Detailed Mathematical Modelling of Liquid-Liquid Extraction Columns

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Abstract
A comprehensive bivariate population balance model for the dynamic and steady state simulation of extraction columns is developed. The model is programmed using visual digital FORTRAN and then integrated into the whole LLECMOD program [23]. As a case study, the simulation tool LLECMOD is used to simulate the steady state performance of pulsed packed and sieve plate columns. Two chemical test systems recommended by the EFCE are used in the simulation. Model predictions are successfully validated against steady state and dynamic experimental data, where good agreements are achieved.

Keywords: LLECMOD, Extraction Columns, Population Balance, Simulation.

1. Introduction
Liquid-liquid extraction is an important separation processes encountered in many chemical process industries [1]. Different kinds of liquid-liquid columns are being used in industries; which can be classified into two main categories: agitated and non-agitated columns. Non-agitated (packed and sieve plate) columns are frequently used in liquid–liquid extraction operations due to their high throughput, high separation efficiency and insensitivity towards contamination of the interface, thus led to its wide applicability, particularly in the extraction of radioactive materials. These columns use difference in the density of the two phases to carry out the contact between them, thus they do not require external energy. Van Dijck [2] devised the use of external energy in the form of pulsing in sieve plate columns; which has found wide applications in nuclear fuel reprocessing. These columns have a clear advantage over other mechanical contactors when processing corrosive or radioactive solutions. The absence of moving mechanical parts in such columns obviates the need for frequent repair and servicing. The internals (packing/ perforated plates) reduces axial mixing; increases drop coalescence and breakage rates resulting in increased mass transfer rates, and affect the mean residence time of the dispersed phase. The performance of these columns can be enhanced by mechanical pulsation of the continuous phase. This is a result of an increase in shear forces and consequent reduction in size of dispersed droplets so that the interfacial area, and hence the mass transfer rate, is increased [3].

To shed more light on the extraction behaviour in the pulsed packed and sieve plate columns, the hydrodynamics as well as the mass transfer characteristics must be well understood. Our present knowledge of the design and performance of extraction columns is still far from satisfactory. The reason is mainly due to the complex behaviours of the hydrodynamics and mass transfer [4]. It is obvious that the changes in
the characteristics (holdup, Sauter diameter, etc.) of the drop population along the
column have to be considered in order to describe conveniently the behaviour of the
column. The dispersed phase in the case of liquid-liquid extraction undergoes changes
and loses its identity continuously as the drops break and coalesce. Accordingly,
detailed modelling on a discrete level is needed using the population balance equation
as a mathematical framework. The multivariate non-equilibrium population balance
models have emerged as an effective tool for the study of the complex coupled
hydromechanics and mass transfer in liquid-liquid extraction columns.

The development of computational tools to model industrial processes has increased in
the last decades. However, to the best of the authors’ knowledge, there are no
comprehensive non-equilibrium population balance models to describe in sufficient
detail the behaviour of extraction columns. The main objective of this work is to
develop a model that is capable to describe the dynamic and steady state behaviour of
pulsed packed and sieve tray extraction columns. The models of both columns are
integrated into the existing program: LLECMOD [Reference], which can also simulate
agitated extraction columns (RDC and Kühni). LLECMOD can simulate the steady
state and dynamic behaviour of extraction columns taking into account the effect of
dispersed phase inlet (light or heavy phase is dispersed) and the direction of mass
transfer (from continuous to dispersed phase and vice versa) [5]. Therefore, scale-up
and simulation of agitated and non-agitated extraction columns based on population
balance modelling can now be carried out successfully.

2. Mathematical model

Mathematical modelling of pulsed extraction columns is considered by many
researchers [6-13]. An empirical model for predicting the hydrodynamics in pulsed
sieve plate columns was proposed by Kumar and Hartland [7]. A stagewise model for
the transient behaviour of a sieve-plate extraction column taking into account the back
flow and assuming constant hold-up was developed by Blass and Zimmerman [8].
Hufnagl et al. [9] evaluated a differential model of a Kühni column. Steiner et al. [10]
modelled a packed column using differential contact model without axial mixing.
dynamic model considering the influence of drop size distribution was developed by
Xiaojin, et al. [12]. Several population balance models have been proposed by various
authors: Garg and Pratt [13] developed a population balance model for a pulsed sieve-
plate extraction taking into account experimentally determined values for drop breakage
and coalescence. Casamatta et al., [14] proposed a population balance model as
described by Gourdon et al. [15]. Al Khani et al. [16] and Milot et al. [17] applied this
model for dynamic and steady state simulations of a pulsed sieve-plate extraction
column. Recently extensive work has been done on the population balance modelling of
extraction columns many researchers [15, 18-23].

2.1. The population balance model

The general spatially distributed population balance model describing the coupled
hydromechanics and mass transfer can be written as [21]:

$$\frac{\partial f_{d,c_v}(\psi)}{\partial t} + \frac{\partial [u_y f_{d,c_v}(\psi)]}{\partial z} + \sum_{i=1}^{2} \frac{\partial [c_i f_{d,c_v}(\psi)]}{\partial \xi_i} =$$

$$\frac{\partial}{\partial z} \left[ D_y \frac{\partial f_{d,c_v}(\psi)}{\partial z} \right] + \frac{Q_{in} \rho_{in}}{A_c} \frac{c_y}{\bar{w}_{in}} (d, c_y, t) \delta(z - z_y) + r \{ \psi \}$$  (1)
In this equation the components of the vector \( y = [d, c_y, z, t] \) are those for the droplet internal coordinates (diameter and solute concentration), the external coordinate is \( z \) and \( t \) is time. The velocity vector along the internal coordinates is given by \( \zeta = [d, c_y] \). The source term \( y_\zeta \) represents the net number of droplets produced by breakage and coalescence per unit volume and unit time in the coordinates range \( [\zeta, \zeta + \partial \zeta] \). The droplets axial dispersion is characterized by the dispersion coefficient, \( D_y \). The second term on the right hand side is the rate at which the droplets entering the LLEC with volumetric flow rate, \( Q_{y,in} \), that is perpendicular to the column cross-sectional area, \( A_c \), at a location \( Z_y \) with an inlet number density, \( f_y^{in} \). The dispersed phase velocity, \( u_y \), is relative to the walls of the column [23].

2.2. Model parameters
Equation (1) is general for any type of extraction column. However, what makes the equation specific is the internal geometry of the column as reflected by the required correlations for hydrodynamics and mass transfer. Experimental correlations are used for the estimation of the turbulent energy dissipation and the slip velocities of the moving droplets along with interaction frequencies of breakage and coalescence. In this work, correlations for packed and sieve plate columns concerning droplet velocity, coalescence and mass transfer are taken from the work of Henschke [24]. The slowing factor and the droplet breakage frequency are taken from the work of Garthe [25].

2.3. Numerical solution
The resulting model is composed of a system of integro-partial differential and algebraic equations that are dominated by convection and hence it calls for a specialized discretization approach. The model solved using an optimized and efficient numerical algorithms developed by Attarakih et al. [19, 21, 22].

3. LLECMOD program
These aforementioned mathematical models, and in particular for pulsed extraction columns, are programmed in LLECMOD using Visual Digital FORTRAN. Recent correlations for fluid dynamics and mass transfer are now available and are extensively validated against experimental data collected from pilot and industrial columns. The graphical interface of the LLECMOD program contains the main input window and sub-windows for parameter and correlation inputs. The main window contains all correlations and operating conditions that can be selected using drop down menus. The basic feature of this program is to provide an easy tool for the simulation of coupled hydrodynamics and mass transfer in liquid-liquid extraction columns based on the population balance approach for both transient and steady states conditions. Details about LLECMOD can be found in [23].

4. Results and discussion
To completely specify the model, the following geometry is used for a pilot plant scale LLEC (packed pulsed column): column height \( H = 4.4 \) m, inlet of the dispersed phase \( z_y = 0.85 \) m, inlet of the continuous phase \( z_x = 3.8 \) m, column diameter \( d = 0.08 \) m, the inlet feed is normally distributed with mean equals to 3.2 mm and standard deviation of 0.5 mm. The two EFCE test systems (toluene-acetone-water and butyl acetate-acetone-water) are used. The direction of mass transfer is from the continuous to the dispersed phase. The inlet solute concentrations in the continuous and dispersed phases
are taken for the toluene–acetone–water as 5.73 and 0% and for the second system (butyl acetate–acetone–water) as 5.22 and 0% respectively. The pulsation intensity \( (a, f) \) = 1 cm/sec and the total flow rate of the continuous phase: \( Q_c = 40 \text{ lit/hr} \) and dispersed phase: \( Q_d = 48 \text{ lit/hr} \).

Fig.1: Simulated mean droplet diameter along the column height compared to the experimental data [25]. Left panel the test system is (toluene–acetone–water) and the right panel is (butyl acetate–acetone–water).

Fig.(1) shows the variation of the mean droplet diameter along the column height compared to the experimental data for both chemical systems. A fairly good agreement between the experimental and simulated profiles is achieved for both systems. A comparison between the simulated holdup profiles along the column height and the experimental data [25] is shown in Fig.(2). Again, a very good agreement is achieved for both test systems.

Fig.2: Simulated holdup profiles along the column height compared to the experimental data [25]. Left panel the test system is (toluene–acetone–water) and the right panel is (butyl acetate–acetone–water).

Fig.(3) shows the simulated and experimental solute concentration profiles as function of column height in both phases. The agreement between the simulation and experiment is excellent for both test systems.

Fig.3: Simulated solute concentration profiles in both phases along the column height compared to the experimental data [25]. Left panel the test system is (toluene–acetone–water) and the right panel is (butyl acetate–acetone–water).
LLECMOD provides also dynamic simulations to describe the transient behaviour of the extraction columns. Using the LLECMOD program, the transient column behaviour can be investigated numerically. To analyse the dynamic behaviour of the column, step- and exponential changes can be applied to the inlet variables to get the dynamic step response of the model. In the transient module, the following step and exponential changes can be applied: Inlet solute concentration in the dispersed phase, \( C_{y,in} \), inlet solute concentration in the continuous phase, \( C_{x,in} \). The dynamic evolution of solute concentration in the extract along with the experimental data will be discussed in a separate publication. It is obvious that LLECMOD is able to catch the dynamic behaviour of the extraction column with a good accuracy.

5. Conclusions

The present nonequilibrium bivariate population balance model can be considered as an effective tool to describe the steady state and dynamic behaviour for hydrodynamics and mass transfer in extraction columns. In this work, pulsed packed and sieve plate extraction columns are considered. The transient and steady state performance of a pulsed packed extraction column is studied using the present model as an alternative to the commonly used models (backmixing and dispersion models). The simulation results from the present model are found in good agreement with the available experimental data.

References