Design of Extractive Reaction Systems

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DOI: 10.1002/cite.201900163

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Product selectivity and yield in chemical reactions can be limited by side product formation or low conversions due to equilibrium limitations. Extractive reaction systems (ERS) employ an in situ liquid-liquid extraction that separates the product from the reaction phase to overcome these difficulties. The design of ERS requires a broad knowledge of the discipline of process intensification and extraction and reaction engineering. Furthermore, specific knowledge about the interplay of reaction and extraction phenomena is unique to ERS. This review gives an overview of the design of ERS and enables their application to any suitable reaction.

Keywords: Extractive reaction systems, In situ extraction, Liquid-liquid systems, Multiphase reaction systems

Received: October 01, 2019; accepted: October 09, 2019

1 Introduction

There are two major motivations for the employment of an extractive reaction: a desire to optimize the reaction outcome and overall process optimization through integration of separation and reaction in a single unit. An overview of technologies aimed at reactions with in situ separation is given in [1], pointing out their potential to improve conversion and selectivity and lower capital investment.

In this review, the discussion of extractive reaction systems (ERS) focuses on biphasic liquid-liquid systems with product formation in one phase and in situ product extraction into a second phase. By application of an ERS, the product is separated from catalyst and/or educts within the reactor. Phase transfer catalysis systems can be considered ERS if the product is transported out of the catalytic phase during the reaction. The catalyst enables the reaction of educts that are distributed among immiscible phases by transferring one of the educts to the reaction phase while activating it [2]. As phase transfer catalysis systems are not further discussed in this review, see [3] for an overview. In general, the rules for the design of ERS can be applied to extractive fermentation systems, since these systems follow the same principle as ERS. However, biochemical processes have their own characteristics and challenges. Thus, the reader is referred to Görak and Staniewicz [4] for further information.

ERS should be distinguished from thermomorphic solvent systems and reactive extraction systems. In thermomorphic solvent systems, the extraction can only occur after a change in temperature. Thus, unlike in ERS, a separation during the reaction is not possible. Reactive extraction employs the reaction to extract components, whereas extractive reaction employs the extraction to improve the reaction performance.

From a perspective of process design, extractive reaction can be classified as process intensification, which, according to [5], “combines reaction, separation, and other phenomena in multitasking units and reduces the cost, energy consumption, and footprint of chemical plants”. In their review on process intensification, Tian et al. [6] list “combined reaction separation processes” as one of the four main categories of process intensification among advanced separation and advanced reaction technologies and the use of alternative energy sources. Within this category, mostly reactive distillation, membrane separations, and reactive adsorption are addressed [6], being the most studied reaction separation processes [7]. However, extractive reaction processes fulfill the same objective and are often designed using analogies and transferability of the same methods.

Utikar et al. [7] discuss that a reaction system with multiple phases does not necessarily represent a process intensification but may need to be intensified itself. Common challenges in multiphase reaction engineering are intensification of mixing, mass transfer and heat transfer, overcoming equilibrium limitations and scale-up based on fundamental principles [7–9]. Some of these challenges also have to be solved during the design of ERS.

2 Reaction and Phase Equilibrium

The challenges that arise in the early design of ERS due to the interaction of liquid-liquid phase equilibrium and reaction

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equilibrium are discussed in the following, based on illustrations from a design framework by Samant and Ng [10].

For a three-component isothermal, isobaric system, both phase and reaction equilibria can be depicted in a ternary diagram, see Fig. 1. Both subfigures show the same binodal curve through a, P, and b, marking the region within which the system splits into two phases. For the reaction $A \rightleftharpoons B$ with an inert component C, the reaction equilibrium between components A and B can be plotted in the phase diagram as a function of the mole fraction of component C. The resulting dotted reaction equilibrium line depends on the equilibrium constant. In Fig. 1a, the reaction equilibrium line does not cross the two-phase region. In this case, an in situ extraction is not possible. In Fig. 1b, the two lines intersect in the points d and e. The system splits into a reaction phase (point e) and an extraction phase (point d). In this example, the equilibrium concentration of the product B can be raised from point c in the single-phase system to point d within one equilibrium stage of an ERS.

### 2.1 Modeling of Phase Equilibria

As demonstrated above, the knowledge about phase equilibria is essential for designing ERS, as it influences the efficiency or even the general feasibility of the process. As measuring every state point of interest (temperature, pressure, composition) requires a prohibitive effort, thermodynamic models are used for correlation. The most popular types of thermodynamic models are excess Gibb's free energy ($G^E$) models and equations of state [12]. $G^E$ models allow for calculation of phase equilibria of highly non-ideal mixtures but neglect the pressure dependency and cannot calculate volumes and $pVT$ behavior [12]. Well-known examples for $G^E$ models are the NRTL [13] and UNIQUAC [14]. Equations of state, on the other hand, allow for a comprehensive modeling, e.g., of $pVT$ behavior, caloric properties, and phase equilibria [12]. While cubic equations of state like Suave-Redlich-Kwong (SRK) [15] and Peng-Robinson (PR) [16] are used to model systems that deviate only slightly from ideal behavior, physically-based equations of state like the statistical associating fluid theory (SAFT) [17, 18] describe even associating mixtures well. Examples for modern versions of SAFT are perturbed-chain polar SAFT (PCP-SAFT) [19, 20–23] and SAFT for variable range interactions of the generic Mie form (SAFT-VR Mie) [24].

All of the above-mentioned models require the determination of model parameters. Parameters for $G^E$ models are typically fitted to binary liquid-liquid equilibrium data [25]. Pure component parameters for equations of state can be obtained with a small amount of pure component vapor pressure and liquid density data points [26]. Using PCP-SAFT, a single adjusted binary parameter often suffices for an accurate description of liquid-liquid equilibria even for strongly non-ideal systems [27].

A way to avoid the need for experimental data is the usage of group contribution methods [28, 29] or quantum-mechanics-based approaches [30–33]. A combination of information from prediction and experimental data can greatly improve accuracy with a minimal amount of experimental data [34, 35].

### 2.2 Modeling of Reaction Equilibria

At the equilibrium of a reaction, the Gibb's free energy at constant temperature and pressure is minimal [12]. Using thermodynamic models, the relation between the composition at reaction equilibrium and the Gibb's free energy change for the reaction can be established [12]. For the sake of convenience, this relation often is expressed in terms of a reaction equilibrium constant.

### 3 Reaction and Mass Transfer Kinetics

The operating point of an ERS is defined not only by the thermodynamic equilibrium but also by kinetic effects. The dimensionless quantities used to describe the relation between reaction and mass transfer kinetics are the Hatta...
number $Ha$ (Eq. (1)) [36], the Damköhler numbers $Da_r^\Phi$ [37] and $Da_m^\Phi$ [38] (Eqs. (2) and (3)) and the second Damköhler number $Da_{II}$ (Eq. (4)) [37].

The Hatta number is the ratio of the reaction rate without transport limitation to the pure mass transfer rate of a component. Its expression depends on the reaction order and constants, the local concentrations, and diffusion coefficients. If the educts are located in two different phases, the Hatta number classifies the reaction into interfacial reaction ($Ha > 2$), bulk phase reaction ($Ha < 0.02$), and an intermediate regime. [36]

The first Damköhler number links the reaction time (index $r$) or extraction time (index $m$) to apparatus design by introducing a residence time for each phase $\Phi$.

$$Ha^2 = \frac{\text{maximum possible conversion in the film}}{\text{maximum diffusion transport through the film}}$$  \hspace{1cm} (1)

$$Da_r^\Phi = \frac{\text{Residence time of phase } \Phi}{\text{Characteristic reaction time with phase } \Phi \in \{E, R\}}$$  \hspace{1cm} (2)

$$Da_m^\Phi = \frac{\text{Residence time of phase } \Phi}{\text{Characteristic mass transfer time with phase } \Phi \in \{E, R\}}$$  \hspace{1cm} (3)

$$Da_{II} = \frac{Da_r^\Phi}{Da_m^\Phi} = \frac{\text{Characteristic mass transfer time}}{\text{Characteristic reaction time}}$$  \hspace{1cm} (4)

To illustrate the influence of kinetic effects, in Fig. 2a an isothermal, isobaric system with a reaction equilibrium of reaction $A+B\rightleftharpoons C$ and an intersecting phase equilibrium is shown. For instant mass transfer and reaction, the system would operate in points $R$ for the reaction phase and $E$ for the extraction phase. In reality, there is a range of kinetically hindered operating concentrations belonging to the equilibrium points $R$ and $E$ between phase and reaction equilibrium line. Fig. 2b shows this range for point $R$ with the operating point depending on the reaction phase Damköhler numbers for reaction and mass transfer $Da_r^R$ and $Da_m^R$ [38].

### 3.1 Modeling of Mass Transfer and Reaction Kinetics

The rate of mass transfer is a function of the mass transfer coefficient and the driving concentration difference. The definition of the mass transfer coefficient depends on the chosen mass transfer model, e.g., the two-film model and penetration theory, see [39].

The temperature-dependent reaction rate constant can be described by the Arrhenius equation depending on the frequency factor $k_0$, activation energy $E_a$, ideal gas constant, and temperature [40]. Both, $k_0$ and $E_a$ can be described with thermodynamic principles using transition state theory (TST) [12, 40]. Combined with quantum mechanics and statistical thermodynamics, TST can be used to quantitatively predict rate constants [41]. Quantum-mechanics-based approaches can also capture solvent effects on reaction kinetics [42–44].

### 4 Process Design

Using the methods presented in Sect. 3 it is possible to assess whether an ERS can improve a reaction and the consecutive process or not. This is the starting point of process design. In the following, several methods specifically extended or developed for ERS are presented. These methods can be grouped into heuristic methods, attainable region methods, and optimization-based methods. They are based on classical process design methods, are adapted from process intensification methods, e.g., for reactive distillation, or stem from the field of reactor network synthesis. According to Chen and Grossmann [45] reactor network
synthesis always includes the steps of targeting, problem formulation and optimization. Indeed, these steps can be identified in most of the presented design frameworks.

4.1 Heuristic Methods

Heuristics are a simple way to radically reduce the number of feasible options in process design, going back to Douglas [46]. Schembecker and Tlatlík [47] proposed a heuristic method for considering reactive separation systems, including ERS, in early process design. For the stand-alone design of a reactive separation, first the chemical reaction system and the physical properties of the components are analyzed. If the separation seems beneficial and feasible, operation windows for reaction and separation are defined. If an intersection of the operation windows exists, an additional apparatus operation window is defined. An intersection of all three operation windows proves feasibility of the reactive separation. In a consecutive step, a conceptual process design is performed, considering options with and without reactive separation. Due to mass integration, this is an iterative process, including renewed reactor design. Finally, the best process design is determined.

Gorissen [48] developed a method to identify reaction systems that benefit from an integrated extraction and to enable conceptual design of the extractive reaction system in a countercurrent device. Given a new reaction system, they search for conflicting requirements of the system. A simple example for such a conflict is given for an equilibrium of phase and reaction equilibrium in a phase diagram. Their framework builds on the representation. After a transformation of the phase equilibrium concentrations, the phase equilibrium is displayed in the new diagram and a process can be designed using standard geometrical methods, e.g., the lever rule [10, 11, 38].

Figure 3. Projected reaction and phase equilibrium from Fig. 1b.

Olán-Acosta et al. [54, 55] used a similar but modified projection in order to determine the necessary number of reaction-liquid-liquid equilibrium stages and develop an algorithm for the design of extractive reaction columns during conceptual process design. Samant and Ng [38] went a step further and included kinetic effects in their representation by using the Damköhler numbers, as described above. In order to evaluate the reaction systems, a simple two-film reaction-diffusion model is used in a system with cocurrent, ideally mixed bulk phases and a defined interface. Maxwell-Stefan diffusion and reaction rate equations based on mole fractions and activity coefficients are solved simultaneously. The resulting reaction yield is a function of the Damköhler numbers.

Thus, investigations lead to desired values of $Da_{r}^{\phi}$ and $Da_{r1}$, both a function of the residence time and the latter decreasing with increasing interfacial area. The requirements for the Damköhler numbers then can be translated into guidelines for reactor design and operation, e.g., build-up or interfacial area, completing the design framework [10].

4.2 Attainable Region Methods

Attainable region methods go back to Horn [49]. They are used for targeting in reactor network synthesis, i.e., visualization of the best possible reaction outcome reachable through mixing and reaction by a combination of continually stirred reactors (CSTR), plug-flow reactors (PFR), and recycles [50, 51]. Attainable region methods have been extended to combined reaction and separation processes with application to reactive distillation [52].

Samant and Ng [11] developed a geometrical attainable region method. Their framework builds on the representation of phase and reaction equilibrium in a phase diagram (Fig. 1). An adaption of a method developed by Ung and Doherty [53] for vapor-liquid reaction systems enables the reduction of the degrees of freedom by the number of independent reactions. A coordinate transformation, thus, makes it possible to investigate systems with a large number of components in a phase diagram. To give an example, Fig. 3 shows how the system depicted in Fig. 1b can be reduced from a two-dimensional to a one-dimensional representation. After a transformation of the phase equilibrium concentrations, the phase equilibrium is displayed in the new diagram and a process can be designed using standard geometrical methods, e.g., the lever rule [10, 11, 38].

\[ X_A = x_A + x_B \]

4.3 Optimization-Based Methods

4.3.1 Superstructure Optimization

Mehta and Kokossis [56, 57] developed a synthesis tool for non-isothermal multiphase reaction systems with the explicit goal of finding novel reactor concepts for optimal reaction outcome. The framework has been applied to an ERS [58].

The superstructure elements used are depicted in Fig. 4 from top to bottom. The process is generated from streams that connect synthesis units and elements on all levels. Reaction and separation units can be combined to form...
synthesis units. A reaction unit can consist of one or more compartments, with ideal CSTRs or PFRs [57]. These units are themselves made up of basic CSTR elements, stream mixers and splitters.

The concept of shadow compartments extends the structure to multiphase systems [58]. If several phases are in contact in a reaction unit, the original compartment is assigned to one phase. For each additional phase, a shadow compartment of the original compartment is added. Where the phases are in contact, the subunits of the compartments and shadow compartments are connected (Fig. 5). The stochastic optimization via simulated annealing starts from a feasible network that is perturbed by predefined moves to reach new states. Simulation of the new system yields the objective value and the process is repeated until convergence is reached.

4.3.2 Elementary Process Functions

A hybrid optimization and heuristic method by Freund and Sundmacher [62] aims at finding a fundamentally new way of looking at process design, not restrained by predefined unit operations. The framework has been applied to the design of multiphase reactors and processes for hydroformulation reactions in thermomorphic gas-liquid-liquid and gas-liquid-ionic liquid systems [63–65].

Instead of unit operations that are already associated with an apparatus, five functional modules are defined: contacting, activating, chemical reaction, heat supply/removal, and separating. Preprocessing and product formulation are regarded as additional steps. The functional modules are decomposed into elementary process functions (fluxes) that change the state of a volume element traveling through state space [62].

The design method presented in [66] and [67] is conducted on three levels with increasing model complexity, starting from reaction kinetics. The first level imposes no limitations on the fluxes that can enter or exit the fluid element in which the reaction occurs. Restrictions like maximal catalyst temperature, thermodynamic equilibrium of the phase and system kinetics are considered. Fluxes are then optimized with regard to a defined objective, e.g., minimal residence time. This yields an optimal trajectory of the volume element through state space, which serves as a benchmark, and might be considered as a targeting step. The second level imposes transport limitations and kinetics. Control variables that can be used in order to control the fluxes are identified. The third level employs a detailed reactor model chosen to approximate the determined trajectory by adding further limitations such as geometry or velocity equations. Few degrees of freedom remain. A last optimization run yields the final trajectory and results.

4.3.3 Phenomena-Based Modeling

Phenomena-based methods are similar to elementary process functions in decomposing the unit operations but use a higher level of aggregation [68]. The basic building blocks are phenomena building blocks, e.g., reaction or liquid-liquid [69]. Kuhlmann et al. [68] combined these phenomena building blocks with the reactor network building blocks CSTR, PFR, and side stream reactor. A superstructure then is able to generate, e.g., an ERS. Furthermore, identified phenomena building blocks can be aggregated to simultaneous phase building blocks that combine to form unit operations in a design framework by Garg et al. [70].

5 Apparatus Design
following section, disperse phase phenomena are introduced, before moving on to computational models.

5.1 Disperse Phase Phenomena

The efficiency of extraction processes is dominated by the interfacial area between the disperse and the continuous phase and residence time of the phases. Therefore, extensive research has been conducted in the modeling of drop breakage and coalescence, drop sedimentation and mass transfer across the phase boundary [71–75]. These submodels can readily be integrated into an ERS model, describing the extraction of one or several components out of a reactive phase.

The focus of the following sections is to give a brief overview of the modeling approaches for the disperse phase phenomena currently applied in extraction modeling.

5.1.1 Coalescence

A general distinction between coalescence modeling approaches can be made between physical and empirical models. This review focuses on physical models, since they promise a higher flexibility regarding applicability [75]. From a phenomenological perspective, coalescence is initiated by two drops colliding in a fluid continuum [73]. The liquid film between two drops drains, leading to surface rupture between the drops such that a coalescence bridge is formed. The process is completed by drop fusion. Accordingly, two aspects are considered for the description of coalescence: collision frequency and coalescence efficiency. The collision frequency is based on turbulent fluctuations, capturing of the drops in turbulent eddies and velocity gradient-induced collisions. Collisions based on turbulent fluctuations are the most important coalescence cause in turbulent flow [71]. The latter two effects are important in case of similar or significantly different densities between the disperse and the continuous phase [71]. The coalescence efficiency takes into account that not all collisions lead to coalescence and corresponds to the probability of drop coalescence during collision. The various models documented in literature can be divided into energy models evaluating the ratio of kinetic collision and interfacial energy, the critical collision velocity models, and the film drainage models. The latter are the most accepted in the evaluation of immobile interfaces. The efficiency is estimated in terms of the contact time and the drainage time. If the contact time exceeds the time needed for drainage of the liquid film between drops, the two drops coalesce [71, 73].

5.1.2 Breakage

The drop surface is subject to a force balance between internal viscous stresses and external stress caused by the continuous phase hydrodynamics. If the external stress outweighs the internal stabilizing forces, the drop surface ruptures leading to the formation of new drops. The four main reasons for drop breakage discussed in literature are interfacial instabilities, viscous shear stress, shearing-off processes, and turbulent fluctuations and collisions [71, 75]. In extraction devices with typical drop size distributions only the drop breakage by turbulent fluctuations and collisions is of relevance. Therefore, research focuses on these breakage phenomena. Both effects are assumed to deform the drop's spherical form, leading to surface oscillations. Finally, the oscillations lead to the drop surface rupture causing the formation of (at least) two daughter drops. Various modeling approaches exist, which vary mainly in the definition of necessary conditions for a drop to break [74].

For the prediction of the number of daughter drops and daughter drop size distribution, statistical and phenomenological models exist. In statistical models, the daughter drop size is considered as a random variable, which can be depicted by a statistical approach such as a normal distribution. Contrary, the phenomenological models incorporate empirical data. These are commonly classified by the shape of the distribution (U shape, M shape, etc.) [71].

5.1.3 Drop Sedimentation Velocity

The drop velocity in chemical reaction vessels results from a superposition of the forces acting on and deforming the shape of the dispersed drops. The forces considered are the gravity, the buoyancy, the drag, and the inertia force. Considering steady state, the inertia force may be neglected, thus, resulting in the steady-state velocity or terminal velocity a drop would reach in an infinite fluid continuum. A major challenge in determining the terminal velocity is the quantification of the drag coefficient $C_D$, introduced to describe the drag force. Methods to determine $C_D$ can be grouped into correlations for rigid and viscous spheres, depending on the viscosity ratio between the disperse and continuous phase. In this regard, two extreme cases can be defined: spheres with immobile and fully mobile interfaces, representing rigid sphere and spherical bubbles respectively. This distinction can be visualized by the velocity field across the drop surface (see Fig. 6) [72].

Small drops are commonly regarded as rigid spheres. With increasing diameters, the shear forces at the drop surface cause internal circulation. This decreases the drops' drag resistance, increasing the drop velocity. At this transition state, the terminal drop velocity reaches a maximum, which is commonly characterized by a critical Weber number. An additional increase in diameter leads to drop oscillations and finally to deformed and slower drops [76]. Fig. 7 depicts the transition of the drop's hydrodynamic state from a rigid sphere to oscillating/deformed bubble.

5.1.4 Mass Transfer Across Drop Surface

The mass transfer across the phase boundary inherently depends on the mass transfer resistances in the continuous and the disperse phase. Depending on the magnitude of the
Resistance, the mass transfer modeling can be divided into external, internal, and conjugate problems, where the transfer resistance is predominantly in the continuous, disperse, or in both phases respectively. In most mass transfer models the resistance is calculated by a mass transfer coefficient $b$, which in turn is estimated by a correlation for the Sherwood number for each phase. An overview of internal and external problems can be found in [72]. In case of a conjugate problem, an overall mass transfer coefficient $k_d$ is derived from the two-film theory:

$$\frac{1}{k_d} = \frac{1}{\beta_d} + \frac{K^*}{\beta_c}$$

(5)

where $1/\beta_d$ and the $K^*/\beta_c$ are resistances in the dispersed and the continuous phase, respectively. The validity of transfer resistances additivity is limited to large partition coefficients and high convection rates [72].

5.2 Computational Models

In order to depict an ERS, the disperse phase phenomena have to be embedded into an overall reactor model, which is defined by its hydrodynamic modeling depth. Therefore, four reactor modeling approaches with varying levels of detail are presented below: equilibrium stage models (Sect. 5.2.1), rate-based models (Sect. 5.2.2), computational fluid dynamics (CFD) (Sect. 5.2.3) and compartment models (Sect. 5.2.5). The choice of the reactor model and, thus, the level of detail of the continuous phase hydrodynamics depends on the modeling objective. A fast and robust dispersion model might be preferred in an online process control, whereas a CFD approach could be best for a detailed analysis of a reactive device. A part of the detailed reactor models, the population balance theory (Sect. 5.2.4) is briefly introduced as the state-of-the-art method to connect disperse phase phenomena with continuous phase hydrodynamics.

5.2.1 Equilibrium Stage Models

Equilibrium stage models are an established method for the description of separation units. These models describe a countercurrent apparatus as a sequence of equilibrium stages of the contacting phases. The stages have a theoretical height and may include a stage efficiency [77, 78]. For ERS systems, an equilibrium stage is an ideally mixed reaction phase with instant phase equilibrium, e.g., [79, 80], or instant reaction and phase equilibrium, e.g., [55].

5.2.2 Rate-Based Models

From a computational point of view, a simple way to model a chemical reactor is in terms of a differential mass balance (Eq. (6)). A chemical reaction can be accounted for by a term $r_i$, the mass transfer across the phase boundary by a term $r_{i,MT}$. The hydrodynamics of the reactor are considered in a convective term with an absolute flow velocity $v_{abs}$ and a dispersive term with an axial dispersion coefficient $D_{ax}$. This allows the formulation of partial differential equation for the concentration of a species $i$:

$$\frac{\partial c_i}{\partial t} = v_{abs} \frac{\partial c_i}{\partial z} + D_{ax} \frac{\partial^2 c_i}{\partial z^2} - r_i - r_{i,MT} \quad (6)$$

The mass balance can be formulated for every species in each phase occurring in the reactor, thus, constituting a model for an ERS.

The axial dispersion coefficient $D_{ax}$ indicates the degree of spreading of a species after passing a chemical reaction vessel, describing the reactor hydrodynamics as either closer to a PFR or a CSTR. Inserting $D_{ax}$ into the differential mass balance enables the prediction of the concentration course as a function of time and space. This concept originates from the residence time theory, which has been reviewed comprehensively in [81, 82] including modern extension such as genetic and learning algorithms. In case of considerable deviations from plug flow, the validity of this method is limited [36].
Assuming steady state and dividing the reactor domain into a discrete number of layers in axial direction, allows a simplified and fast simulation of an ERS. A rate-based model has recently been applied to the synthesis of hydroxymethylfurfural [83].

5.2.3 Computational Fluid Dynamics

The basic concept of computational fluid dynamics is the discretization of the reactor domain by a mesh in which the hydrodynamic behavior is numerically calculated. For each element of the mesh, conservation equations are defined and solved, balancing physical properties such as mass, momentum, and energy. Two fundamental approaches for modeling fluids can be distinguished: In Eulerian approaches the fluid phase is modeled as a continuum, whereas with a Lagrangian approach dispersed phase particles are tracked. Hence, the two most basic CFD models are the Euler-Euler and the Euler-Lagrange model. In the Euler-Euler model, both phases are regarded as interpenetrating continua, which are characterized by their volume fractions. For either phase, the Navier-Stokes equations are solved, while the interphase interactions are described by source terms. This model can depict complex flow, also in case of high or varying disperse volume fractions [71]. In contrast, in the Euler-Lagrange model the dispersed phase is tracked in the velocity field of the continuous phase, which is calculated with an Euler approach. This approach for the disperse phase demands the computation of momentum, mass, and energy exchange between every drop and the continuous phase. The demand on computational effort increases with increasing number of drops, which limits the practical application to low disperse volume fractions (< 10 vol %) [84], [71, 85].

5.2.4 Population Balance Models

A part of the hydrodynamics, the disperse phase behavior accounts for the drop size evolution along a reaction vessel, which results from a balance between coalescence and breakage processes. A well-established way to integrate models for these phenomena is the application of the population balance model (PBM).

A PBM is a modular approach to balance the number of drops inside a quantity of a chemical vessel. Based on PBM, the transient number of drops \( f(d,p,t) \) is accounted by:

\[
\frac{\partial f(d,p,t)}{\partial t} = B_b - D_b + B_{coa} - D_{coa} + f_{in} \tilde{V}_{in} - f_{out} \tilde{V}_{out} \quad (7)
\]

where \( f_{in} \tilde{V}_{in} \) and \( f_{out} \tilde{V}_{out} \) are the convective flows of the dispersed drops. The terms \( B_b \), \( D_b \) and \( B_{coa} \), \( D_{coa} \) are the birth and death terms for drops by breakage and coalescence, respectively [73]. Accordingly, phenomenological models can be inserted as submodels (kernels) into the CFD model, thus, allowing a space-dependent evolution of the drop size distribution. Examples for the integration of PBM in a CFD environment have recently been published [86, 87]. However, these examples do not consider reactions due to high computational demands. The modeling of ERS in a CFD environment can be regarded as a demanding challenge for future investigations.

5.2.5 Compartment Modeling

Despite the advantages of the rigorous modeling of multiphase hydrodynamics, the computational time limits the application of CFD for large or complex multiphase reactor geometries. The main cause for this limitation is the high number of cells in a CFD mesh, demanding a high calculative effort for the evaluation of the conservation equations. Therefore, considerable scientific efforts are conducted in order to construct broader meshes, the elements of which are referred to as compartments. These compartments constitute reactor parts, which can be represented by simplified reactor models such as a PFR or a CSTR. A distinction of the compartment modeling approaches can be made based on the compartment definition technique. According to the method of successive volume division, the reactor domain is divided into compartments, based on experimental, geometrical or CFD investigations of the reactor device. In the method of successive aggregation, the CFD cells representing the reactor domain are merged to create compartments. Due to the large number of CFD cells, algorithms aggregate cells into compartments based on chemical and/or physical criteria defining the similarity of cells [82].

Compartment modeling approaches for multiphase fluid systems have been published for reactive bubble columns [88], airlift reactors [89], and gas-liquid CSTRs [90]. More recently, Weber established a liquid-liquid extraction model for a Kühni column [91] and multiphase loop-reactor [92], incorporating a detailed PBM approach for the disperse phase. An extension of this work by a reactive model would enable a detailed simulation of an ERS.

6 Conclusion and Future Challenges

The design of extractive reaction systems has been described from reaction kinetics to process and detailed apparatus design. The importance of a reliable model for phase and reaction equilibrium was discussed and suitable models were presented. A number of examples for process design methods specifically developed for ERS were given and put into context with current process design methods. Finally, apparatus design was discussed starting with the individual modeling of the disperse phase phenomena and moving on to computational models of different level of detail.

Regarding apparatus design, ERS and extraction research face many of the same challenges. Detailed models for each disperse phase phenomenon require considerable experimental effort in order to parametrize new systems, with the
experiments mostly based on the evaluation of highly pure systems [72, 73]. Yet, small impurities can cause large deviations from the predicted behavior, both of equilibrium and droplet interactions. Reactive systems, incorporating catalysts and side products, deviate considerably from the behavior of pure systems.

Furthermore, models originating from research on extraction are based on investigations at ambient conditions. Reactive systems rarely meet these premises. Advances in temperature dependent phase separation behavior are currently made by Sibirtsev et al. [93]. Also, reactive systems are often characterized by turbulent hydrodynamics in the continuous phase as opposed to comparatively low Reynolds numbers present in extraction systems.

These limitations should be carefully considered when extrapolating the disperse phase models from liquid-liquid extraction on reactive systems. Further research should focus on the extension and validation of existing models, under standard extraction as well as reaction conditions present in ERS.

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### Symbols used

- \( c \) [mol m\(^{-3}\)]: concentration
- \( C_d \) [-]: drag coefficient
- \( D_{ax} \) [m\(^2\) s\(^{-1}\)]: axial dispersion coefficient
- \( E_a \) [J]: activation Energy
- \( f \) [-]: number of drops
- \( G^e \) [J]: Gibb’s free energy
- \( k_0 \) [-]: frequency factor
- \( k_d \) [m s\(^{-1}\)]: overall mass transfer
- \( K^* \) [-]: partition coefficient
- \( p \) [bar]: pressure
- \( R \) [m]: radius
- \( T \) [K]: temperature
- \( v \) [m s\(^{-1}\)]: velocity
- \( V \) [m\(^3\)]: volume
\( \dot{V} \) [m s\(^{-1}\)] volume stream
\( \beta \) [m s\(^{-1}\)] mass transfer coefficient

### Sub- and Superscripts
- abs: absolute
- b: breakage
- coa: coalescence
- c: continuous
- d: disperse
- in: inlet
- m: extraction time
- MT: mass transfer
- out: outlet
- r: reaction time

### Abbreviations
- CFD: computational fluid dynamics
- CSTR: continuously stirred tank
- ERS: extractive reaction system
- NRTL: non-random two liquid (model)
- PBM: population balance model
- PC-SAFT: perturbed-chain SAFT
- PCP-SAFT: perturbed-chain polar SAFT
- PFR: plug flow reactor
- SAFT: statistical associating fluid theory
- SAFT-VR: SAFT variable range
- SRK: Suave-Redlich-Kwong (model)
- TST: transition state theory
- UNIQUAQ: universal quasichemical (model)

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