

Continuous-Molecular Targeting for Integrated Solvent and Process Design

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An integrated design of processes and solvents is a prerequisite for achieving truly optimized solvent-based processes. However, solving the full integrated problem in a single optimization is usually not possible even for a predefined process topology due to the required discrete choices between molecular structures. Current approaches therefore mostly decompose the integrated problem into a process design and a molecular-design subproblem. The interaction between these subproblems is usually limited in practice, and a direct link between process performance and molecular characteristics of the solvent is not achieved. In this work, a novel methodology for the integrated process and molecular design problem is suggested where the discrete molecular decisions in the integrated design problem are circumvented by defining a hypothetical molecule. The approach is building upon a molecular-based thermodynamic model, where the parameters representing a molecule are treated as continuous. These parameters are optimized together with other process parameters, leading to an ideal hypothetical target molecule (represented by a set of parameters) and a corresponding optimized process. Only in a subsequent step, the parameters of the thermodynamic model representing the hypothetical molecule are mapped onto an existing optimal solvent. The method is illustrated for the design of solvents for carbon dioxide capture where the benefits of the integrated design approach are demonstrated. The perturbed-chain-polar-statistical-associating-fluid theory (PCP-SAFT) equation of state is used as a thermodynamic model. The framework introduced is generic in nature and thus applicable beyond the study of solvents to the integrated design of materials and processes in general.

Introduction

Solvent design is one of the hallmark examples of product design due to the important role that solvents play in the chemical industries.¹ Solvent-based separations are employed in almost all chemical, petrochemical, biochemical, and pharmaceutical processes. The selection of a suitable solvent is thereby the key enabling step for the feasibility and the efficiency of a separation. Selectivity for specific compounds is often an important requirement for a solvent but other properties such as capacity, viscosity, or toxicity have also to be considered. A final choice for a solvent should therefore reflect the trade-off between these properties.²

However, the definition of an objective set of target properties for a solvent is by itself an intricate problem due to the strong interaction between solvent properties and the process at hand. This interaction is crucial for the sound trade-off among the target properties. The ultimate goal is therefore the integrated design of the solvent molecule and the corresponding process.³

Due to the discrete nature of the selection among molecules, the solution of such a fully integrated design problem in a single mathematical optimization is usually prohibitive for most practical problems.⁴ Available approaches have therefore focused on the decomposition of the integrated design problem into interlinked subproblems.^{5,6}

With this study, we propose to utilize the detailed molecular picture underlying modern thermodynamic models in order to achieve a close integration between solvent and process design. In recent years, improvements in the theory of dense complex fluids led to the development of advanced thermodynamic models such as the COSMO-RS approach⁷ or the SAFT family

of equations of state,^{8–13} based on the statistical associating fluid theory.^{14–18} Since these thermodynamic models are based on a coarse-grained but still very detailed molecular picture, they achieve a close correspondence between a set of model parameters and a specific compound. This feature is exploited in the proposed methodology to establish a new route toward computer-aided molecular design.

In this work, a real solvent is represented by a set of pure component parameters of an advanced thermodynamic model. For the integrated solvent and process design, we propose a two-step procedure: First, a hypothetical target molecule is obtained by regarding the solvent pure component parameters as free continuous variables during process optimization. This *continuous-molecular-targeting* approach to *computer-aided-molecular design* (CoMT-CAMD) thus achieves the direct coupling between solvent and process properties while circumventing the discrete selection in the integrated design problem. Only in a second step, the hypothetical target molecule is mapped onto real solvent molecules.

The suggested CoMT-CAMD framework is generic in nature and it is here based on the perturbed-chain-polar-statistical-associating-fluid theory (PCP-SAFT) equation of state.^{9,19–22} Whereas most previous CAMD approaches employ thermodynamic models applicable at low pressures only, the integration of an equation-of-state model allows for a sound description of high-pressure systems.²³ Furthermore, the molecular picture underlying PCP-SAFT has recently been extended to account for multipole interactions.^{19–22} The latter development is particularly important for the study of solvent systems where the right polarity is often a crucial property.

The integrated solvent and process-design problem and current methods for approaching this problem are briefly introduced next. Then, the proposed CoMT-CAMD approach is presented. The method is subsequently demonstrated for the case of carbon dioxide capture by an absorption/desorption process. The results show that the CoMT-CAMD method

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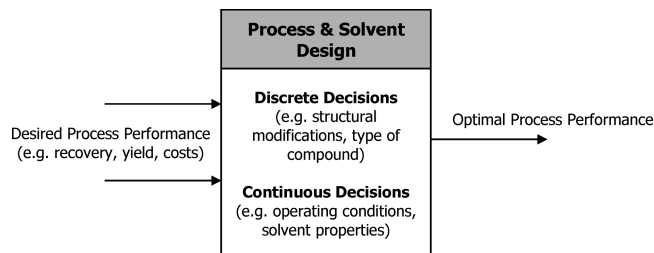


Figure 1. Desired integrated solvent and process-design problem.

provides a framework for a truly holistic design and allows for nonincremental advances in the development of novel solvents.

Integrated Solvent and Process Design

In practice, solvent selection is often still based on experience and simple heuristics leading to suboptimal solutions. If experiments are involved, this selection procedure adds further cost and becomes time-consuming.²⁴ To provide for a systematic means to identify suitable solvents, computer-aided-molecular-design (CAMD) methods have been developed in recent years.¹ CAMD can be interpreted as the inverse of the property prediction problem: Given a set of target properties, a combination of structural groups of a molecule is sought that satisfies the property specifications.

It is difficult to a priori set these target properties for a solvent because they strongly depend on the considered process. The final evaluation of a solvent will usually be based on a process-wide objective (e.g., cost-, energy-, or entropy-efficiency). Plant-wide environmental issues have also to be taken into account.²⁵ Thus, solvent design should actually be linked to the process level. For extractive-distillation processes, Kossack et al.²⁶ recently showed that the assessment of solvents based upon shortcut process models already leads to significantly improved solvent candidates compared to the use of simple heuristic criteria.

The integrated design of the solvent molecule and the corresponding process is therefore highly desirable.³ The integrated design problem is illustrated in Figure 1. While it is quite straightforward to propose a general problem formulation for the integrated design,²⁷ its solution within a single mathematical optimization is prohibitive in most cases of practical interest due to the large amount of discrete variables. In practice, it is thus very difficult to simultaneously design solvents and processes.⁴

Molecular and process design have therefore traditionally been addressed in two separated problems with no or limited feedback between them as sketched in Figure 2.⁵ To achieve this decoupling, many design decisions have to be taken a priori usually based only on qualitative knowledge and experience.⁵ For example, the objective in the molecular-design subproblem as well as the candidate molecules considered in the process-design subproblem have to be specified as input to the procedure. Most importantly, while such a decoupled approach is convenient to apply, the interdependence between solvent properties and process variables is not reflected any more.

To introduce feedback between the two design subproblems, a reverse engineering approach has been followed in the literature: First, constraints on property values are obtained from a process-design optimization. In a second molecular design phase, components are generated that meet these constraints (Figure 3).^{5,6} While the reverse engineering CAMD-approach allows for the derivation of process-specific targets, a direct link between process performance and molecular characteristics of

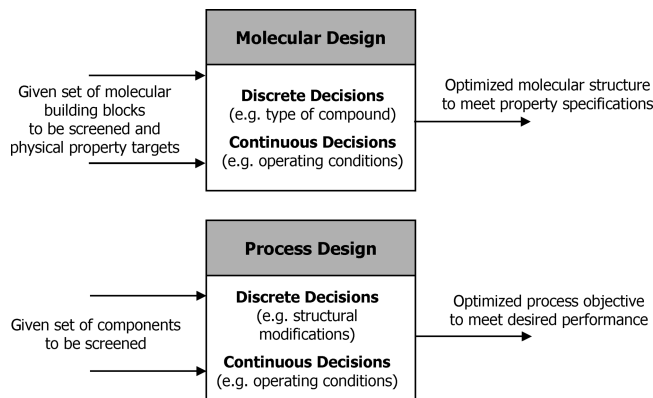


Figure 2. Traditional design approach based upon decoupled process- and molecular-design problems (adapted from the work of Eden et al.⁵).

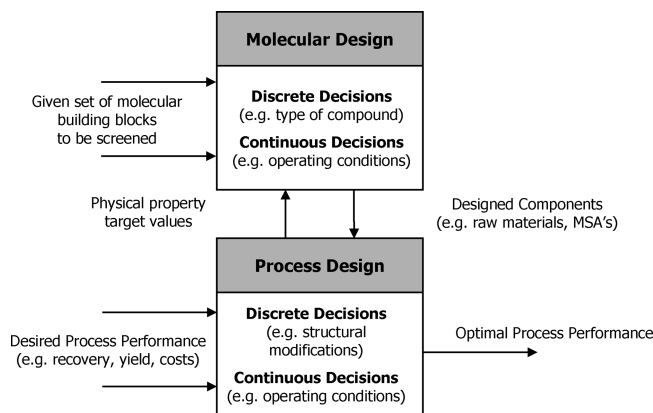


Figure 3. Reverse problem formulation for integrated process-product design (adapted from the work of Eden et al.⁵).

the solvent is not achieved. For the class of linear alkanes, Pereira et al.²³ recently developed a method to optimize the solvent chain length as part of process optimization by suitable preparameterization of their thermodynamic model for this class of molecules. The continuous-molecular-targeting framework introduced in the following provides a systematic framework to establish the direct link between solvent and process properties for general solvents.

Continuous-Molecular-Targeting Framework

Framework. In our view, a physically based thermodynamic model is central to truly link molecular characteristics to process performance. In a physically based model, a molecule is represented by a set of pure component parameters which correspond to clearly defined molecular attributes. In contrast to earlier thermodynamical models, these parameters do not lump many molecular-scale effects into one coefficient. Thereby, a close correspondence between a parameter set and a specific molecule is achieved. This correspondence is the key factor in the suggested approach.

Here, such a physically based model is employed for process design. Every candidate solvent is hereby represented by a discrete set of model parameters. Integrated solvent and process design thus corresponds to the simultaneous optimization of the process and the optimal selection between the discrete solvent model parameter sets. Due to the complex nonlinear structure of process-design problems combined with the vast discrete molecular-design space, the solution of such a mixed-integer nonlinear programming (MINLP) problem is very difficult for practical problems.

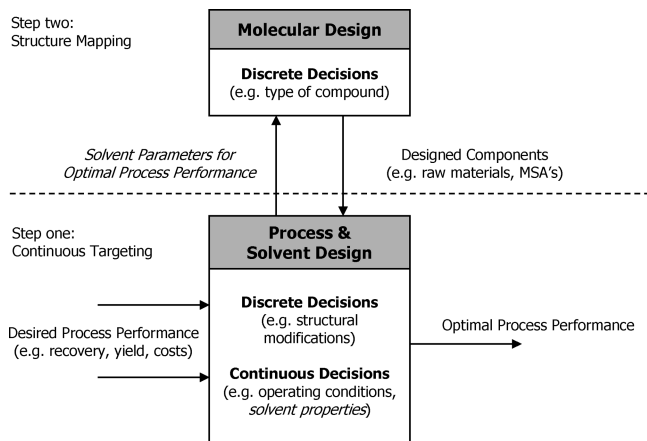


Figure 4. CoMT-CAMD problem formulation for integrated solvent and process design using a physically based thermodynamic model.

In the suggested approach, the MINLP problem is avoided through relaxing the discrete model parameters representing the solvent and allowing for a continuous search within the solvent parameter space. Thereby, continuous optimization methods can be employed to simultaneously optimize process settings and molecular characteristics of the solvent. The thermodynamic model thereby ensures the sound reflection of molecular properties on the process level such that the trade-offs between molecular and process-design decision are properly captured. While the approach is generic in nature, a prerequisite for it to be successful is a thermodynamic model that predicts mixture behavior with sufficient accuracy.

Relaxing the model parameters from their discrete values corresponds to introducing a hypothetical target solvent. The suggested approach thus truly achieves the integrated optimization of the process and the solvent—at the cost that the solvent found does no longer correspond to existing components. Still, by employing a physically based thermodynamic model, the hypothetical solvent found is described through a set of very realistic molecular attributes. These values form targets for a subsequent search of existing molecules showing similar attributes.

The resulting *continuous-molecular-targeting* approach to computer-aided-molecular design (CoMT-CAMD) thus achieves the integrated solvent and process-design problem in two steps (Figure 4):

- **Step one: Continuous targeting**
Both process variables and solvent parameters are simultaneously optimized in a continuous fashion by relaxing the solvent pure component parameters from their discrete values. This optimization yields both settings for optimal process performance and a hypothetical target molecule.
- **Step two: Structure mapping**
The hypothetical target molecule (characterized by a parameter set of a thermodynamic model) is mapped onto real substances. Only here, discrete decisions have to be taken.

While the approach still consists of two parts, molecular attributes are now directly assessed in process design. The two steps are described in more detail in the following.

Step one: Continuous Molecular Targeting. The goal of step one of the procedure is to obtain both the process-design settings and the parameter set for a hypothetical solvent from a simultaneous continuous optimization problem. For this purpose, the discrete solvent parameter set of the thermodynamic model is relaxed and a continuous search in the full parameter space

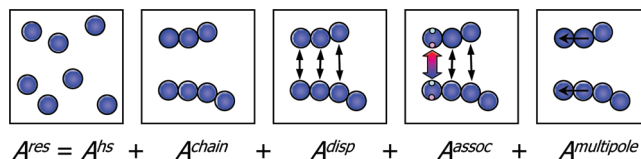


Figure 5. Resolved contributions to the residual Helmholtz energy in PCP-SAFT: hard spheres (hs), chain of hard spheres, dispersion, association interactions, and multipole effects.

is performed. The resulting optimization problem is then of the form

$$\max_{x,y} f(x) \quad (1)$$

$$\text{s.t. } h[x, \tilde{g}] = 0 \quad (2)$$

$$\tilde{g} - g(x, y) = 0 \quad (3)$$

$$c(x, y) \leq 0 \quad (4)$$

where x denotes the process variables and y denotes the pure component solvent parameters. The latter typically do not appear directly in the design objective $f(x)$ but could be integrated in principle. The process model is given by the equality constraints $h(x, g)$ where the thermodynamic quantities \tilde{g} computed from the models $g(x, y)$ enter. Process and solvent inequality constraints are summarized in $c(x, y)$.

For the integrated design problem (1), a standard NLP solver may be employed. Thereby, optimal process settings x^* and pure component parameters y^* of a hypothetical solvent are obtained. The resulting objective gives an upper bound for the process performance achievable by any molecule describable within the chosen thermodynamic framework. This information by itself is valuable in assessing the process design.

To perform the CoMT-step, three elements are required: the thermodynamic model, a process model, and an objective function. These are discussed next.

Thermodynamic Model: PCP-SAFT Equation of State. With the PCP-SAFT model,^{9,19–22} a physically based equation of state is employed in this work. This equation of state has been shown to allow for good predictions of phase behavior in complex mixtures. The molecular model underlying the PCP-SAFT equation of state is illustrated in Figure 5. For a detailed description of PCP-SAFT, the reader is referred to the original literature cited.^{9,19–22} In the present context, it is important that each molecule is represented in PCP-SAFT by a set y of seven pure component parameters. These seven parameters correspond to clearly defined molecular attributes:

- two geometric parameters describe the size and elongation, σ_i, m_i ;
- three energy-related parameters describe the dispersive attraction, the association energy, and the association volume, $\varepsilon_i/k, \varepsilon_i^{AB}/k, \kappa_i^{AB}$;
- two polar parameters specify the point dipole and the quadrupolar moments, μ_i, Q_i .

The idea of a physically based model is demonstrated by the fact that, e.g., the parameters for polar interactions can be based upon the dipole and quadrupolar moments obtained from independent sources such as quantum chemical calculations.^{19,20,28}

As an equation-of-state, PCP-SAFT provides a consistent description of all residual thermodynamic properties of a molecule. Given the seven parameters, the behavior in any process application is thus defined. Separate—and probably inconsistent—physical property models describing, e.g., phase transition enthalpies and saturation pressure are not required.

Even kinetic properties such as viscosity can be described based on the same molecular picture.^{29,30} In the present work, PCP-SAFT is used to compute residual heat capacities and enthalpies, pressures, densities, and equilibrium constants. For the ideal-gas contribution to the heat capacity, a simple correlation valid for organic solvents is introduced.

Process Model. The proposed method is very flexible with respect to the process model employed. In separation processes, process equations typically consist of material balances, equilibrium balances, summation equations, and energy (heat) balances (MESH). In addition, constraints on process variables (e.g., pressure limitation for safety) may be added. The process model obtains thermodynamic input from PCP-SAFT. The degrees of freedom of the process model serve as optimization variables in the continuous targeting step.

Objective Function. While classical solvent design methods had to focus on solvent properties only, process-wide objective functions can be incorporated in the presented CoMT-CAMD framework. The trade-off between different solvent properties is thus directly addressed through their implications on process behavior.

Process-wide objective functions could reflect aspects of cost, energy, or second-law efficiency. Even dynamic aspects such as process responsiveness could be taken into account in the process design as suggested in the work of Almeida-Rivera and Grievink.³¹ Different objectives can be employed to study the implications on solvent selection and process design.

Step Two: Structure Mapping. The continuous molecular targeting step outlined above yields process settings and optimal PCP-SAFT parameters y^* of a hypothetical solvent molecule. To implement these findings in practice, the solvent parameters have to be mapped onto real substances in the second step. Here, discrete decisions have to be taken.

Various approaches can be envisioned to implement this mapping. Group-contribution methods could provide a suitable tool. For the most advanced SAFT models, these methods are currently being developed.^{32–36}

In the present work, the structure mapping is performed by a database search. In the PCP-SAFT database, the potential solvents are represented by their parameter vector y . A preliminary criterion to find the real molecule closest to the hypothetical solvent could be based on the average absolute distance in parameter space

$$\Delta\text{AAD}(y) = \frac{1}{n_p} \sum_{i=1}^{n_p} |y_i - y_i^*|, \quad \text{with here: } n_p = 7 \quad (5)$$

Such a criterion can be computed very efficiently. The quality of the result would, however, strongly depend on the scaling of the individual parameters and different sensitivities with respect to different parameters are not accounted for.

For this purpose, a Taylor approximation is performed around the CoMT-optimum y^* to predict the expected loss in the objective function $f(x)$ for all database entries

$$\Delta\text{TA}(y) = J(y^*)(y - y^*) + \frac{1}{2}(y - y^*)^T H(y^*)(y - y^*) \quad (6)$$

$$\text{with } J_i(y^*) = \left. \frac{\partial f}{\partial y_i} \right|_{\{h=0, g=0, c \leq 0\}}, \quad \text{and } H_{ij}(y^*) = \left. \frac{\partial^2 f}{\partial y_i \partial y_j} \right|_{\{h=0, g=0, c \leq 0\}} \quad (7)$$

where J and H denote the Jacobian and the Hessian of problem (1) available from the optimization in step one. The Taylor

approximation criterion allows for a more sound assessment of the database entries. On the basis of the predicted performance, a ranked list of real molecules is obtained. For a final assessment, a process optimization for this limited number of solvent candidates is performed.

Case Study

Motivation. The following case study is motivated from the problem of CO₂ capture and storage (CCS). CCS is regarded as one major possible element in the mitigation of climate change.³⁷ In CCS, carbon dioxide is captured at its major stationary sources (e.g., power plants) and subsequently transported to underground storage. The separation of carbon dioxide from other gases is a standard operation in the chemical industries where usually absorption processes are applied. For CCS applications, however, it is unreasonable to employ these existing technologies on a large scale because of the enormous energies required. Power plants would lose about 10–40% of their efficiency.³⁷ CO₂ capture contributes to 75% of the CCS cost.³⁸ This cost could be significantly reduced if the absorption solvents would be better designed for the specific process conditions.³⁹ The example of CCS therefore demonstrates the need for an integrated design of the solvent and the specific process at hand.

The main aim of the following case study is to demonstrate the suggested CoMT-CAMD approach. For this purpose, a simplified setup is studied to allow for a clear interpretation of the results. Settings resembling precombustion CO₂ capture conditions are chosen.³⁷ The inlet stream consists of an equimolar mixture of carbon dioxide and hydrogen at a pressure of $p = 5$ MPa. The arbitrary inlet flow rate is set to $V_{\text{in}} = 10$ mol/s. Methanol is used as a reference solvent since it is used commercially in the so-called Rectisol process.⁴⁰ To prevent solvent loss of the reference solvent methanol, a low inlet temperature of $T = 230$ K is assumed. Comparable temperatures are also established in real Rectisol plants.⁴⁰ Hong and Kobayashi reported binary phase equilibrium measurements of methanol and carbon dioxide at $T = 230$ K with the lowest composition of carbon dioxide in the liquid phase of $x_{\text{CO}_2} = 0.384$.⁴¹ The bubble-point pressure as calculated from PCP-SAFT without introducing a k_{ij} correction, $p = 0.729$ MPa, compares well with the experimental value of $p = 0.690$ MPa for these conditions. All variables used during optimization have been scaled according to the lower and upper bounds given in Table 1.

Single-Stage Absorption. As a proof-of-concept, a very simple flowsheet is considered consisting of a single-stage absorber. Thus, only the carbon dioxide absorption step is regarded. The objective function is to maximize the separation of carbon dioxide while ensuring a capture rate of 90%, i.e.,

Table 1. Scaled Variables Used in the Case Study

variable	unit	lower bound	upper bound
segment number, m_i		0.8	10
segment diameter, σ_i	Å	2.5	6
segment dispersion energy, ε_i/k	K	250	350
effective association volume, κ_i^{AB}		2.5	6
depth of association potential, $\varepsilon_i^{\text{AB}}/k$	K	0	4000
dipolar moment, μ_i	D	0	4
quadrupolar moment, Q_i	D	0	6
molar flow rates, L, V	mol/s	0	1000
temperature, T	K	200	400
pressure, p	MPa	0	5

$$\max \frac{x_{\text{CO}_2, \text{out}}}{y_{\text{CO}_2, \text{out}}} \quad (8)$$

$$\text{s.t. MESH equations for absorber} \quad (9)$$

$$\text{bound constraints on variables} \quad (10)$$

$$y_{\text{CO}_2, \text{out}}^{\text{absorber}} V_{\text{out}}^{\text{absorber}} - 0.9 y_{\text{CO}_2, \text{in}}^{\text{absorber}} V_{\text{in}}^{\text{absorber}} \leq 0 \quad (11)$$

where x_i and y_i denote here liquid and vapor flow mole fractions of component i , respectively. The free variables are the solvent parameters as well as the solvent flow rate.

In the continuous-targeting step, the expected separation (8) increases by more than a factor of 6 from 1.02 for methanol to 6.3. The normalized PCP-SAFT parameters for the reference solvent methanol as well as the target molecule found are given in Table 2. The target solvent shows rather extreme properties. All parameters lie at one of their given boundaries. The association energy ϵ_i^{AB}/k has an intermediate value. This is, however, only due to parameter insensitivity as the association volume κ_i^{AB} is zero and association does thus not occur any more. Since the increase in separation indicates a major potential to improve the CO_2 separation, the target molecule is mapped onto existing substances in the next step.

The results from the molecular mapping step are given in Table 3. For reference, the values for methanol are included. All solvent candidates improve the separation with respect to the benchmark methanol. The order suggested based on the Taylor approximation criterion, however, does not match the actual process performance found in subsequent process optimization. The Taylor approximation criterion (6) works better than the simple average deviation criterion (5) which even produced clear outliers with worse performance than methanol (not shown here). Still, the molecular mapping procedure does not seem very robust. This, however, is mainly caused by the problem definition, where we have asked for the highest separation that PCP-SAFT is mathematically able to describe within the given parameter bounds. A rather extreme hypothetical molecule with parameters far from any real molecule has to be the result. One can introduce convex hull constraints⁴² to ensure the final parameters to be closer to existing molecules. However, we here prefer to proceed by simply introducing a more relevant and realistic problem formulation as a second case study, where a trade-off of properties is better reflected. A practical absorption solvent has to release the solute in the desorption step and more balanced molecular properties immediately also lead to more balanced molecular parameters, as seen below.

Flowsheet with Solvent Recycle. The previous study has focused on carbon dioxide absorption only. Due to the molecular richness available in the suggested approach an extreme target molecule is found which maximizes all attractions for CO_2 . Real solvents used in absorption–desorption processes require a high enough affinity of a solvent for CO_2 in the absorption step but also the ability to release CO_2 during desorption again. It is thus expected that the consideration of a whole process flowsheet including absorption–desorption leads to balanced values for the target solvent.

The flowsheet considered is sketched in Figure 6. The shifted syngas is sent to the gas inlet of the absorber. The rich solvent loaded with CO_2 leaves the absorber. Through pressure reduction, the carbon dioxide is released in a flash unit. To accommodate for solvent losses, fresh solvent is added in a make-up stream before the lean solvent enters the absorber. The pressure in the flash is fixed at atmospheric conditions.

Table 2. Normalized Solvent Parameters for Reference Solvent Methanol and Optimized Target Solvent

parameter	m_i	σ_i	ϵ_i/k	κ_i^{AB}	ϵ_i^{AB}/k	μ_i	Q_i
methanol	0.16	0.25	0.38	0.89	0.58	0.43	0.00
target solvent	1.	1.	1.	0.	0.512	1.	1.

Table 3. Ranked Top Five List of Candidate Solvents Found from the CoMT-CAMD Approach Using Taylor-Approximation Criterion $\Delta T_A(y)$ and the Separation Found from a Subsequent Process Optimization

compound	$\Delta T_A(y)$	separation
dimethylformamide	−5.3	2.53
dimethyl sulfoxide	−5.5	1.94
butyronitrile	−5.8	2.70
propionitrile	−6.4	2.59
nitroethane	−6.9	2.15
methanol	−15.0	1.02

Since solvent loss is an issue for methanol, the objective of the integrated process and solvent design is to minimize the makeup solvent flow rate $L_{\text{solvent, in}}$ while keeping the performance of methanol with respect to CO_2 -capture rate and purity of the CO_2 stream. Thus, the objective function is given by

$$\min L_{\text{solvent, in}} \quad (12)$$

To validate the assumption that the study of the whole process scheme, indeed leads to a trade-off in solvent properties only a single molecular property is varied initially. Starting from the reference molecule methanol, each of the seven PCP-SAFT parameters is optimized individually while keeping the remaining values fixed. The resulting makeup solvent flow rates are shown in Figure 7. The expected trade-off in the molecular properties is indeed found for all properties except the dipole moment μ_i . Thus, studying the absorption–desorption cycle leads to less extreme target properties. Figure 7 further supports the commercial use of methanol as a solvent: Most of its individual molecular properties are already very close to the optima found (keeping the other molecular parameters fixed).

On the basis of this preliminary study, the full optimization of the flowsheet including all solvent and process parameters is approached. The target solvent found from the continuous-

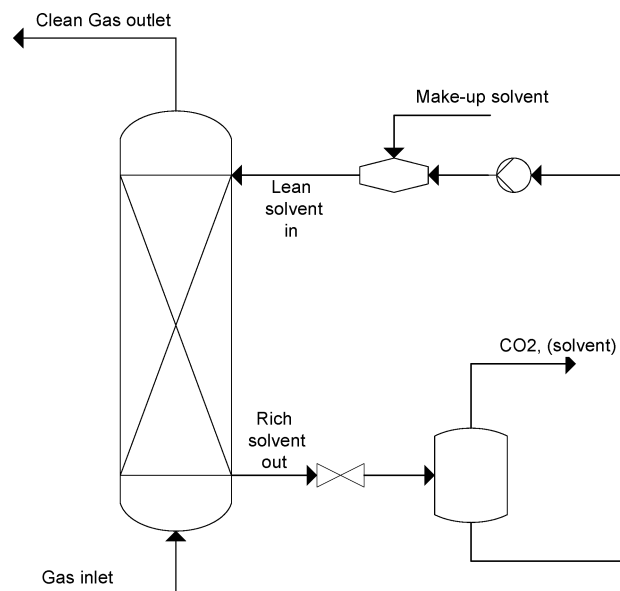


Figure 6. Absorption–desorption process studied consisting of an absorber at high pressures (left) and a flash unit (bottom right) at low pressures.

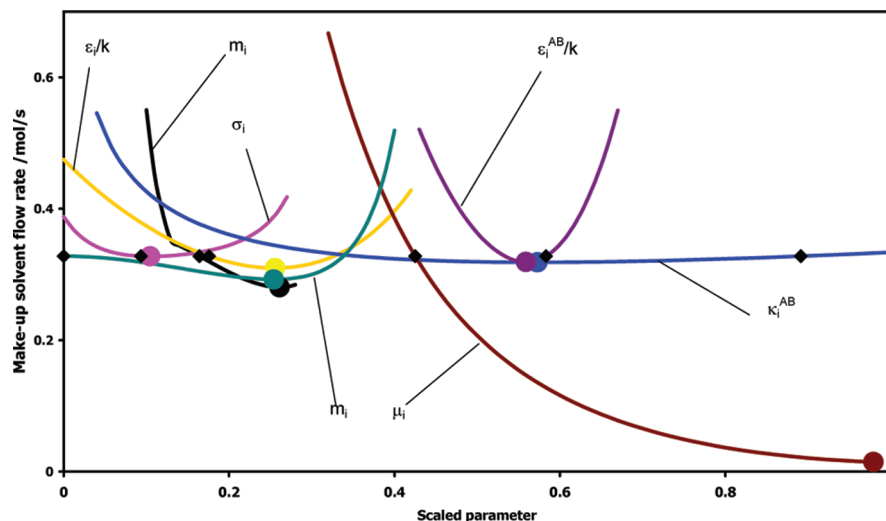


Figure 7. Make-up solvent flow rate as function of molecular solvent parameters individually varied from base case molecule methanol. Circles indicate optima found by the optimization algorithm. Diamonds denote reference values for methanol.

Table 4. Normalized Solvent Parameters for Reference Solvent Methanol and Optimized Target Solvent for Absorption–Desorption Cycle Optimization

parameter	m_i	σ_i	ε_i/k	κ_i^{AB}	ε_i^{AB}/k	μ_i	Q_i
methanol	0.16	0.25	0.38	0.89	0.58	0.43	0.00
target solvent	0.37	0.39	1.00	0.02	0.43	1.00	0.19

Table 5. Ranked Top Five List of Candidate Solvents Found from the CoMT-CAMD Approach using Taylor-Approximation Criterion $\Delta T_A(y)$ and the Make-up Solvent Flow Rate Found from a Subsequent Process Optimization for the Absorption–Desorption Cycle

compound	$\Delta T_A(y)$	make-up solvent (mol/s)
dimethyl sulfoxide	0.049	0.21×10^{-3}
dimethylformamide	0.050	0.54×10^{-3}
butylbenzene	0.230	0.52×10^{-3}
styrene	0.400	2.4×10^{-3}
xylene	0.420	2.6×10^{-3}
methanol	4.600	0.33

molecular-targeting step is compared to methanol in Table 4. For most properties, the properties of the target solvent show intermediate values. The target molecule thus no longer consists of the combination of all extremum points in the parameter space. The makeup solvent flow rate is reduced from $L_{\text{solvent,in}} = 0.33$ mol/s for methanol to $L_{\text{solvent,in}} = 0.26 \times 10^{-6}$ mol/s. The target solvents thus allows for an improvement of the objective by more than 6 orders of magnitude.

The results of the molecular mapping step are summarized in Table 5. The molecular mapping procedure using the Taylor-approximation criterion now yields a robust result. The order of the molecules predicted corresponds to the one found from subsequent process optimization. The properties of the hypothetical target solvent differ only by 15% from the closest existing molecule. The local Taylor approximation is therefore suited as a selection criterion.

The identified solvent candidates reduce the solvent loss by more than a factor of 1000 while still offering the same carbon dioxide capture performance. It should be noted that the database employed is still very limited and is currently being expanded. Still, opportunities for major improvements are already identified through the holistic approach integrated solvent and process design.

The case studies presented here serve as a validation of the suggested design framework. Due to the generic nature of the

approach a broad range of possibilities exist for immediate extensions. Most naturally, the studied processes can be expanded to a full process flowsheet to be studied together with a truly process-wide objective function. Thereby, novel solvents and processing concepts can be studied simultaneously. Reactive systems could be included.⁴³ Chemical solvents for CO₂ capture such as MEA have recently been successfully modeled using transferable parameters within the SAFT framework.⁴⁴ Further physical properties such as viscosity^{29,30} or surface tension^{45,46} can be integrated naturally. The power of the approach increases with improvements toward more predictive thermodynamic models. As in classical CAMD approaches, the mapping step could lead to novel solvent molecules by employing group-contribution concepts.

Conclusions

The integrated design of processes and solvents is highly desirable due to their strong interdependence. In this work, the continuous-molecular-targeting method (CoMT-CAMD) is presented to establish the integrated design in practice. The CoMT-CAMD approach achieves the sound integration of molecular degrees of freedom into process optimization while circumventing the prohibitive complexity of the discrete choice between individual molecules. The result of the first step is an optimal process and a hypothetical solvent. The parameters of the optimal hypothetical solvent are in a second step mapped onto an existing optimal solvent. The CoMT-CAMD approach is versatile with respect to the applications and to the thermodynamic models. It relies on a model that, on the one hand, adequately predicts mixture (phase) behavior and, on the other hand, represents molecules with a set of meaningful, physically based molecular parameters.

The general framework of the suggested CoMT-CAMD approach certainly reaches beyond the specific example of solvent design to general integrated materials and process-design problems. Once a sufficiently detailed molecular model for the problem at hand is available, its application should be straightforward.

Acknowledgment

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