ReDrop: Single-Drop Based Modelling of Extraction Columns

Marc PHILIPPART DE FOY, Andreas PFENNIG

Department of Chemical Engineering, PEPs - Products, Environment, and Processes, Université de Liège, Belgique

Introduction

Traditionally, liquid-liquid extraction columns are designed based on pilot-plant experiments with simple evaluation of the results. Concepts such as theoretical stages are used to model the performance of the column. It is also necessary to design and build a pilot plant before any experiments are carried out. An alternative approach has been developed for more than two decades: the ReDrop (REpresentative DROPs) algorithm. This approach is based on the simulation of the behavior of a large number of drops along their trajectory in the column. The various phenomena that can occur for each drop and that are modelled include sedimentation, mass transfer, chemical reactions, coalescence, splitting, axial dispersion, swarm effects, etc. Each of these phenomena is influenced by the geometry of the column and the internals, which is also considered in the algorithm.

The ReDrop algorithm leads to a transient simulation of the behavior of the column until steady state is reached. It is a powerful numerical tool for modelling extraction columns, as it requires only a few minutes of simulation to reach steady state. To use the program, the model parameters must be known for the specific material system under study. Laboratory-scale experiments are therefore performed to evaluate the parameters. These experiments are standardized and require only a few liters of both phases. This is a considerable advantage over the conventional design method based on pilot-plant experiments, which require a large amount of solution and a long experimentation time.

ReDrop also has the advantage of allowing any type of column to be designed based solely on generic single-drop experiments at the laboratory scale. Different configurations can therefore be studied numerically in order to choose the optimal column type for the desired application.

Algorithm

A graphical representation of the ReDrop algorithm is presented in Figure 1. The first step is to initialize the parameters and define the geometry of the column. All components used in the system are specified, with their properties such as density, viscosity, etc. These input values are either taken from the literature or from laboratory experiments. The operating conditions are encoded, such as flow rates, system temperature and initial concentrations as well as the characteristics of the column type and geometry, and a description of the internals used.

Other inputs are also needed to use the models in the simulation. These include diffusion coefficients, reaction equilibrium constants, kinetic rates, and other variables specific to the system under study. If not available in the literature, these parameters can be determined by standardized single-drop experiments. Before starting the simulation, the extraction column is subdivided into height elements. These height elements contain the drops present at that height in the column at a given time. They represent control volumes for the drop balances during the simulation.

Once all the input variables are specified, the simulation starts. The core of the program consists of two main loops. The ReDrop algorithm allows transient simulations, so a time loop is considered to model the behavior of the system over time. At each time step, all phenomena acting on the drops are modeled in the drop loop. These phenomena include sedimentation, mass transfer, chemical

reactions, breakup and coalescence, among others. ReDrop follows a Monte-Carlo approach to model the behavior of a representative number of drops along the column. The balances of the drops leaving and entering the elements of different heights are calculated for each time step.

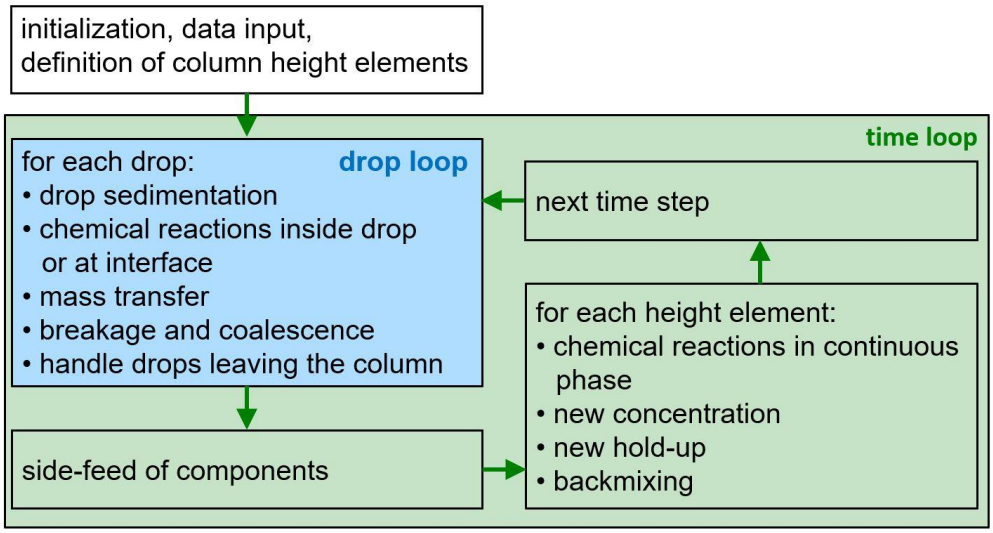

Figure 1: Graphical representation of the ReDrop algorithm.

Once the drop loop is complete, the continuous phase properties are updated for each height element. The solute concentration in the continuous phase is evaluated, as well as the new hold-up. Potential chemical reactions and secondary fluxes are also taken into account.

A new time step can then start. The algorithm is applied until steady state is reached and the performance of the column is characterized. Reaching steady state in an extraction column requires only a few minutes of computer time (Kalem et al., 2011).

Models and Experiments

In the drop loop, the behavior of individual drops is modeled. Models for all phenomena occurring at the drop scale are therefore required. Four phenomena are considered for each drop: sedimentation, mass transfer, splitting and coalescence. Interactions between several drops creating a swarm effect are accounted for, as well as interactions between drops and column internals.

An example of a model used is the model developed by (Henschke, 2004) for the calculation of the sedimentation velocity of a drop. Different models have been proposed, depending on drop diameter. Each model is valid in a certain diameter range, which corresponds to a characteristic drop behavior. These types of drop behavior are respectively, for an increasing drop diameter, rigid drops, drops with internal circulation, oscillating drops, and deformed drops. The final global sedimentation model combines all the individual models and accurately predicts the relationship between the sedimentation velocity and any drop diameter. The comparison between the model prediction and the experimental measurements is shown in Figure 2, where the individual models for each drop behavior are also shown as dashed lines.

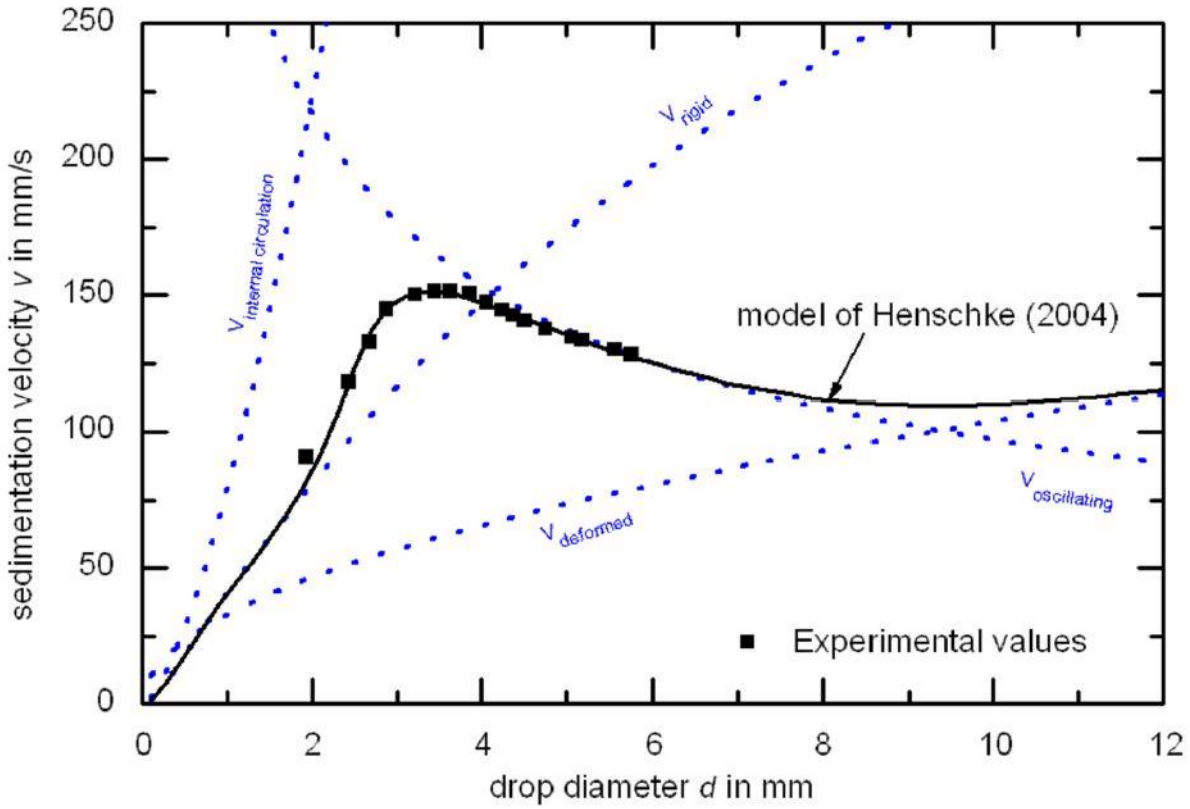

Figure 2: Henschke model for sedimentation velocity (Henschke, 2004).

A second phenomenon occurring at the drops is mass transfer. Since the purpose of an extraction column is to transfer a solute from one phase to another, modelling this phenomenon is essential. It has also been shown that mass transfer at a drop affects its sedimentation velocity (Kalem et al., 2010). Mass transfer models have therefore been developed and implemented in ReDrop. To use such models, parameters specific to the system under study are required. If not available in the literature, these parameters can be measured experimentally. In the latter case, a standardized single-drop cell has been designed to evaluate these variables. The standardized mass-transfer cell is shown in Figure 3.

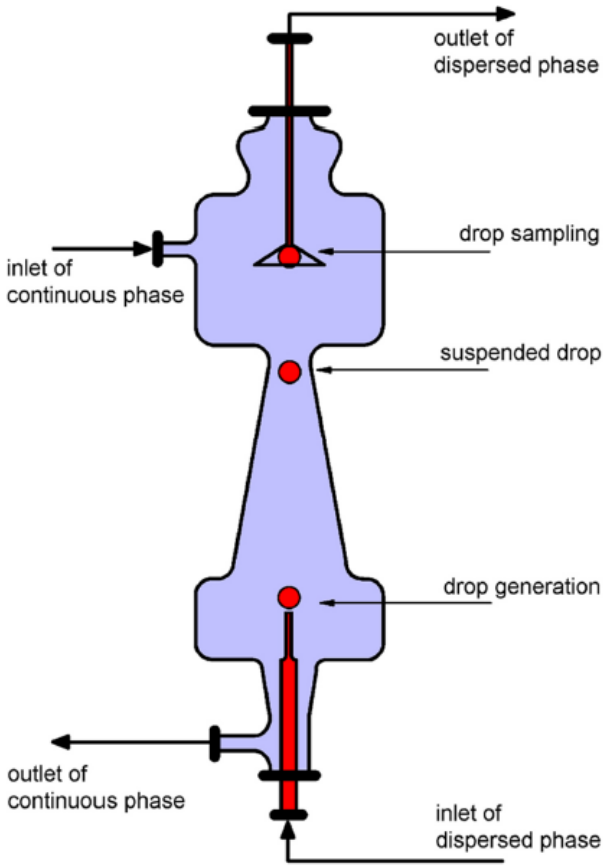

Figure 3: Single-drop mass-transfer measuring cell.

The single drop cell is made of glass. Individual drops of a dispersed phase are generated at the bottom of the cell with a constant diameter. They rise into the cell, where a continuous phase flows in counter-current. By adjusting the flow rate of the continuous phase, the movement of the drop can be stopped and the drop can be levitated. The two phases are thus in contact for a specified residence time. During this time a solute is transferred between the phases. When the desired contact time is reached, the counter flow is stopped, the drop rises to a drop collection funnel, where the drop is collected. The experiment proceeds for a large number of drops. Once a sufficient amount of dispersed phase is collected, it is analyzed to quantify the mass transfer that has occurred. The single-drop cell thus allows the evaluation of the mass-transfer efficiency between a drop and a continuous phase for a specific contact time. Testing different contact times gives information on the mass-transfer kinetics of the system. An example of a resulting graph is shown in Figure 4 (Altunok et al., 2012). It represents the mass-transfer rate of zinc from a continuous aqueous phase to organic droplets, as a function of the contact time between the two phases.

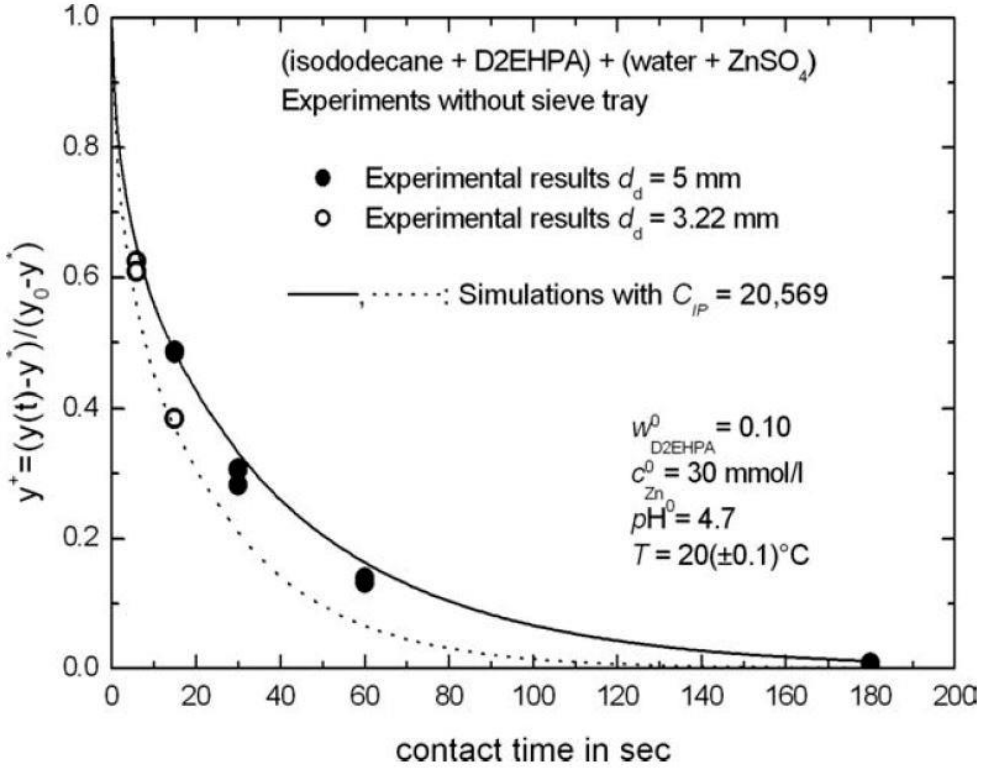

Figure 4: Mass-transfer rate of zinc in organic droplets (Altunok et al., 2012)

The single-drop cell shown in Figure 3 is just one example of equipment used to obtain the relevant parameters involved in ReDrop. A sedimentation cell is also used, as well as adapted versions of the mass-transfer cell. If, for example, the influence of internals on mass transfer is to be studied, a cylindrical section is included in the cell, which can accommodate internals. Trays or packing have been used, as well as rotating internals (Ayesterán et al., 2017). The drop can be stopped below or above the internals, in order to evaluate the influence on the mass transfer of the internals themselves.

Applications

The ReDrop algorithm has been used to simulate several situations over the years. For each application, the relevant models have been improved and adapted to the case under study. First, the models developed by Henschke (Henschke, 2004) were used to predict the behavior of drops with respect to sedimentation velocity, mass transfer, splitting and coalescence, and axial dispersion in the continuous phase. Then the influence of chemical reactions on mass transfer was added by Altunok (Altunok et al., 2006).

Kalem then studied RDC columns (Kalem et al., 2011) and Buchbender Kühni columns (Buchbender, 2013), i.e. columns with rotating internals. The drop models were adapted to account for the effects of these internals. Different material systems, column types, and column diameters were investigated. Hold-up values calculated by ReDrop are compared to experimental values in Figure 5 as a parity diagram (Ayesterán et al., 2015). Essentially all points calculated by ReDrop have less than 20% deviation from the experimental values with an average deviation of 10.2%.

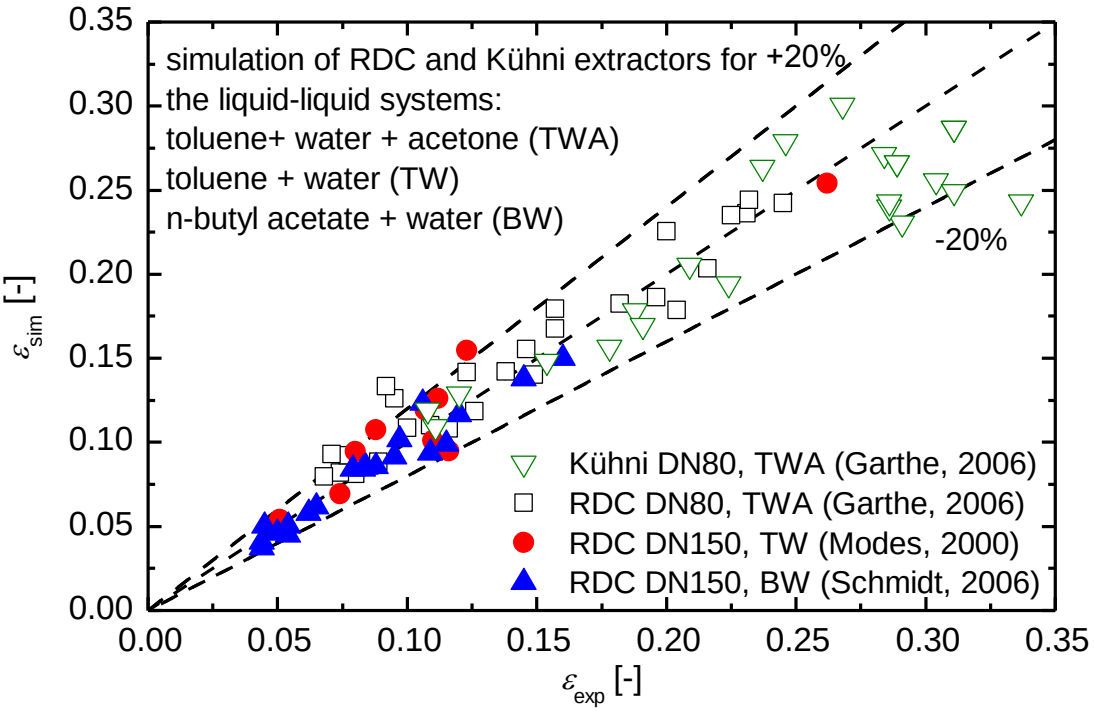

Figure 5: Parity diagram between experimental and predicted hold-up values for different column types and material systems (Ayesterán et al., 2015)

To investigate the influence of the concentration gradient in columns on mass transfer, Kalvoda designed a new single-drop cell (Kalvoda, 2016). In this new cell a concentration gradient in the continuous phase could be realized, which thus allowed the study of mass transfer between a drop and the continuous phase under these conditions. Kalvoda also validated a corresponding mass-transfer model, which accounts for such a gradient. Knowing that mass transfer influences the sedimentation velocity of a drop (Kalem et al., 2010), her results improved the accuracy of the overall ReDrop simulations.

A final important application of ReDrop is the prediction of the flooding point of extraction columns. Although the program is based on single-drop modelling, a large-scale phenomenon such as flooding can be predicted by ReDrop. There is no flooding model implemented into the algorithm. If flooding occurs in the simulation, it results as a consequence of drop behavior (Altunok et al., 2012). Therefore, the operating limits can be consistently detected by ReDrop. The algorithm was applied to technical systems also regarding this flooding limit. The numerical predictions were correct by about 10% (Bart et al., 2004).

Currently, ReDrop is being extended to simulate a new reactive extraction equipment dedicated to metal recycling in urban mining. Existing models are used to predict the behavior of the system, and single-drop experiments are conducted to study the reactive extraction of metal ions with different extractants under varying conditions. The experimental results will allow to select an appropriate material system with respect to mass-transfer kinetics, and to apply ReDrop simulations to predict the performance of the new process.

Advantages of ReDrop

The ReDrop program has many advantages. It is flexible to all types of columns and internals. Multiple configurations and material systems can be tested with only a few changes in the input files and a

defined set of single-drop experiments. The program is also fast, as only a few minutes of computation are required to reach steady state (Kalem et al., 2011).

ReDrop represents an alternative to traditional methods of modelling and designing large-scale equipment. It saves time and cost as compared to conventional design based on pilot-plant experiments.

Different column and internals configurations can be tested and compared numerically, allowing for an informed choice of type of column and internals. The single-drop experiments are standardized and only a few single-drop experiments are required to determine the model parameters.

Another advantage of ReDrop is its ability to predict system behavior up to and including its operating limits. Based solely on drop-scale models, the algorithm can accurately describe the flooding that occurs in the extraction columns with an accuracy of about 10% (Bart et al., 2004).

Conclusions

The ReDrop algorithm is a simulation tool not so much for process, but for equipment design. It is the result of the work of several collaborators for more than two decades. The simulation is based on drop-scale models, describing all phenomena occurring on the drop level. Using a transient approach and balances on the drops over time, the algorithm is able to predict the behavior of the system until it reaches steady state typically with less than 10 % deviation. The operating limits of the system are also detected by the program.

A global, user-friendly version of the ReDrop program is currently under development, which will allow easy application of the ReDrop algorithm for any column type.

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