Conceptual Screening of Reactive Separation Process Options Using Aggregated Process Models

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Reactive liquid-liquid extraction (RLLE) is a process design option with the potential to improve product yields for systems involving equilibrium reactions or reactions that are inhibited by product formation. Existing process synthesis tools are limited in their ability to handle such systems. Graphical methods are limited by dimensionality problems and modelling flexibility, whereas superstructure optimisation methods struggle to cope with the highly non-linear kinetic and phase equilibrium models involved. As a result, it is currently not possible to reliably screen promising RLLE process options and judge their potential as compared to that of possible alternatives quickly. Technology that would allow such a quick screening would be highly beneficial as it could be used to guide the allocation of process design and retrofit project time. Clearly, the more quickly the promising conceptual process design options can be identified, the more focussed the detailed investigations can be carried out.

We propose a new network optimisation-based approach that allows to quickly determine if the application of RLLE is a promising candidate for the system under consideration. Based on previous superstructure developments for single-phase systems (Kokossis and Floudas, Chem Eng Sci, 46: 261) we have developed a reaction/reactive separation superstructure comprised of synthesis units which can represent either a reactor (cstr, pfr, dssr), a reactive separator or a mass exchanger (Figure 1). The latter two multiphase options consider countercurrent contacting between the reactive and the mass separating agent phases. The synthesis units are connected in every physically possible combination through mixers and splitters. The approach also provides conceptual information on the design of the reaction process in terms of feeding, bypassing and mixing patterns for the reactive phases as well as on the existence of reactive separation sections within the network.

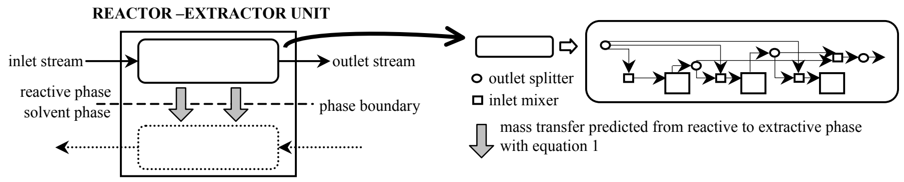

Figure 1: Illustration of reactive-extractive units.

The approach is highly computationally efficient as the information regarding the mass separating agent (solvent) phase is mapped onto the superstructure model of a single-phase reactor network. Thus, the superstructure model only contains the balance equations for the reactive phase. The aggregation is achieved with the help of a transfer rate expression for the LLE processes to predict possible mass transfer out of the reactive phase. This expression allows to predict the mass transfer rate in LLE systems based on the composition of the reactive phase. The mass transfer rate expression has been derived following the work by Zheng et al. (Chem Eng Sci, 53:13, 2327) and validated with rigorous simulations for a large number of LLE systems. The expression for the transfer of each component is:

$$T_{rate,i} = \frac{\dot{F}_{out}^{Carrier} \cdot K_D \cdot R}{\left(1 + K_D \cdot R\right)} \cdot C_{i,out}^{Carrier} \cdot \left(1 - exp\left(Param \Big/ \dot{F}_{out}^{Carrier} \cdot \delta\right)\right) \tag{1}$$

where Carrier indicates the reactive phase, $\dot{F}_{out}$ the outlet volumetric flow (m^3/s) from the unit, K_D the distribution coefficient, R the volumetric ratio between extractive and reactive phase, C_i the concentration (kg/m^3) of the component being extracted, δ the interfacial layer thickness (m) and Param is given by:

$$Param = -8.83 \cdot 10^{-14} \cdot \left(10\eta_C\right)^{1.40} \cdot \left(10\eta_S\right)^{0.38} \cdot \left(10V_{molar,i}\right)^{1.28} \cdot K_D^{1.64} \cdot F_C^{-0.05} \cdot F_S^{1.10} \cdot MW_i^{0.36} \tag{2}$$

where sub-indexes C refer to carrier and S to solvent phases. η is the viscosity (cP), F the mass flow (kg/h) entering the unit and MW_i and $Vmolar,_i$ are the molar weight (kg/kgmol) and volume (m^3/kgmol) of the component being extracted. The interfacial layer thickness calculation follows A. M. Bollen (1999, PhD Thesis, Dept. of Math. and Natural Sciences, University of Groningen), and is related to the viscosity of the mixture (η_{mixt}) by:

$$\delta(\eta) = 10^{3 \cdot 0.5 - 5} \cdot \eta_{mixt}^{0.5} \tag{3}$$

The RLLE networks can be searched efficiently using customised stochastic search methods to robustly and quickly extract optimal solutions (V.M. Ashley and P. Linke, 2004, Chem Eng Res. Des, 82:A8, 1). In this work, we have chosen Tabu Search to optimise the networks.

The approach will be illustrated with two examples in biochemical reactions. The first case study addresses extractive fermentation and will be presented to explain the individual aspects of the presented approach. We will then present an application to a complex biochemical reaction system: the aerobic growth of Saccharomyces Cerevisiae.

Results obtained in this work, compared with those obtained using detailed equilibrium & mass transfer models show that CPU times are reduced between 3 and 4 orders of magnitude. The resulting reactive extraction network superstructures are of similar size and numerical complexity as the corresponding homogeneous reactor networks. The approach has been proved to be highly computationally efficient as compared to reactive separation superstructure optimisation approaches. Model accuracies have been found suitable for high-level decision-making.