounting for additional drop characteristics with a bearably higher mathematical effort. The ReDrop approach has been successfully applied to pulsed sieve-tray, random and regular packings. Besides predicting the steady-state behavior of a column, it is possible to determine the limits of operatibility, namely the flooding point. First simulations for reactive extractive have shown the principal applicability for reactive extraction. The general formulation of the ReDrop model and its easy extensibility makes it also suitable for simulating other unit operations in which droplets or bubbles habe to be considered e.g. fiber-bed coalescers.

4. Current Work

The simplified approach for mass transfer in reactive extraction will be replaced by a more detailed model. Therefore a module will be added to ReDrop which can calculate reaction equilibria and kinetics. Simulation results will be compared to parallel pilot-plant experiments in sieve-tray columns.

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