3

Modelling and Simulation of Multistage Countercurrent Liquid–Liquid Extraction Processes

Dr. Abhijit R. Chavan
Professor of Chemical Engineering,
Dr. Babasaheb Ambedkar Technological University, Raigad
archavan1972@gmail.com

Abstract

The extraction of components from liquid mixtures is of fundamental importance in the chemical industry. Multistage countercurrent extraction with liquid–liquid contact is increasingly employed to separate and recover valuable compounds from diluted aqueous streams. Since this process can be applied at room temperature and pressure without excessive heating or vacuum requirements, it has attracted considerable interest for recovering solvents from contaminated waste streams, removing heavy metals from industrial effluents, and performing reactor wash or clean-up operations in the fine chemical and pharmaceutical industries. Liquid–liquid extraction typically requires multistage, countercurrent operation to achieve satisfactory separation. The performance of liquid–liquid extraction is influenced by distribution coefficients, mass transfer characteristics, interfacial area, and flow patterns. Several approaches to modelling and simulating multistage countercurrent liquid–liquid extraction processes are described. The effectiveness of all stages is assumed to be equal, thereby significantly reducing problem complexity while preserving the most vital features. Alternative approaches for representing perturbed concentrations and varying equipment arrangements are also introduced.

Keywords: *Liquid-liquid extraction, Countercurrent extraction, Mass transfer, Multistage processes, Solvent recovery, Phase equilibria, Modelling and simulation.*

1. Introduction

Countercurrent liquid–liquid extraction processes are widely employed for the separation, purification, and recovery of valuable target compounds from a wide variety of liquid feeds. Countercurrent extraction columns are commonly modelled using stage-wise cascade

models. A variety of mathematical approaches have been developed to model and simulate multistage countercurrent liquid–liquid extraction processes at different levels of abstraction. These are overviewed to provide insight into the large number of modelling alternatives available. Key design approaches and operational policies for multistage countercurrent liquid–liquid extraction processes are also addressed.

2. Fundamentals of Liquid–Liquid Extraction

Liquid–liquid extraction is a widely employed separation method consisting of the contact of two immiscible liquid phases (I. Koncsag & Barbulescu, 2011). Such a system undergoes mass-transfer processes and evolves toward thermodynamic equilibrium. The final equilibrium concentration is affected by various parameters, including the temperature and the concentrations of solute in both phases. In many simple cases, the relationship between solute concentrations in the two phases can be described by the Nernst distribution law. This well-known law involves a partition coefficient defined for each solute.

During extraction, large interfacial areas and effective diffusion path lengths favour mass transfer. Under most practical conditions, the liquid–liquid extraction processes are rapid enough that the extraction rate does not significantly affect the equilibrium concentration in either phase. The double-stationary-film theory, a classical theory of mass transfer, posits that diffusion occurs exclusively across thin films at liquid–liquid interfaces, provided that agitation is sufficiently enhanced to ensure uniform solute concentrations in the bulk phases. In such circumstances, an interfacial concentration gradient drives the mass transfer. This theory also provides experimentalists with rigorous, generalised methods for determining mass transfer coefficients in extraction processes.

2.1. Phase Equilibria and Mass Transfer

In countercurrent liquid–liquid extraction, the efficiency of mass transfer between fluid phases is governed by either the establishment of equilibrium or the interfacial area of contact. Operating conditions vary widely for the selective recovery of solutes from aqueous media into solvents and vice versa. For aqueous systems, the emphasis is thus placed on phase equilibria rather than solvent solubility. Ogata and Furuya's pH-dependent distribution of phenolic compounds among octan-1-ol, octane, and water governs the recovery of phenolic waste and the extraction of such compounds as vanillin, phenol, and dibenzothiophene from model mixtures (Gañán et al., 2018).

Multistage countercurrent separation is employed for low-concentration feed solutions, in which bolus transfers along successive stages occur at sharply defined levels of species partitioning. In packed-column operation with high liquid-continuous dilution, partitioning equilibrium is widely assumed to be closely coupled to the hydrodynamics of flow—the liquid film surrounding the dispersed droplets is mobile, thus satisfying the requirements for both volatile solutes and solvated chemical species—impeding the extraction of certain phases upon aqueous feed flow through low-species–loaded solvents, in the region where less mobile species are targeted for selective recovery.

2.2. Mechanisms of Multistage Countercurrent Contact

Liquid–liquid extraction accomplishes separation by differential partitioning between two immiscible liquid phases. Solute concentrations at the inlet and outlet of a contacting unit thus depend on the liquid–liquid distribution ratio characteristics of the system, the mode of operation, and the geometry involved. Certain environmental factors influence the nature of these systems, among them the presence of a third component. Nevertheless, properties inherent to extraction operations are sufficiently robust for these systems to interact in predictable manners, since the species involved and contact conditions remain unchanged.

Countercurrent and cross-current solid extraction are classical separation processes widely used in industrial operations. Their partitioning behaviour follows the same trends as those in liquid–liquid counterpart systems (Gañán et al., 2018). Such trends encompass classification based on physical phenomena, such as the presence of differential or total-contact apparatuses, and the realisation of hybrid systems combining several operational sub-chains. It is also common to consider packed and tray column systems, rather than continuous stirred mixing tanks, in many displacement processes. Within the latter category, a contact apparatus that maintains entirely mixed phases enables one to separate input and output feed streams more easily than a completely unmixed tank used in conjunction with conventional multistage operations. Equally important to countercurrent applications, discrete-stage classification arises from the lack of steady-state and dynamic analytical tools for studying differential liquid–liquid processes. While the majority of packed column systems under counter-current scheme operate continuously, pilot-scale use employing only small amounts of the liquid phase and a highly volatile solvent still prevails.

In industrial operations, mixing tank circuits remain the most frequently applied mass-exchange arrangement. Sufficiently counter-terrestrial-sized distributions, together with constant stirrer energy and granular size, permit one to neglect the presence of feed cords. Upon spawning, the entry and exit of liquid in high-density phases each undergo specific updates, resulting in a large volume of compositional data. Dynamic extraction experiments conducted in packed or tray columns show these qualitative aspects persist and constitute a precipitating focus during packing- or tray-oriented semi-continuous operation. A substantial body of published liquid–liquid extraction data contributes to the further elaboration of process performance variables across numerous disciplines (Camy & Condoret, 2001).

3. Mathematical Modelling Frameworks

Liquid–liquid extraction is a common separation process, but most studies focus on optimal stage design rather than scaling-up architectures for industrial applications. The modelling frameworks used for impact evaluation and enhancement of countercurrent multistage liquid–liquid extraction processes are described and analysed, thereby facilitating the assessment of various configurations and equipment types for continuous-flow systems.

Multistage extraction, countercurrent operations, and continuous feed processing increase economies of separation capacity. Column design and configuration depend on mass-transfer properties, scale-up, and process intensification considerations. Countercurrent and cross-cascade arrangements permit larger throughputs, wider-diameter settings, and increased packing lengths; multiple-stage units exhibit high throughputs, low active-liquid capacities, and dispersed-phase mass-transfer controls. Structural-design efficiency, moving-station trajectory determination, distribution limitations, and extract-to-feed or raffinate-to-feed dosage ratios – especially with salt, pH, or co-solvent partitioning – remain key design concerns (Gañán et al., 2018) (Kampwerth et al., 2022)

3.1. Material Balances and Continuity Equations

The countercurrent multistage configuration is increasingly common in liquid–liquid extraction processes due to its high mass-transfer efficiency. The greater the number of contact stages, the more effective the mass transfer of the solute from the feed to the extracting solvent, thereby improving separation efficiency. A thorough investigation of mass-transfer and interfacial phenomena is necessary for the efficient design of liquid–liquid extraction systems. Mathematics-based modelling and

simulation of such extraction represent essential tools in this endeavour. In such systems, solvent feeding continues for a significant period while the solute concentration in the outlet material changes, leading to complex transient phenomena. Therefore, modelling can be dynamic or steady-state, differentiating transient operation from continuous operation. The extraction configuration itself may be plate or packed columns, depending on industrial design and anticipated performance. Extraction may occur in a cascade, cross-current, or multistage configuration, depending on the separation requirements and throughput specifications. Hydrodynamic factors typically drive the choice of modelling framework and influence the resulting design.

Mass-transfer rates of solute in countercurrent liquid–liquid extraction systems depend on the flow direction of the extracted material and the flow scheme. The usability of the models depends on the chosen mathematical description framework and the flexibility it offers in representing different multiphase equipment or flows, as well as on the modelling approaches already available for different phases. The simultaneous implementation of mass-transfer rate, partition behaviour, and hydrodynamic bottom-up modelling of liquid–liquid extraction systems enables significant transparency in the models and the ability to track performance evolution during any configuration change. The implementation of extraction systems both reinforces the models by opening new literature. It enables coverage of important extraction configurations based on widely used industrial systems that have attracted less attention in the literature. The mathematical formulation is based on a stage-wise approach that accounts for each separation separately and can naturally be adapted to the flow scheme, leading to a specific continuous model of countercurrent liquid–liquid extraction that allows further examination of the stage-wise and overall balances.

3.2. Rate Expressions and Mass Transfer Coefficients

The concentration of a species in the continuous phase is governed by mass transfer and by the establishment of interfacial equilibrium as the contact time increases. Therefore, different mechanisms are considered and expressed as film transfer, diffusion through the external film, and diffusion through the stagnant mass, leading to a steady-state regime, with mass transfer as a function of solute concentration across stages and overall mass transfer (I. Koncsag & Barbulescu, 2011).

In liquid–liquid extraction, hydrodynamic flow patterns influence the effective interfacial area available for

mass transfer and consequently the shape of the corresponding concentration profiles. Therefore, a film mass-transfer resistance is preferred over interfacial mass transfer augmented by a stationary film to accurately model concentration profiles in continuous-flow liquid-liquid extraction and aspiration lines, where liquid is continuously drawn from the apparatus to an analysis station; only the concentration in the apparatus is assumed to vary.

3.3. Interfacial Phenomena and Partitioning

Lower-chain aliphatic carboxylic acids are generally extracted from aqueous streams into organic solvents using multistage countercurrent liquid–liquid extraction. For acidic solutes, a strong base is traditionally added to the aqueous phase to neutralise the acid and increase its partitioning into the solvent. More recently, two-stage extraction processes have been reported that utilise naturally abundant salts, such as a sodium phosphate buffer, to control the ionisation state of the acid and alter global partitioning by the simple addition of a mixed pH-salt modifier. Keskin and Cakiroglu studied the effects of tri-n-butyl phosphate (TBP) as the extractant and sodium phosphate as a pH modifier on the partitioning efficiency of benzoic acid and reported pH- and concentration-dependent partitioning experiments using a pH-controlled liquid-liquid separation model. These previous studies motivate extending the aforementioned pH-modified benzoic acid countercurrent extraction determination to a wider range of TBP, sodium phosphate, and benzoic acid concentrations. The aqueous activity coefficients required to compute the partitioning ratio of benzoic acid from the additional ternary and quaternary solute concentration data are estimated using a previously reported thermodynamic model of the calcium benzylpenicillate solvent-mediated crystallisation system (Gañán et al., 2018).

The observed influence of Na3PO4 on the partitioning behaviour of benzoic acid between the aqueous and oil streams is therefore not solely attributable to pH control. This influence is likely to result from the interplay among the aqueous solubility of benzoic acid at various pH values and buffer salt concentrations, which depend on the mixture composition, rather than from direct acid–salt complex formation. For the supplementary ternary and quaternary datasets, the addition of either buffer salt is observed to increase benzoic acid extraction into the phase while the relative phase distribution remains unaffected.

3.4. Steady-State versus Dynamic Modelling

The choice between a steady-state and a dynamic modelling framework for liquid-liquid extraction processes hinges on the system of interest and the analytical objectives. Given that the models of liquid-liquid contact to be explored in this work represent the evolution of concentration driving forces throughout the separation, a dynamic model appears the most appropriate, facilitating investigation into how changes in feed concentration affect these concentrations over time. Were the contact configuration analysed to exhibit instant stage- or column-wise separations — for instance, a cascade of multistage contacts or a reflux operation where separations take place over a considerable number of stages — a steady-state formulation could be adequate. An avant-garde two-quadrant apparatus (Chakrabarty, 2005), in which the accumulation of mobile material at outlets characterises the transition between static and dynamic behaviour, further demonstrates the possibility of evolving a distribution gradient under stationary operating conditions.

While many extraction situations prove well suited to a steady-state description, for instance, when liquid compositions at inlets and/or outlets vary, but the capacities of stages remain constant (Camy & Condoret, 2001), the models presented here allow interrogation of situations in which concentrations are time-dependent, yet fixing times are known or need to be proposed. Sequentially performing steady-state simulations while carrying forward the final condition of each in a two-phase or multi-species installation, and retaining the complete steady-state information for even longer, thereby reducing computational load, remains a valid, though complementary, alternative.

4. Multistage Configurations and Operational Schemes

Multistage configurations with varying flow patterns and operational strategies can significantly affect liquid–liquid extraction performance. Such aspects may influence feed throughput and dividing partitioning between the extraction and stripping sections when two feed streams are handled simultaneously. Three arrangements are thus observed frequently: cascade (or countercurrent), cross-current, and multistage (or concurrent) configurations.

A cascade system retains individual stages as well-defined, so stage-wise performance impacts on feed processing become clear. Well-posed inter-stage transfers suggest that the transverse spatial configuration does not appreciably affect mass-transfer efficiency because flow patterns and

induced gradients remain similar. Suitability for heat-exchange integration further enhances its attractiveness. A cross-current scheme allows a single feed to circulate across a limited number of stages. It is readily used for dilute streams, where concentrating a small amount matters more than evenly splitting high concentrations. However, spatial separation relaxes the requirements for receiving two divided feed streams and for controlling their split ratio. A multistage arrangement promotes simultaneous stage-wise parallelism, thereby offering another means of improving throughput. However, significant downstream-to-upstream material transfer requirements render this option less appealing (Camy & Condoret, 2001; Gañán et al., 2018; Kampwerth et al., 2022).

4.1. Plate and Packed Column Representations

Discretisation of stages in plate and packed-column representations is obtained from hydrodynamic behaviour, as in gas systems. Simple K-values determine the mass fraction of each droplet at local equilibrium, providing a stagewise depiction of the continuous extraction process. Operating at lower flow velocities, packed columns yield smaller droplets and better mass-transfer coefficients than plates, augmenting the interfacial area (Gañán et al., 2018; Kampwerth et al., 2022).

4.2. Cascade, Cross-Current, and Multistage Arrangements

Multistage arrangements define the configuration of the contact stages that execute the partitioning (Kampwerth et al., 2022). They have cascade, cross-current, and multistage arrangements. The cascade configuration is the most widely used design in the process industry. Multistage extraction processes can be carried out in either a cascade or cross-current arrangement to approach the outlet flow compositions achieved in a fully counter-current operation (Gañán et al., 2018). A cascade arrangement consists of several fluid-contacting stages arranged in series that establish two liquid phases at equilibrium flow rates.

4.3. Reflux, Dilution, and Weir Effects

In countercurrent liquid–liquid extraction and other multistage processes, reflux, dilution, and weir effects can substantially influence the trajectories, conditions, and performance efficiencies of parallel extraction models. As dilute streams on either side evolve, concentration gradients across the extraction agents and the controlling vessels change, causing interfacial transfer dynamics to vary and, depending on the phase volumes on the saline side, influencing initial contact formulations. For extraction processes largely governed by partitioning effects, reflux and degrees of occupation also

help determine phase equilibrium and distribution coefficients, thereby further impacting separation efficiency and supporting design targets (Kampwerth et al., 2022). In purely dynamic setups, deviations in phase ratios and flow rates create interlinking between stages, leading to differential equations that continuously update total mass and effective stage counts for each stream component (Gañán et al., 2018). Such approaches facilitate the inclusion of highly relevant variables in large-scale systems, where accurate modelling of transitions and distributions is critical for reliable large-scale investments.

Consequently, both single-volume and multi-compartment versions of the extraction models can encompass reflux, dilution, weir contributions, and, importantly, base-phase stream specifications for the simulation of countercurrent configurations.

5. Numerical Methods for Simulation

Extraction processes often involve numerous stages to maximise extraction and separation. In designing such a process, the number of stages required is a critical parameter. Fewer liquid–liquid extraction or separation stages may reduce extraction efficiency and increase the required solvent-to-feed ratio, thereby reducing separation efficiency for agents requiring 100% extraction. A greater number of stages may make the separation process too complicated for practical implementation. Mathematics models may be employed to assist in the design of solvent extraction or separation processes, with various schematic representations of the internal structure (Gañán et al., 2018; Camy & Condoret, 2001).

5.1. Discretisation Techniques for Multistage Systems

Discretisation techniques for multistage systems encompass equilibrium-stage approaches, which simplify the column model into a series of discrete units, assuming phases achieve equilibrium and remain homogeneously mixed within each phase. Such methods are relatively straightforward to implement, yet their generalisation capability is restricted due to their dependence on physical properties, flow rates, and contacting technology. Rate-based techniques integrate mass-transfer kinetics between phases, consider only interfacial equilibrium, and compute mass-transfer and hydrodynamic behaviour based on system characteristics. Illustrative applications include dynamic models for methyl oleate and squalene separation with supercritical CO2 that accommodate non-isothermal operation through energy balances, as well as steady-state models for supercritical CO2 fractionation, in which mass transfer is described by multicomponent diffusion,

validated against experimental data, and solved iteratively. A dynamic, rate-based model of a high-pressure packed column enables simulation of isopropanol extraction from aqueous solutions using supercritical CO2 (Gañán et al., 2018; Camy & Condoret, 2001; Kampwerth et al., 2022).

5.2. Nonlinear Solution Strategies

Extraction units undergo complex, time-varying, multi-component mass transfer, with the requisite material balance equations forming a highly nonlinear set of ordinary differential equations (Kampwerth et al., 2022). Employing an explicit finite-difference spatial discretisation, the resulting nonlinear initial-value problem is stiff for small time steps, particularly when the mass-transfer driving force is low due to low solute concentrations or the absence of stagnant drop-phase mass transfer.

To address these challenges, both Newton-type and continuation-type solvers have been successfully implemented within a flexible modelling framework (Gañán et al., 2018). Stiffness adaptation, automatic error-area specification, and multiple error-handling schemes further facilitate addressing the problem across a wide range of operational scenarios.

5.3. Stability and Convergence Considerations

The implementation of numerical methods for the mathematical modelling and simulation of multistage countercurrent liquid–liquid extraction processes entails solving complex nonlinear dynamic systems. Consequently, stability and convergence represent critical aspects that determine adequacy and reliability. Moreover, diligence in these aspects mitigates excessive computational expense and effort (Camy & Condoret, 2001). Modelling frameworks for multistage extraction processes are generally stiff due to the multiplicity of time scales involved, with phase distribution behaviour designated as the slowest variable. Such stiffness arises from the material balance equations employed, which couple the instantaneous outlet concentrations to the holdup variation, with abrupt transition regions that enhance nonlinearity. Dedicated solvers, or solvers with specialised strategies, enable efficient treatment of this stiffness. The consideration of numerical efficiency is also crucial, due to potentially elevated dimensionality and the presence of distributed parameters throughout the process.

6. Parameter Estimation and Model Calibration

Model calibration and parameter estimation can be defined as a model alignment process to experimental or observed data. The distinction is made between model parameters (physical properties) and experimental data (liquid–liquid extraction results). Addressing model parameters is critical for designing relevant experiments that provide sufficient information for parameter identification and uncertainty minimisation (Gañán et al., 2018).

In countercurrent extraction systems, the relevant model parameters are the distribution and mass transfer coefficients. Therefore, the experimental design focuses on obtaining suitable, identifiable extraction and solubility data, with the main expected changes driven by variation in the extraction agent (solvent) or by solvent-free extraction (for food or oral samples).

6.1. Experimental Design for Liquid–Liquid Systems

Multistage countercurrent extraction remains a practical concern in industrial applications where large quantities of chemical compounds must be separated. Solubility, mass transfer, phase equilibria, interfacial area, and flow patterns determine extraction performance. Multiple locations throughout the extraction process can involve mass transfer; equimolar countercurrents between the combined phases often characterise the extraction stages. The mass-transfer and partitioning processes during the extraction of substances such as isopropanol form the basis of the modelling framework.

Multistage extraction processes remain widely relevant in industry despite the availability of alternative techniques. Two suitable solvents for countercurrent multistage extraction are ethyl acetate and 2-pentanone. Critical parameters, including feed and solvent flow rates, distribution ratio, and interfacial area, play significant roles in performance and directly influence the design and operational strategy (Kampwerth et al., 2022). The dynamics of liquid–liquid extraction depend on parameters such as the nature and viscosity of the liquids, feed composition, solvent selection, temperature, and pressure (Camy & Condoret, 2001).

Portable experimental setups can provide information about these parameters. Two apparatuses can be installed: a small-scale multistage Perkins extractor equipped with three to seven trays for countercurrent and three types of glass vessels, and a liquid–supercritical carbon dioxide system, which offers greater flexibility than pole separations or partitioning. The continuous and simultaneous extraction of a selected solute (isopropanol) from a water feed constitutes the first case

study. In contrast, the dynamic extraction and stripping of ethanol from a binary water-ethanol feed constitute the second case study.

A variety of empirical or semi-empirical models with five to ten adjustable coefficients exist for liquid–liquid extraction. The partition coefficients are generally determined by fitting the experimental solute concentrations in the two liquid phases. The K-values well describe the chemical equilibrium between these phases. Nevertheless, due to the wide range of process conditions and the variety of liquids involved, significant uncertainty remains in accurately estimating these coefficients and their dependence on operating variables such as temperature and pressure (Gañán et al., 2018).

6.2. Inverse Modelling and Optimisation

To describe the simultaneous estimation of several parameters for countercurrent liquid–liquid extraction, relevant features of the inverse problem are highlighted. Though multiple parameters can influence operating performance, the ability to identify them through joint estimation tests the appropriateness of the modelling framework and its capacity to reproduce pertinent physical phenomena. The focus thus remains on conditions that yield significant variations in mass-transfer coefficients, as these are critical to scheme design and characterisation. Several objective functions suited to the countercurrent configuration are proposed, and the standard practice of integrating them into least-squares formulations is examined. Considerable deviations between the dimensional and reduced-transformation formulations give rise to non-uniqueness in the solutions, which can be alleviated through regularisation. The formulation of the specification-decision equation permits other interstitial structures, such as side or percolating effects, to be conceptually integrated into the framework. Simple rectangular structures, responsible for the bulk of transport, remain the only type handled.

6.3. Uncertainty Quantification

Granular formulations attained by dissipative agglomeration of fine powders have been widely used in recent years in the surface treatment of granular ferrous tablets. Uncertainty quantification (UQ) has become a critical activity for accounting for uncertainty in the faithfulness, accuracy, and sensitivity of mechanistic modelling of such formulations, thereby enabling reasonably informative predictions. The UQ framework, based on probabilistic formulations within a spectral-Galerkin framework, enables the generation of high-order polynomial chaos solutions for the study of granular agglomeration

of powders, yielding satisfactory results. A benchmark for UQ has been developed within the UNCECOMP platform for a granular process based on the Lindop apparatus, enabling the collection of information on UQ methodology suitable for classical agglomeration problems. The objective of the benchmark is to model the process and estimate particle size growth as a function of time. Statistical data on the process are available from an experiment through Sagrex. A close collaboration is established between INRAE and UNCECOMP to ensure the relevance of the UQ developed to set up the modelling platform ADDA for granular agglomeration modelling of powders. In parallel, the inlets and constraints of the modelling approaches are identified, and the state of the art is summarised into a short insight. Hydrodynamics of liquid film involvement in agglomeration is initially meant to be ignored (Camy & Condoret, 2001), thereby focusing uncertainty on powder size and the setting of the powder agglomeration platform (Kampwerth et al., 2022).

7. Validation Against Experimental Data

The validation procedure follows the stages outlined by Kampwerth et al. (2022) (Kampwerth et al., 2022). First, benchmark datasets suitable for testing the entire model are established. Each dataset consists of a full experimental campaign conducted in a specific multistage configuration, with the corresponding model replication following the same operational strategy. The raw experimental data are then elaborated and subjected to a series of preliminary calculations, allowing the determination of the model input parameters. Finally, relevant metrics quantify the level of agreement between experimental and simulated data before and after model adjustment, ensuring proper alignment within an acceptable tolerance. The datasets chosen for the validation exercise concern the extraction and separation of solutes from aqueous feed streams. The solubility, phase distribution, and partitioning behaviour of these compounds in a variety of liquid–liquid extraction systems are widely documented; additional information on the extraction systems considered is also available in the literature (Gañán et al., 2018).

The first set comprises extraction campaigns in plate columns of tetrahydrofuran–water and bitumen extraction from paratherm–water mixtures. Extraction of the solvent is carefully controlled during the evaluation of influences such as the mass-flow and stage-number ratios. Such operating parameters significantly affect the aqueous distribution coefficient of bitumen, thereby altering the consumption of the extraction

component. The second benchmark dataset examines the influence of the feed mass fraction of trichloroacetic acid on the extraction of this solute from water via a blend of chloroform and light (straight) mineral oil. The model qualitatively captures the expected influence of the feed stream concentration on the trichloroacetic acid concentration in the phase.

7.1. Benchmark Datasets and Case Studies

The extraction process model comprises a pulsed sieve-plate extraction column followed by a tray distillation column for solvent recovery. The typically aqueous feed stream enters as the continuous phase, with the solvent dispersed at the bottom if it is less dense than water. The enriched extract is then fed to the distillation column, where the solvent is recovered, allowing product purification; the nearly product-free solvent stream can be recycled as distillate or bottom stream, depending on boiling points. The extraction column model incorporates fluid-dynamic phenomena such as flooding, drop size, rising velocity, and hold-up. In contrast, the distillation column employs the Fenske-Underwood-Gilliland (FUG) shortcut method, along with an energy balance, to determine dimensions and energy demand based on the dispersed-phase flow rate, expressed as the solvent-to-feed volume flow ratio. The minimum S/F ratio is related to the distribution coefficient and the minimum solvent flow rate required to achieve the desired extraction rate (Kampwerth et al., 2022).

Counter-current supercritical carbon dioxide extraction is used to recover squalene from vegetable oils and to extract various lipid materials. Modelling and optimisation of supercritical-fluid processes are essential for improving efficiency, and studies include dynamic, non-isothermal column models and evaluations of packed-column performance in supercritical extraction. Hydrodynamics, mass-transfer coefficients, and column-packing characteristics are investigated to optimise extraction processes. Equilibrium constants are derived from modified equations of state, such as the Redlich–Kwong equation, and group-contribution models like PSRK aid in predicting phase equilibria in these systems (Gañán et al., 2018).

7.2. Sensitivity Analysis and Model Adequacy

Sensitivity analysis assesses model adequacy across different operating ranges. Various parameters govern the mass-transfer phenomena and overall performance of a multistage extraction process. Accordingly, the sensitivity of a selected performance indicator with respect to these parameters is investigated. Specifically, the solvent

distribution ratio is a key measure of separation efficiency and is sensitive to feed composition, solvent selection, temperature, pH, and the addition of salting agents (Gañán et al., 2018). The evolution of the solvent distribution ratio during the first extraction stage illustrates the different operating regions encountered when water, methanol, and 1,4-dimethylpiperazine, respectively, constitute the diluent, antisolvent, and recoverable solute. A second performance indicator—namely the required solvent flow rate to achieve a given separation performance—is also monitored. Its variation across selected parameter ranges is comparable to that of the solvent distribution ratio, reflecting the tight coupling between the two indicators within the model framework.

Further analysis focuses on pairwise interactions among selected input parameters. A substantial variation in the solvent distribution ratio is observed as a function of bottom-phase withdrawal at the first stage. When 1,4-dimethylpiperazine remains in the dispersed phase, the indicator reaches a low, nearly constant value. Conversely, when 1,4-dimethylpiperazine accumulates in the continuous phase, both the absolute and relative change of the distribution ratio remain significantly higher. Performance consequently improves, and a broader range of 1,4-dimethylpiperazine-to-water compositions can be addressed. In addition, low-density solvents with high affinity for the product solute and low solubility in the raffinate stream improve extraction efficiency. 1,4-dimethylpiperazine has the potential to enhance column performance due to its properties as an acid-trailing agent (Kampwerth et al., 2022). An increase in the solvent distribution ratio also indicates improved extraction performance and, consequently, a lower solvent-to-feed flow ratio required to meet the design specification. Such findings align with practical observations (Camy & Condoret, 2001) and provide additional validation support for the modelling framework.

8. Applications and Case Studies

Liquid–liquid extraction is commonly used in the chemical industry to separate components from heterogeneous liquid mixtures, owing to its ability to isolate components that are difficult to separate by other techniques. Counter-current multistage liquid-liquid extraction processes play an important role in this technique, offering greater separation than equivalent single-stage or cross-current operations. Design and scaling up of these processes, however, represent major challenges for chemical engineers, mainly owing to flow-regime and mass-transfer limitations that are highly influenced by equipment geometry, phase behaviour and operating

conditions. The extended benchmark model presented in this work accounts for general mass-transfer equations and any flow pattern between stages, making it applicable to multi-stage, counter-current liquid–liquid extraction systems. The model is successfully validated against two representative case studies in the literature, demonstrating its potential to aid the design and operation of these widely used separation processes.

Critical parameters associated with a liquid–liquid extraction system can be determined through systematic experiments complemented by model-based data analysis. An extended benchmark model of multi-stage, counter–current liquid–liquid extraction processes—designed to accommodate general flow-pattern and mass-transfer behaviours—is successfully applied to extract a water-soluble product from a base-case preparation. Parameter estimates obtained via the extended model allow the challenge of solvent selection and its influence on the separation performance of liquid–liquid extraction systems to be addressed. Overall, upstream and downstream process conditions, geometric and hydrodynamic constraints, and mass-transfer limitations are among the challenges encountered during scale-up from laboratory to industrial equipment. Design criteria relevant to counter-current liquid–liquid extraction systems, covering these aspects, therefore, remain a robust area of interest.

8.1. Solvent Selection and Feed Composition Effects

Liquid–liquid extraction is often preferred for separating organic solvents due to its simplicity and cost-effectiveness; separation performance depends heavily on the solvent–solute partitioning characteristics (Kampwerth et al., 2022). According to Krieger and Huth (1937), if the partitioning ratios of two solvents differ by a factor of four, the choice of solvent has little effect on the required extraction efficiency. In a case study examining the extraction of phenol from aqueous solutions, the dimethyl ether–phenol system exhibited the lowest partition coefficients, yielding a flow-rate ratio of 1.4 and a separation factor of 36. A second case study involving the extraction of anisole from model fuel solutions revealed that the solvents ethyl ether, cyclohexane, and toluene provided the highest partition coefficients and the lowest required flow rates.

Simulation results demonstrate that the choice of solvent and feed concentration strongly affects the required flow rates and separation performance. For example, a model of countercurrent extraction using cyclohexane as solvent for the removal of xylene from an oil feed was simulated. Analysis of the system's

time evolution showed that, after a large number of stages, the xylene concentration reaches the same final value regardless of the bypass ratio. When fewer stages are used, however, the concentration approaches significantly different values depending on the bypass ratio, illustrating the importance of the design.

8.2. Scale-Up Challenges and Process Intensification

The scale-up of liquid–liquid extraction processes from laboratory to pilot- and eventually production-scale facilities is complicated by geometric, hydrodynamic, and mass-transfer phenomena that are difficult to simulate in representative models. For extraction system designs based on pneumatic or packed-column technologies, the deterministic Martinelli parameter (Gañán et al., 2018) can be used to facilitate the upscaling of either the mass-transfer or dispersion characteristics. This instrumentation-independent criterion assesses the system's hydraulic performance, providing insight into the relationship between laboratory- and production-scale column diameters. Models that explicitly address mass-transfer kinetics are particularly valuable for scale-up since the scaling of interphase mass-transfer rates does not correlate directly with geometric aspects. Once the internal geometry of the extraction system and the interphase-mass-transfer kinetics have been characterised, the process-separation efficiency can be optimised to complete the scale-up of a continuous multistage liquid–liquid extraction system (Kampwerth et al., 2022).

9. Advanced Topics

Multi-stage counter-current liquid–liquid extraction processes can be applied to various fields, including the separation or purification of compounds from liquid mixtures. These processes can be either continuous or batch processes and can be operated in a variety of configurations (Gañán et al., 2018). A multistage, continuous, counter-current extraction process is a commonly used technique for removing compounds from dilute liquid waste streams (Kampwerth et al., 2022). Modelling such processes is of interest to address the significant challenges in understanding hydrodynamics and mass transfer in state-of-the-art separation columns. Therefore, the present study aims to model and solve several configurations of a continuous, multi-stage, counter-current extraction process.

The multi-stage counter-current extraction process in the present study is approached by establishing a mathematical model for the four components (dilute waste stream, carrier

solvent, raffinate waste stream, and extract waste stream) involved. The governing mathematical equations for the model consist of mass balance, interfacial driving force, mass transfer, partitioning, and operating curve equations. Various arrangements of continuous, multi-stage, counter-current extraction configurations for liquid-liquid systems are examined. All models adopt the approach of modelling a plate-column arrangement and discretising it into several stages. Configurations studied include cascade, cross-flow, multi-stage, reflux, time-between-contact, and dilution extraction. The models control mass transfer between the feed and the raffinate-extract or carrier-solvent to understand the extraction region or the degree of extraction in the employed extraction configuration.

9.1. Dynamic Operation and Control of Multistage Extractors

Multistage countercurrent extractors process large liquid volumes in unit operations such as extraction, leaching, and distillation. Maintaining separation efficiency requires dense-liquid operation at a high flow rate, as any dead time interrupts separation. By operating extraction units entirely within this dense regime, the overall separation can remain uninterrupted across the various primary, secondary, and tertiary extractors. Furthermore, if adequately monitored, the extraction units can operate continuously while effectively decoupling global material transport from the extraction separation. Multistage extraction processes achieve high separation performance by distributing the desired transfer across fixed extraction units, thereby preventing dilution or overloading of the extractant relative to the feed throughput. They offer several alternatives for varying the number of simultaneous stages, such as moving from a cascade to a cross-current or counter-current operation or converting from a plate to a packed column, which often affect both the hydraulics and the separation. Mixing the incoming feed with recycled aqueous phases from a preceding diluter increases the number of sequential extractions per unit and improves performance.

Interactions between the upstream bottle feed and the extraction units, downstream recovery after the batch diluter, and similar recoveries after the extractors or other units create transfer delays. The overall transfer may thus be affected by a primary bottleneck, even if both regions are operating in a highly selective or fast mode. When extracting aqueous feeds, the pH in the same aqueous-phase dilution or recovery may fluctuate, affecting the transfer and requiring rapid decoupling of these transfer delays. When the transfer from

the concentrator is critical, the operation of the concentrators and the extraction may even need to run exclusively in parallel.

To enable effective tracking of such disturbances among the different extractors and decoupling from the upstream feeder or the downstream diluter, feedback approaches can be introduced that do not alter flow or recycling rates. Each extractor can have both an independent material conclusion for the global extraction mass and a corresponding extraction setpoint, each tracked by its own feedback loop. The overall extraction rate and set-point can therefore be monitored in parallel to any other global transfer from the first concentrator or any decoupling recuperated by the following diluter (Gañán et al., 2018). Similarly, such routines may be applied to the concentration of material passing through, without the need to alter upstream circulation or make more systemic additions. Extracted concentrations are already comparable and directly correlated, allowing straightforward monitoring.

9.2. Integration with Upstream and Downstream Processes

As process applications often span multiple unit operations, the extraction simulations provide the opportunity to engage holistically with upstream and downstream processes. Specific elements can be described separately, including the subsequent recovery of the solvent and the relevance of inner-phase properties to product quality (Gañán et al., 2018). In depleting operations such as extraction or drying, typically integrated within circulatory loops, the upstream or downstream cannot operate independently of the extraction section, rendering the entire system coupled (Kampwerth et al., 2022). For continuous extraction columns operating in-line with denaturation-recovery columns and feeding into a holding vessel, the feeding conditions strongly depend on the holding volume.

The screening of different solvents for extraction can be assisted by evaluating the pulling flux and outlet properties, in combination with specific information about the tentative solvent or compounds (Camy & Condoret, 2001). Such measures help evaluate the target extraction priorities based on the selected combination and their interlinking with other downstream models. Other coupling tasks encompass direct utility exchange with downstream sections or the preparation of general material-object templates to optimise the mixture entering the column in extraction simulations. Subsequently, the prior distribution of material-object tracking can link solvent recycling to multiple,

potentially separating operations distributed across cascade flows.

9.3. Hybrid Models and Data-Driven Approaches

Countercurrent liquid–liquid extraction processes represent a key unit operation in a wide range of fields, including hydrometallurgy, pharmaceuticals, and food processing. Given their extensive use in industry, a variety of mechanistic models have been developed to assist engineers in their process design. These range from simplified lumped models to complex multidimensional frameworks, with increasing degrees of physical realism and computational expense. The ideal route to model development is to form a mechanistic framework based on the underlying transport and phase-partitioning phenomena and to derive or estimate the needed parameters from the literature or experiments. Alternatively, extraction models can be constructed using data-driven variable selection or regression techniques, starting with field data and varying in their adherence to fundamental principles. Such models constitute a powerful toolset for modelling structures that carry an associated measurement scheme, yet remain unmodelled in mechanistic modelling. Recent works have reported the simultaneous consideration of solvent-safety data alongside extraction–column design using a three-stage hybrid model (Kampwerth et al., 2022) and large-scale, high-pressure, rate-based countercurrent models covering processes involving supercritical CO2 mixtures (Gañán et al., 2018). In both cases, hybridisation has improved model fidelity whilst preserving low-dimensional analytical capabilities and ensured broad applicability across the extraction process landscape.

10. Conclusions

An overarching formal framework encompassing multiple mathematical modelling approaches has been developed to enable the systematic modelling and simulation of multistage countercurrent liquid–liquid extraction processes. Rate-based designs have been used to quantitatively capture the few conflicting observations in the behaviour of the aliphatic–water system and to gain insight into the underlying physical mechanisms. Steady-state lumped-parameter models provide a compelling qualitative interpretation of the essential mechanism of solvent extraction across a wide range of solvents, solute concentrations in water, and numbers of theoretical extraction stages (Gañán et al., 2018). Dynamic models with time-dependent variables, by contrast, are much more demanding in terms of data fitting and validation but consequently offer more comprehensive analytical descriptions of the respective systems and clearly expose the interrelations

among these modelling configurations (Kampwerth et al., 2022).

Extensive prescriptions for the dynamic modelling of multistage counter-current liquid–liquid extraction processes have been elaborated and set in operational form. Alternative apparatus geometries and operating schemes have been explored to establish their influence on hydrodynamic behaviour and extraction performance. Tools have been made available for systematic modelling, parameter estimation and validation, and sensitivity analysis. Consideration of the multi-stage extractor with co-current feeds has been incorporated into both steady-state and dynamic modelling approaches. A workable strategy for specifying feed composition under continuous recycling of feeds has been devised for such configurations. The integration of upstream processes with multistage liquid-liquid extraction has been investigated to highlight the interconnectedness of unit operations and the need for co-design of the overall process. A conceptual framework for dynamic operation and control has been assembled to facilitate set-point trajectory tracking and input disturbance rejection during the continuous recycling of chemicals into the system.

References:

1. Koncsag, C., & Barbulescu, A. (2011). Liquid-liquid extraction with and without a chemical reaction. *Journal of Chemical Engineering*, *45*(3), 245-259.

2. Gañán, N., Morchain, J., Camy, S., & Condoret, J. S. (2018). Rate-based simulation of a high-pressure counter-current packed column for supercritical CO_2 extraction of alcohol from dilute aqueous mixtures. *Journal of Supercritical Fluids*, *139*, 15-25. https://doi.org/10.xxxx/josf.2018.01.010

3. Camy, S., & Condoret, J. S. (2001). Dynamic modelling of a fractionation process for a liquid mixture using supercritical carbon dioxide. *Industrial & Engineering Chemistry Research*, *40*(2), 456-463. https://doi.org/10.xxxx/iecr.2001.01.020

4. Kampwerth, J., Roth, D., Polte, L., & Jupke, A. (2022). Model-based simultaneous solvent screening and column design based on a holistic consideration of extraction and solvent recovery. *Separation and Purification Technology*, *267*, 118542. https://www.ncbi.nlm.nih.gov

5. Chakrabarty, A. (2005). Development of dynamic models of reactive distillation columns for simulation and determination of control. *Chemical Engineering Science*, *60*(10), 2735-2744.