

## **Rapid screening of conceptual reactive separation process options**

Daniel Montolio-Rodríguez, Patrick Linke\*

Centre for Process & Information Systems Engineering

School of Engineering, University of Surrey, Guildford, Surrey, GU2 7XH, U.K.

### **Abstract**

We present a novel network optimisation-based approach that allows to quickly determine, whether the application of reactive liquid-liquid extraction (RLLE) is a promising option for reactive equilibrium systems, or for systems where reactions are inhibited by product formation. The approach provides conceptual information on the design of the reaction process in terms of feeding, bypassing and mixing patterns for reactive phases as well as on the existence of reactive separation sections within the network. The approach is highly computationally efficient since the superstructure model contains only the balance equations for the reactive phase. Such simplification is achieved with the help of a LLE transfer rate expression that has been developed from the work by Zheng et al. (1998), to predict the mass transfer from the reactive phase. A stochastic optimisation method, in the form of Tabu Search (TS), is used to explore the network. The approach is illustrated with two biochemical examples. The first one addresses extractive fermentation and will be presented to explain the individual aspects of the presented approach. The second presents an application to a complex biochemical reaction system: the aerobic growth of *Saccharomyces Cerevisiae*.

**Keywords:** Reactive Liquid-Liquid Extraction, Tabu Search, Conceptual Process Synthesis

### **1. Introduction**

A vast range of design options for chemical processes are available and engineers constantly face the difficult task to judge whether or not a design option is beneficial. Process choices in early design stages is challenging due to the limited time available, a lack of conceptual support tools and the large number of possible options. Optimisation can help to choose the most outstanding option, but tools are currently limited by the mathematical and combinatorial complexities of the problem and graphical methods (Horn, 1964, Glasser et al., 1987) are limited by dimensionality problems and modelling flexibility. Typical superstructure optimisation methods require high computational efforts to handle the highly non-linear kinetic and phase-equilibrium models involved.

---

\* Author to whom correspondence should be addressed: p.linke@surrey.ac.uk

Accordingly, it is currently impossible to screen reliably and quickly RLLE process options to compare their potential with that of other alternatives.

We present here a conceptual design tool that allows quick screenings of RLLE process options in order to identify trends of structures, which will guide a posterior optimisation process. The initial search area will be highly conceptual so that later optimisations with rigorous models can be initialised. In the following section we present the modelling and theoretical aspects of the approach presented here in order to tackle these problems. Section 3 presents results and comparisons of two case studies followed by the conclusions.

## 2. Modelling and theoretical aspects

### 2.1 Superstructure network optimisation

Superstructure optimisation of reactive systems was first presented by Achenie and Biegler (1986), who applied deterministic techniques in the form of non-linear programming (NLP). Later work on superstructure optimisation in reaction networks includes Kokossis and Floudas (1991), Marcoulaki and Kokossis (1996), Mehta and Kokossis (1997), Linke and Kokossis (2003). Efforts addressed isothermal reactor networks and were later extended to include nonisothermal and multiphase systems, including reaction/reactive separation. These extensions quickly lead to model complexities which resulted in severe computational problems if applied to complex problems. The long computational times limit the suitability of the multiphase and reaction-separation developments for conceptual screening of processing options at initial project stages.

Based on previous superstructure developments for single-phase systems (Kokossis and Floudas, 1991) 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. Conventional chemical reaction and LLE processes as well as both processes integrated, are explored in every unit. Conceptual information on the design of the reaction process in terms of feeding, bypassing and mixing patterns only for reactive phases are provided. Information regarding the mass separating agent (solvent) phase is mapped onto the superstructure model of a single-phase reactor network. The aggregation is achieved with the help of a transfer rate expression for the LLE processes, which predicts possible mass transfer from the reactive phase based on composition and solvent properties. The mass transfer rate expression has been derived following the work by Zheng et al. (1998) and validated with rigorous simulations for a large number of LLE systems. The expression for the transfer of component  $i$ , is:

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

where *Carrier* indicates the reactive phase,  $\dot{F}_{out}$  the outlet volumetric flow (m<sup>3</sup>/s) from

the unit,  $K_D$  the distribution coefficient,  $R$  the volumetric ration between extractive and reactive phase,  $C_i$  the concentration ( $\text{kg}/\text{m}^3$ ) of the component being extracted,  $\delta$  the interfacial layer thickness (m) and  $Param$  is given by:

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

where sub-indexes  $C$  refer to carrier and  $S$  to solvent phases.  $\eta$  is the viscosity (cP),  $F$  the mass flow ( $\text{kg}/\text{h}$ ) entering the unit and  $MW_i$  and  $V_{\text{molar},i}$  are the molar weight ( $\text{kg}/\text{kgmol}$ ) and volume ( $\text{m}^3/\text{kgmol}$ ) of the component being extracted. The interfacial layer thickness calculation follows Bollen (1999), and is related to the viscosity of the mixture ( $\eta_{\text{mixt}}$ ) by:

$$\delta(\eta) = 10^{3-b-5} \cdot \eta_{\text{mixt}}^b \quad (3)$$

The viscosity is assumed to depend on the composition of the mixture as follows:

$$\ln(\eta_{\text{mixt}}) = \sum_i x_i \cdot \ln(\eta_i) \quad (4)$$

where  $x_i$  and  $\eta_i$  are the mass fraction and viscosity for each component in the mixture.

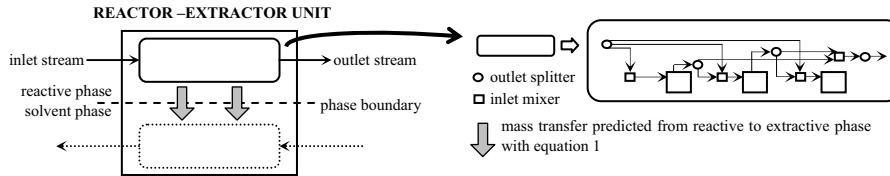


Figure 1. Illustration of reactive-extractive units

## 2.2 Optimisation

Tabu Search (Glover 1993) is an iterative neighbourhood stochastic search method that incorporates artificial intelligence techniques. TS applications are found in batch plant process design (Cavin et. al., 2004), heat exchanger networks (Lin & Miller, 2004) and reaction-separation systems (Linke & Kokossis, 2003). At each iteration, a neighbourhood around the current state is explored and several moves (the number of which equals the size of the neighbourhood), are executed in order to search for a better performance than the current state. A short-term memory is incorporated in the form of a Tabu List. The list contains the latest movements, and reverse ones associated with them are not considered when applying acceptance criteria, thus avoiding cycling in certain locally optimal states. The best objective in the new neighbourhood is chosen, and if not related with the current tabu list, this new state corresponds to the initial one for the next iteration. Aspiration criteria are introduced to decide if a move is executed despite being in the Tabu List to take into account that moves in the list can attain potential previously unvisited states. In this work TS is terminated either when the number of iterations without objective improvement reaches a certain number (here  $IT_{\text{unsuccessful}} = 50$ ) or when a maximum number of iterations has been completed (here  $IT_{\text{max}} = 500$ ). The last criterion is included to avoid excessively elevated CPU times.

### 3. Examples

#### 3.1 Production of Ethanol

Liquid-Liquid extraction is commonly used to recover ethanol from reactors where fermentations have taken place. Fournier (1986) considered improving the ethanol (EtOH) productivity by extracting it, as it is being produced through glucose (Glu), by the biological scheme:



Linke (2001) optimised reaction/reactive separation superstructures for the ethanol extractive fermentation using dodecanol as solvent. The objective function for this case was set to:

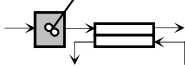
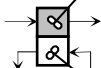
$$J = \frac{N_{\text{EtOH},S}^2}{N_{\text{Glu},C} \cdot N_S} \cdot 100 \quad (6)$$

Where  $N$  is expressed in kg/hr and  $N_{\text{Glu},C} = \max(N_{\text{Glu},C}, N_{\text{min}})$  with  $N_{\text{min}} = 1.0$  kg/hr. Kinetics (Fournier, 1986) are given by:

$$r_{\text{Cell}} = 0.461 \cdot \frac{C_{\text{Gluc}} \cdot C_{\text{Cell}}}{C_{\text{Gluc}} \cdot 0.315} \left(1 - \frac{C_{\text{EtOH}}}{87.5}\right)^{0.36}, \quad r_{\text{Gluc}} = -9.452 \cdot r_{\text{Cell}}, \quad r_{\text{EtOH}} = 4.254 \cdot r_{\text{Cell}} \quad (7, 8, 9)$$

Table 1 provides a comparison of results obtained in this work for the optimisation of two reference case studies, with those ones obtained by Linke (2001) using detailed equilibrium & mass transfer models. Both models show very similar results. Conversions, volumes and objective values are practically identical, whereas CPU times for the novel approach presented, are between 3 and 4 orders of magnitude smaller.

Table 1. Comparison of results<sup>1</sup>

	Linke (2001)	This work	Structure ( <input checked="" type="checkbox"/> Reaction <input type="checkbox"/> Extraction)
Objective	3.66	4.46	
Glu. conversions (%)	60.5	60.5	
CPU (sec)	1.50·10 <sup>3</sup>	4.55	
Units volume (m <sup>3</sup> )	8.7 (reactor) 1.3 (extractor)	8.5 (reactor) 1.4 (extractor)	Classical design, S=1680 kg/h
Objective	6.46	5.99	
Glu. conversions (%)	84.2	84.6	
CPU (sec)	1.81·10 <sup>3</sup>	0.55	
Unit volume (m <sup>3</sup> )	10.0	10.0	Extractive fermentor, S=1396 kg/h

<sup>1</sup> CPU times correspond to the optimisation of volumes, recycles and bypasses of the system. Number of units, solvent flow and reaction and/or extraction options were preset.

A complex network is optimised next. Up to three synthesis units are allowed in the network. The network volume is limited to 10 m<sup>3</sup>. Two sets of eleven runs each based on different initial structures with dodecanol as extracting agent are searched using TS. Again a comparison of results between the two works is found in Table 2. The conceptual structures found in this work show a clear trend of countercurrent contacting with reactive separation dominating at the inlet and separation at the outlet of the reactive phase. These conceptual results can be used to set up the detailed, time-consuming optimisations.

Table 2. Resulting structure for a complex network

	Aver	Max	Min	Optimal structure ( <input type="checkbox"/> Reaction <input type="checkbox"/> Extraction)
<b>Screening results</b>				
Objective	$6.48 \cdot 10^3$	$6.48 \cdot 10^3$	$6.48 \cdot 10^3$	
CPU (sec)	$1.06 \cdot 10^2$	$1.89 \cdot 10^2$	71.1	
Conversion <sup>1</sup>		>99.9%		Volume <sup>1</sup> (L) 4.00 4.40 1.49
<b>Detailed optimisation</b>				
Objective		1230		
CPU (sec)		-		
Conversion		>99.9%		Volume (L) 4.33 5.13 0.54
<b>Linke (2001)</b>				
Objective		840		
CPU (sec)		55548		
Conversion		>99.9%		Volume <sup>2</sup> (L) 5.11 1.40 3.48

<sup>1</sup>Best of 11 runs based on different initial structures.

<sup>2</sup>Only direct connections between units in solvent phase are shown in the optimal structure.

For demonstration purposes, we have carried out a detailed optimisation using the structure identified in the screening stage (this took approximately 3 minutes of CPU time). The optimised structure yields an objective function value of 1230, which outperforms the structure identified in Linke (2001). In this respect, in cases where good initial structures are used, the optimisation search is robust and efficient, and better results are obtained. Clear trends are identified with the approach as compared to the many streams that are present in results from detailed superstructures. The detailed optimisation in this work identifies a third unit where reaction takes place. This may be caused by small traces of glucose still reacting.

### 3.2 The aerobic growth of *Saccharomyces Cerevisiae*

Lei et al. (2001) proposed a growth mechanism for *Saccharomyces Cerevisiae* consisting on 12 reactions, which are summarised in Figure 2. Rate equations, parameters, explanation and details about kinetics can be found in Lei et al. (2001).

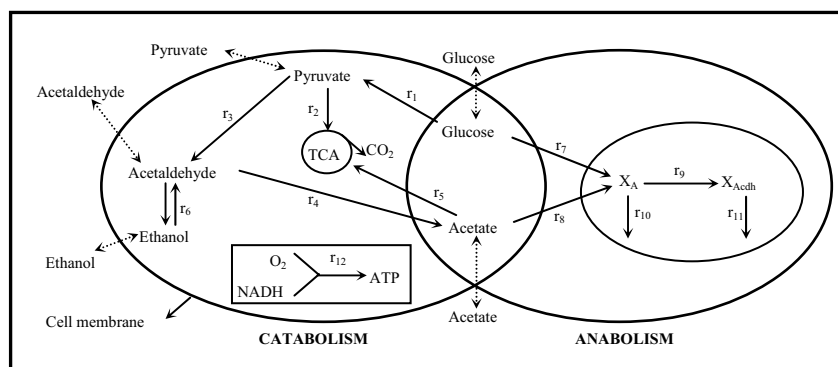


Figure 2. *Saccharomyces Cerevisiae* reaction path (Lei et al., 2001)

Ashley (2004) studied this case for a reactor network and same conditions as she took are adopted: 10 different initial structures, 4 maximum units, 30 litres as a maximum unit volume, 50 litres as maximum structure volume and a neighbourhood size of 10 for TS. Flow rates are: glucose 14 g/s, ethanol 0.13 g/s, biomass X 0.002 g/s, X<sub>A</sub> 0.1g (g

biomass X)<sup>-1</sup>, X<sub>Ac<sub>dh</sub></sub> 0.0075 g (g biomass X)<sup>-1</sup> in 1 kg/s of aqueous solution (Lei and Jorgensen, 2001). Ethanol is once more the desired product, and its total yield, the objective.

Table 3. Results for *Saccharomyces Cerevisiae* case study.

	Aver	Max	Min	Optimal structure <sup>1</sup> ( <input type="checkbox"/> Reaction <input type="checkbox"/> Extraction)
<b>Ashley (2004)</b>				
Objective	4.67	5.25	0.23	
CPU (sec)	3.63·10 <sup>3</sup>	8.37·10 <sup>3</sup>	72.8	Volume (L) 8.04 0.81 1.69 1.11
<b>This work</b>				
Objective	4.75	5.28	0.79	
CPU (sec)	6.95·10 <sup>3</sup>	1.45·10 <sup>4</sup>	1.75·10 <sup>3</sup>	Volume (L) 4.29 1.52 1.95 0.14

<sup>1</sup> Best of 10 runs based on different initial structures.

The use of RLLE for this case at the considered conditions does not improve appreciably the objective function. However it is proved that with an increase only of 90% in the average CPU time, RLLE as a process design option is efficiently screened and its potential can be effectively assessed.

## 4. Conclusions

We have presented a novel approach to screen RLLE networks. The approach is based on mapping the information regarding the mass separating agent (solvent) phase onto the superstructure model of a single-phase reactor network. This work has addressed the implementation of the approach into two biochemical examples. The approach has been proved to be highly computationally efficient as compared to reactive separation superstructure optimisation approaches. Model accuracies appear appropriate for high-level decision-making.

## References

- Achenie, L. K. E., Biegler L. T., 1986, *Ind. Eng. Chem. Fund.*, 25: 621.  
 Ashley, V., 2004, PhD Thesis, School of Engineering, PRISE, University of Surrey.  
 Ashley, V., P. Linke, 2004, *Chem. Eng. Res. Des.*, 82:A8, 1.  
 Bollen, A. M., 1999, PhD Thesis, Dept. of Math. and Natural Sciences, University of Groningen.  
 Cavin, L., Fischer, U., Glover, F., Hungerbuhler, K., 2004, *Comp. Chem. Eng.*, 28: 459-478.  
 Fournier, R.L., 1986, *Biotech. & Bioeng.*, 28, 1206.  
 Glasser, D., Hildebrandt, D., Crowe, C., (1987), *Ind. and Eng. Chem. Res.*, 26: 1803-1810.  
 Glover, F., 1993, A user's guide to tabu search, *Annals in Operational Research*, 41: 3.  
 Horn, F., (1964), Third European Symposium on Chemical Reaction Engineering, 293-303.  
 Kokossis, A. C., Floudas, C. A., 1991, *Chem. Eng. Sci.*, 46: 261.  
 Lei, F., M. Rotboll, S. B. Jorgensen, 2001, *J. of Biotech.* 88, 205.  
 Lin, B., D. C. Miller, 2004, *Comp. Chem. Eng.*, 28: 2287-2306.  
 Linke, P., 2001, PhD Thesis, Dept. of Process Integration, UMIST, University of Manchester.  
 Linke, P., A. Kokossis, 2003, *Comp. Chem. Eng.*, 27: 733-758.  
 Marcoulaki, E. C., Kokossis, A. C., 1996, *Comp. Chem. Eng.*, 20: S231-S236.  
 Mehta, V. L., Kokossis, A. C., 1997, *Comp. Chem. Eng.*, 21: S325.  
 Zheng, Z., J. Lu, D. Li, G. Ma, 1998, *Chem. Eng. Sci.*, 53:13, 2327.

## Acknowledgements

We would like to acknowledge funding from the EPSRC (GR/R61581/01).