

Integrated Design of Optimal Processes and Molecules: A Framework for Solvent- Based Separation and Reactive-Separation Systems

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Abstract

The presented work addresses the integrated design of solvent molecules with separation and reactive-separation process systems. The proposed design philosophy relies on extensive structural optimization both at the solvent and process synthesis stage and allows the identification of solvent molecules based on process performance criteria. It employs multi-objective optimization technology in order to capture the manifold trends and trade-offs characterizing the solvent design space, while avoiding the introduction of unnecessary biases or user defined assumptions. The obtained solvent design information is effectively incorporated into the process synthesis stage through the use of data mining techniques in the form of clustering. The process synthesis framework is sufficiently flexible to accommodate for separation or reactive-separation superstructures of the most general type. The presented method is illustrated through examples on the design of solvents for liquid-liquid extraction, gas-absorption, extractive distillation and extractive fermentation processes.

Keywords: Solvent synthesis, Reaction- separation process synthesis, Multi-objective optimization, clustering

1. Introduction

The design philosophy generally followed in computer aided molecular design (CAMD) solvent synthesis involves screening for solvent molecules based on pre-specified thermodynamic property objectives and constraints that are expected to have a positive impact in process performance (Marcoulaki and Kokossis, 2000a). Clearly, following this approach the synthesis drives involved in process synthesis are misrepresented and the results are prematurely biased towards presumably optimal options.

In contrast, methods that facilitate the integrated CAMD solvent and process synthesis by accounting for process and solvent design interactions have also been proposed (Stefanis and Pistikopoulos, 1998; Hostrup et al., 1999). The design philosophy followed by these methods involves screening for solvent molecules based on pre-specified property targets. The molecules meeting these targets are further screened with regards to their process performance either by participating in process simulation or

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process optimization. In these cases sub-systems of the overall system are targeted, thus the results are liable to assumptions regarding the size of the solvent-process design space. On the other hand, some methods (Marcoulaki and Kokossis, 2000b; Wang and Achenie, 2002; Linke and Kokossis, 2002) propose the simultaneous optimization of the formulated solvent-process superstructure which may involve separation and reactive separation processes. The enormous amount of solvent-process design options and the complexities caused by the non-convexities of the employed models introduce low confidence with regards to the optimality of the obtained results.

This work addresses the previously presented limitations through a generic and systematic methodology that will robustly determine performance targets for integrated solvent and separation/reaction-separation process systems. Based on our previously presented work (Papadopoulos and Linke, 2004) multi-objective optimization is used at the solvent design stage in order to identify optimum solvent candidates without a priori excluding options that will potentially be useful at the process design stage. The obtained solvent design information is systematically introduced into the process synthesis stage through the efficient exploitation of this information using a data mining technique in the form of clustering. This work focuses on the development of an effective clustering strategy as well as on the exemplification of the proposed framework through extensive solvent-separation and solvent-reaction-separation synthesis cases.

2. Synthesis of solvent-separation and solvent-reaction-separation processes

2.1 Multi-objective CAMD solvent synthesis-Overview

In the proposed unified framework for solvent and process design CAMD solvent synthesis is performed using multiple objective optimization (M.O.O.) technology (Papadopoulos and Linke, 2004a). This formulation of the optimization problem allows unnecessarily premature assumptions about the process requirements to become redundant as each objective is treated independently, freed of artificial constraints. While the interactions among a variety of objectives are thoroughly explored, the optimization results in a comprehensive set of solvents that represents molecules with a broad range of structural, physical and economic characteristics regardless of the process task in which they will be utilized. This design philosophy allows all the underlying trends and trade-offs amongst the properties of the candidate optimal molecules, as well as the structure- property relations to be revealed. The design information included in the obtained solvent set can then be systematically exploited in the process synthesis stage so that the computational requirements remain largely unaffected.

2.2 Efficient exploitation of solvent design information in process synthesis

The obtained solvent set from the M.O.O. CAMD solvent synthesis contains all the important solvent design information that must be incorporated into the process synthesis stage. We propose the formation of *molecular clusters* according to physical properties so that all the molecules in each cluster are similar to each other and as different as possible to the molecules in other clusters. The properties of the molecule

that lies closest to the cluster centre can be considered to be approximately representative of the properties of the other molecules within the cluster and a representative molecule from each cluster can be introduced into the process synthesis. The result of the process performance of each representative molecule for each cluster will reveal the cluster that includes the molecules that are ideally suited for the process, thus rejecting the molecules that belong to other clusters. An iterative application of this procedure will result into a tree-like representation for the optimization problem. In each iteration the various branches of the representation will focus the search on a decreased solvent solution space and the size of the problem will decrease without discarding important solvent information.

The appropriate directions for the development of the branches involved in the proposed representation are selected based on a set of decision criteria. In summary four major criteria have been identified: the number of clusters, the distances between the cluster centres and within each cluster, the number of data points in each cluster and the process performance of the molecule closest to the cluster centre. These criteria describe the clusters both in terms of statistical partitioning information and of cost of solvent/process configuration for each cluster.

Each individual criterion provides a sense of quantity of what it describes, but, as the criteria operate independently from each other, they only identify the overall trends and directions of the clustering paths in a qualitative manner. A function is required in order to unite and quantify the proposed criteria under a single index. This function will suggest new clustering paths that are likely to lead to optimal clusters. We therefore define the *clustering heuristic probability* as follows:

$$P = \exp[-(E_{new} - E_{min})/(a \cdot T_{old})] \quad (1)$$

$$a = 1 - SSB/(SSB + SSW) \quad (2)$$

Although the clustering heuristic probability P follows the Simulated Annealing (SA) probability function, the aim of this approach is to model the uncertainties involved in the clustering decisions and not to perform a SA search. This approach capitalizes on the knowledge regarding the physical characteristics of the clusters in order to identify clusters that are likely to include a molecule that can produce a solvent/process configuration with a cost lower than the best existing one. In this context the numerator of the probability fraction compares the cost of a cluster centre E_{new} with the best existing cost E_{min} . In the present case, the annealing temperature T can be appropriately reduced by a quantity a , that is a function of the available clustering information. The term a (Eq.4) is the R-Squared (RS) clustering index (Halkidi et al., 2002) ranging between 0 and 1 and represents a measure of between clusters difference (SSB) and within clusters homogeneity (SSW). For each cluster the annealing temperature is reset to an initial value (T_{old}) which is selected based on the discussion found in Aarts and van Laarhoven (1985). The advantage of using the clustering heuristic probability is that it allows the decision maker to quickly assess the problem and adjust the followed clustering policies. However, the understanding of the conditions of the overall problem at hand through the decision criteria previously discussed should always supplement the decisions made with the clustering probability.

2.3 Process synthesis

The process synthesis framework utilises stochastic optimization in combination with generic superstructures which have proved beneficial for the synthesis and optimization of separation (Papadopoulos and Linke, 2004b) and reaction/separation (Linke and Kokossis, 2003) processes. The process models incorporated in the superstructures represent reaction, reactive separation and separation options in generic reaction mass/exchange (RMX) units. An RMX unit can provide a conceptual or rigorous representation of all possible reaction or mass exchange phenomena taking place during process synthesis. Separation task units supplement the RMX units by offering a conceptual representation of separation options based on emerging separation paths, while leaving the rigorous representation of separation processes to RMX units

3. Illustrative examples

3.1 Design of solvents for separation processes

The proposed method is illustrated with three applications on the integrated design of solvents and liquid-liquid extraction/recovery (P_1), gas-absorption/recovery (P_2) and extractive distillation (P_3). The mixtures that are being separated are n-butanol-water for P_1 , air-acetone for P_2 and cyclohexane-benzene for P_3 . An example of generation of new clustering paths based on the methodology analyzed in section 2 is shown in Figure 2 for P_2 . Each table shows the number of clusters (Cl), the objective function value (OF), the number of points in each cluster (Nm) and the probability (P). Clusters 1 and 4 of iteration 1 present higher probabilities of including a molecule that benefits the process because of low OF values in combination with a large Nm. The information regarding OF and Nm as well as the rest of the decision criteria analyzed in section 2 are transparently represented by the reported probability values. On the other hand, the certainty that clusters 2 and 3 do not include beneficial molecules is high and this is also reflected in the probability values. Therefore, clusters 1 and 4 are further developed into the sub-clusters of iteration 2.

Iteration 1				Iteration 2			
Cl	OF(k\$/yr)	Nm	P	Cl	OF(k\$/yr)	Nm	P
1	1971.7	34	0.83	1	1712.3	4	0.41
2	3155.2	2	0.17	2	1925.9	21	0.56
3	3190.1	6	0.50	3	2030.9	8	0.46
4	1278.3	69	0.89	4	2510.8	1	-

Cl	OF(k\$/yr)	Nm	P
1	1424.3	22	0.86
2	1640.9	38	0.87
3	1457.8	1	0
4	1383.0	8	0.75

Figure 1. Clustering decisions for (P_2)

Following the presented clustering methodology it is possible to significantly reduce the computational time required for the identification of the cluster with the optimal solvent-process configuration. The number of molecules screened with regards to their

process performance in cases P₁, P₂ and P₃ are 18%, 15% and 25% of the initially obtained solvent set, respectively. These results represent a level of reduction from the initial solvent set that can be achieved following an approach that involves a low risk of missing the optimum molecule. Depending on the requirements of the problem, the method allows the user to set the threshold of the probability value below which clusters are rejected.

Table 1 shows the optimum molecules identified for each case using the proposed methodology. For P₁ the best molecule designed using M.O.O. is better in terms of process cost (OF) than the molecules designed using single objective optimization (S.O.O.). Furthermore, it is shown that by changing the objectives in the S.O.O. cases from solvent selectivity (S_s) to solvent distribution coefficient (M) the process performance of the obtained molecules deteriorates. The same happens for case P₂ as well when instead of using vapour pressure (P_{vp}) as the objective in S.O.O. we use solute solubility (S_b). Finally, in case P₃ the process performance of the proposed molecule overcomes the process performance of industrial solvents or solvents reported in published literature.

Table 1. Designed molecules and comparisons

Case	Method	Molecule	OF(k\$/yr)
P ₁	M.O.O.	CH ₃ -CH ₂ -CH(CH ₃)-CH ₂ (C=O)-CH ₂ -CN	153.8
	S.O.O. (S _s)	CH ₃ -C(CH ₃) ₂ -CH ₂ (C=O)-CH ₂ -CN	169.2
	S.O.O. (M)	CH ₂ =CH-C(CH ₃) ₂ -(CH ₂) ₂ -(CH ₃)C(H(C=O)) ₂	183.1
P ₂	M.O.O.	CH ₃ -O-CH(Br)CH(Br)Cl	486.0
	S.O.O.(P _{vp})	FCH ₂ O-C(Br) ₂ -CH ₂ Cl	613.3
	S.O.O.(S _b)	CH ₂ =C(-OCH ₃)-CH ₂ -Cl	657.7
P ₃	M.O.O.	FCH ₂ -O-C-(HC=O) ₃	317.2
	Industrial ^a	Aniline	711.8
	Literature ^a	n-methyl-2-pyrrolidone	913.8

^a Results presented by van Dyk and Nieouwoudt (2000)

3.2 Design of solvents for reactive separation

The second example involves the design of solvents for the extractive fermentation of ethanol. Details regarding the implementation of this example can be found in Linke and Kokossis (2002).

Table 2. Molecules for the design of extractive fermentation processes

ID	Molecule	EF	S_{EF}^{fl} (kg/hr)	EFN	S_{EFN}^{fl} (kg/hr)
S ₁	CH ₃ -O-CH ₂ -C(CH=CH ₂) ₂ -(OH)C(CH ₃)-CH=CH ₂	1630.2	768	8100	400
S ₂	Dodecanol	6.46	1396	960	2326
S ₃	Large aromatic	-	-	3135	2000
S ₄	Octane	13.91	1061	-	-
S ₅	Isopropyl-propionate	15.77	1321	-	-

A desired solvent-process superstructure must facilitate the complete conversion of glucose in the aqueous phase and the complete extraction of ethanol, whilst utilizing a minimum amount of solvent flow that dissolves as little glucose as possible. The

employed objective function is a dimensionless equation incorporating these trends. The clustered solvent molecules are first screened with regards to their process performance in the synthesis of a well-mixed extractive fermentor (EF). Molecules with high process performance in EF synthesis are introduced in generic extraction fermentation network synthesis (EFN). Molecule S_1 of Table 2 is designed using the presented method and molecule S_2 has been proposed by Fournier (1986) as an ideal solvent. Molecule S_3 has been proposed by Linke and Kokossis (2002) and is not shown for space economy. Finally, molecules S_4 and S_5 have been proposed by Wang and Achenie (2002). The results show that the already high performance of the EF structure can be significantly improved by EFN synthesis. The structure of the EFN allows the use of almost half of the solvent quantity (S_{EFN}^f) required in EF (S_{EF}^f). The proposed molecule S_1 performs better than all the molecules presented in literature and has lower toxicity than dodecanol, which is very important for extractive fermentation processes. Furthermore, molecules S_3 , S_4 and S_5 have been reported to be locally optimal, whereas following the proposed methodology we are confident that molecule S_1 is a globally optimal solution.

4. Conclusions

This presented work proposes a new technology for the integrated design of solvent and process synthesis. Molecules are designed for simultaneous optimality in a set of desired objectives using M.O.O. The obtained set of molecules is effectively introduced into the process synthesis through a clustering strategy that is especially designed to exploit the solvent design information, whilst reducing the amount of required computations. The methodology is exemplified through extensive examples in separation and reactive separation process synthesis. In all cases the obtained molecules outperform molecules designed using previously presented approaches. Overall, the proposed methodology demonstrates the systematic selection of solvents based on process performance criteria. This allows the introduction of confidence in the obtained solvent structures even in the most complex cases of the design of extractive fermentation networks.

References

- Fournier, R.L., 1986, *Biotech. & Bioeng.*, 28, 1206
- Halkidi, M., Batistakis, Y., Vazirgiannis, M., 2002, *SIGMOD Record*, 31(3)
- Hostrup M, Harper P.M., Gani, R., 1999, *Comp. & Chem. Eng.*, 23, 1395
- Linke P., Kokossis, A.C, 2003, *Comp. & Chem. Eng.*, 27(5), 733
- Linke, P., Kokossis, A., 2002, In proceedings of ESCAPE-12, Elsevier
- Marcoulaki E.C., Kokossis, A.C., 2000a, *Chem. Eng. Sci.*, 55(13), 2529
- Marcoulaki, E.C., Kokossis, A.C, 2000b, *Chem. Eng. Sci.*, 55(13), 2547
- Papadopoulos A., Linke, P., 2004a, In proceedings of ESCAPE-14, Elsevier
- Papadopoulos A., Linke, P., 2004b, *Comp. & Chem. Eng.*, 28, 2391
- Stefanis, S.K., Pistikopoulos, E N., 1998, *Comp. & Chem. Eng.*, 22(6), 717
- Van Dyk, B, Nieuwoudt, I., 2000, *Ind. Eng. Chem. Res.*, 39(5), 1423
- Wang, Y., Achenie, L.E.K., 2002, *Fluid Phase Equilibria*, 201, 1