

Integrated Design of Solvents in Hybrid Reaction-Separation Processes Using COSMO-RS

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Solvents have a large impact on process performance due to their influence on e.g., selectivity in absorption, equilibrium conversion in reactions or exergy demand in distillation. Optimization of process performance therefore needs to integrate solvents as degree of freedom. In this work, an integrated design approach is presented to select solvent molecules as part of flowsheet-wide process optimization. The design approach is based on COSMO-RS for the prediction of thermodynamic properties and uses advanced pinch-based process models for absorption and distillation. Pinch-based process models allow for rapid and accurate process optimization. Thus, a large design space of solvents can be evaluated efficiently. The design approach is demonstrated for a novel concept for integrated CO₂ capture and utilization (ICCU) to carbon monoxide. The complete flowsheet containing absorption, multiphase reaction and distillation is optimized successfully for more than 4000 solvents to minimize the overall process exergy demand. The approach is shown to discover process inherent trade-offs in molecular properties of the solvents allowing for optimal solvent and process design.

Keywords: process design, solvent selection, ICCU, energy storage

1. Introduction

Solvents strongly influence the economics and environmental impacts of processes, thus careful solvent selection is required for optimal process performance (Adjiman et al., 2014). In particular in reaction-separation processes, solvents need to fulfill various tasks: increase absorption capacity, enhance equilibrium conversion in reactions or facilitate distillation. However, each of these tasks demands different molecular properties of the solvent molecule leading to complex trade-offs in molecular properties for optimal process performance. Thus, the development of novel processes requires a systematic approach for integrated design of process and solvent. To design solvents, knowledge about the thermodynamic properties of the solvent candidates is essential. However, experimental data on properties is frequently missing or too expensive to measure for a large number of solvents. Solvents with unknown thermodynamic properties are excluded from the design, which confines the number of solvent candidates and leads to suboptimal decisions. Thus, a comprehensive approach for solvent selection needs to 1) capture all process inherent trade-offs and 2) employ a predictive thermodynamic property model to cover a large design space of solvent candidates. Common approaches for solvent design balance process level detail and design space due to computational complexity: Either processes are optimized using rigorous process models for a small pre-defined set of solvents (Pereira et al., 2011) or a large number of solvents is considered, but the selection is based on simplified process indicators (Burger et al., 2015).

In this work, the challenge of integrated molecule and process design is tackled by screening several thousand solvents using thermodynamically sound process models and quantum mechanics-based predictive thermodynamics. The screening method is applied for a process for integrated capture and conversion of carbon dioxide (CO₂). The conversion of CO₂ to carbon monoxide is promising and has been studied assuming CO₂ to be readily available as pure feed stream (Scheffczyk et al., 2017). However, providing CO₂ requires a substantial energy demand depending on the CO₂ source (von der Assen et al., 2016). A possible

source of CO₂ is absorption from a gaseous stream, e.g., from natural gas. Natural gas contains up to 70% CO₂ by molar fraction and needs to be purified from CO₂ for sale (Pereira et al., 2011). This CO₂ could be used in the chemical industry. To consider the capture of CO₂ in solvent selection, the design approach is expanded by an advanced pinch-based process model for absorption (Redepenning and Marquardt, 2017). The resulting approach is introduced in Section 2 and demonstrated in a case study in Section 3.

2. Predictive assessment of process and solvent candidates

For integrated design of solvents in complete process flowsheets, a method is required that allows for rapid, automated and reliable evaluation of solvents and process flowsheets. The approach presented in this work is based on the idea by Scheffczyk et al. (2016) and extended towards comprehensive evaluation of complete flowsheets. The approach builds on a hierarchical framework using COSMO-RS and pinch-based process models for predictive assessment of several thousand solvents. The approach uses four steps (Figure 1):

1. Solvent candidates are generated either using computer-aided molecular design (CAMD) or databases.
2. The feasibility of each solvent candidate for the process is evaluated based on molecular properties. Solvents need to fulfill property targets required for the process flowsheet topology such as the existence of a liquid-liquid-equilibrium (LLE) for extraction, a suitable boiling point or the non-existence of azeotropes for feasible distillation. All required thermodynamic properties such as vapor pressures or activity coefficients are calculated using COSMO-RS (Klamt et al., 2010). COSMO-RS is based on quantum chemistry and thus allows for fully predictive assessment of large numbers of solvent candidates, since no experimental data is required.
3. For all solvents fulfilling the feasibility requirements, a process flowsheet is optimized considering continuous process variables such as reactor pressures or flow rates. The process is evaluated and optimized using thermodynamically accurate pinch-based process models (cf. Marquardt et al., 2008). Pinch-based process models exploit the existence of so-called pinch-points, which are characterized by vanishing thermodynamic driving force. Thus, pinch-points mark operating points of minimum solvent demand for absorption and extraction or minimum reflux for distillation and thus give a lower bound on process energy. All process units in this work employ thermodynamic equilibrium properties predicted by COSMO-RS. Thus, the thermodynamics of each solvent are treated consistently for the whole flowsheet.
4. As a result of the design procedure, a ranked list of solvents and corresponding optimal process configurations is obtained. The results are input for further refinement by additional design criteria and validation.

The presented framework allows for integrated design of molecules and processes involving reaction, extraction, distillation and absorption. Thus, the most frequently employed unit operations are covered. Any process containing these unit operations can be optimized flowsheet-wide for each solvent candidate in the presented framework. In the following section, the proposed approach is exemplified in a case study on integrated capture and conversion of CO₂.

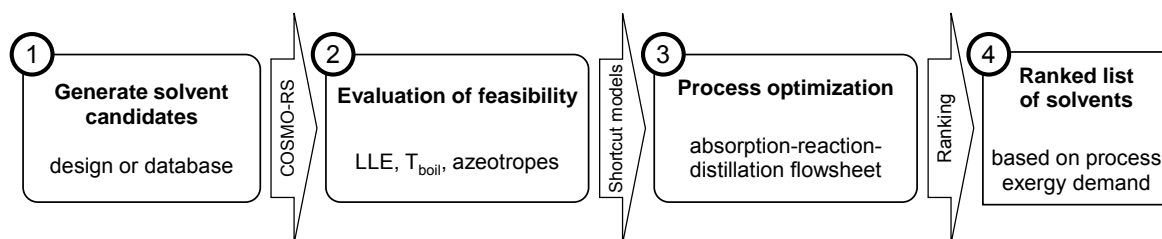


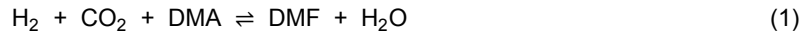
Figure 1: Schematic procedure for integrated solvent and process design

3. Case study

3.1 Problem specifications

Hydrogen (H₂) from fluctuating renewable energy and carbon dioxide (CO₂) can be utilized to produce carbon monoxide (CO) for the chemical industry using intermediate energy storage in a liquid chemical (Behr et al., 2004). The process can be divided into three main steps: Synthesis, Storage and Reforming (SSR-Process)

(Figure 2). In the SSR-Process, H₂ and CO₂ are first converted to dimethylformamide (DMF), which has been identified as the most promising storage molecule by Jens et al. (2016). DMF is formed by reacting H₂ and CO₂ with dimethylamine (DMA) in a multiphase reaction with water (H₂O) as a side product (Eq. 1). Thus, DMA is required as an additional reactant in the synthesis reactor:



After storage, DMF is converted to CO and DMA (Eq. 2). DMA is recovered from the reforming reactor and recycled to the synthesis reactor (Eq. 2):



The most promising process flowsheet using DMF adds a solvent already before the synthesis reactor to enhance the equilibrium conversion (cf. Figure 2), for details see Jens et al. (2016). After reforming, the liquid mixture of H₂O, DMA and solvent is separated by distillation.

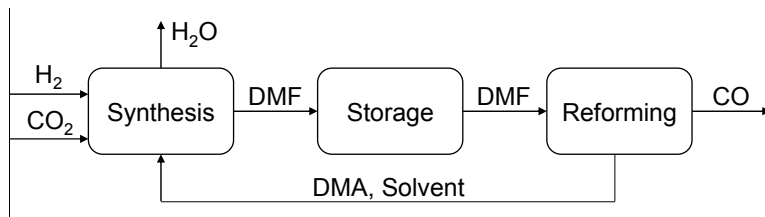


Figure 2: Schematic flowsheet of the Synthesis-Storage-Reforming process using dimethylamine (DMA) as an additional reactant and dimethylformamide (DMF) as liquid energy storage.

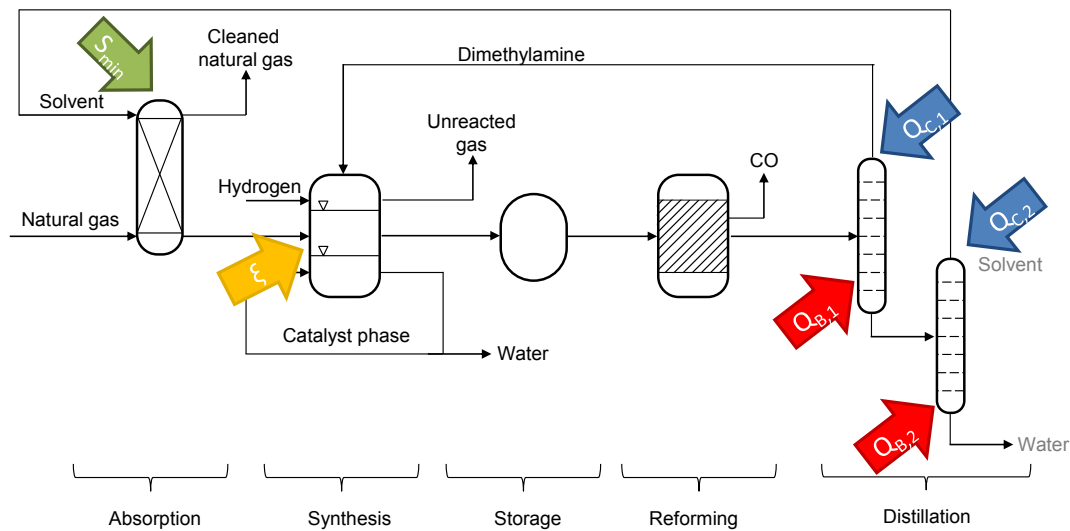


Figure 3: Process flowsheet for CO production from CO₂ via liquid storage of dimethylformamide. The minimum solvent demand in the absorption column is denoted by S_{min} and calculated by the pinch-based process model for absorption (Redepenning and Marquardt, 2017). The equilibrium conversion in the synthesis reactor is denoted by ξ . The minimum condenser and reboiler duties in the two distillation columns are denoted by $Q_{C,1}$, $Q_{B,1}$, $Q_{C,2}$ and $Q_{B,2}$ respectively and are calculated by the pinch-based process model for distillation (Bausa et al., 1998).

Jens et al. (2016) assumed that pure CO₂ was available as input stream. In this work, the capture of CO₂ is included in the process and a solvent is screened that balances absorption, reaction and distillation.

In the considered case study, the pressure in the synthesis reactor and the flow rate of water to the synthesis reactor are optimized to reduce the total exergy demand of the process. The type and amount of solvent is considered as an additional degree of freedom influencing each part of the process (Figure 3), e.g., selectivity of absorption, equilibrium conversion in reaction and exergy demand in distillation. The selectivity of

absorption S_{Abs} is defined as the molar fraction of CO_2 in the liquid absorber outlet divided by the molar fraction of methane in the liquid absorber outlet (Eq. 3):

$$S_{\text{Abs}} = \frac{x_{\text{CO}_2}}{x_{\text{CH}_4}} \quad (3)$$

The objective of the optimization is to minimize the overall process exergy E required by heating and cooling throughout the process for each solvent (Eq. 4):

$$\min E = \sum_{i=1}^2 -Q_{\text{C},i} \left(1 - \frac{T_{\text{u}}}{T_{\text{C},i}}\right) + Q_{\text{B},i} \left(1 - \frac{T_{\text{u}}}{T_{\text{B},i}}\right) \quad (4)$$

The condenser and reboiler duties are denoted by $Q_{\text{C},i}$ and $Q_{\text{B},i}$ at their corresponding temperatures $T_{\text{C},i}$ and $T_{\text{B},i}$. The ambient temperature is T_{u} . Cooling above ambient temperature reduces the exergy demand because utilization of exergy from cooling is assumed, which approximates perfect heat integration.

3.2 Result: Identification of promising solvent candidates

In total, 4488 compounds are used as solvent candidates for the case study (step 1). These candidates are taken from the COSMObase database considering only candidates containing carbon, oxygen and hydrogen atoms for biocompatibility (Scheffczyk et al., 2016). From these 4488 solvent candidates, 1826 compounds fulfill the feasibility requirements (step 2). Thus, process optimization is performed for these 1826 solvents (step 3). Optimization of 1826 solvent-process combinations demonstrates the reliable and efficient evaluation of process flowsheets using the presented method. After optimization, further refinement of promising solvents based on practical considerations excludes another 135 solvents with high experimental melting points.

The resulting exergy demand for each solvent is shown in Figure 4. Generally, the results show that a high absorption selectivity for CO_2 reduces the exergy demand (Figure 4). However, the results reveal complex tradeoffs in molecular properties: Selectivity for CO_2 absorption, equilibrium conversion and exergy demand in distillation are closely linked and need to be balanced for optimal process performance.

In particular, solvents with high absorption selectivity or a high equilibrium conversion do not guarantee low exergy demand of the process: The solvent with the lowest process exergy demand (1-trans-3-pentadiene, red diamond Figure 4) is neither the solvent with the highest absorption selectivity nor equilibrium conversion. Moreover, the importance of considering the absorption of CO_2 is highlighted when comparing the results for 1-trans-3-pentadiene to a solvent screening without considering absorption. 1-trans-3-pentadiene ranks only 93rd, if absorption of CO_2 is not considered. Thus, evaluation of parts of the flowsheet separately would lead to suboptimal choices.

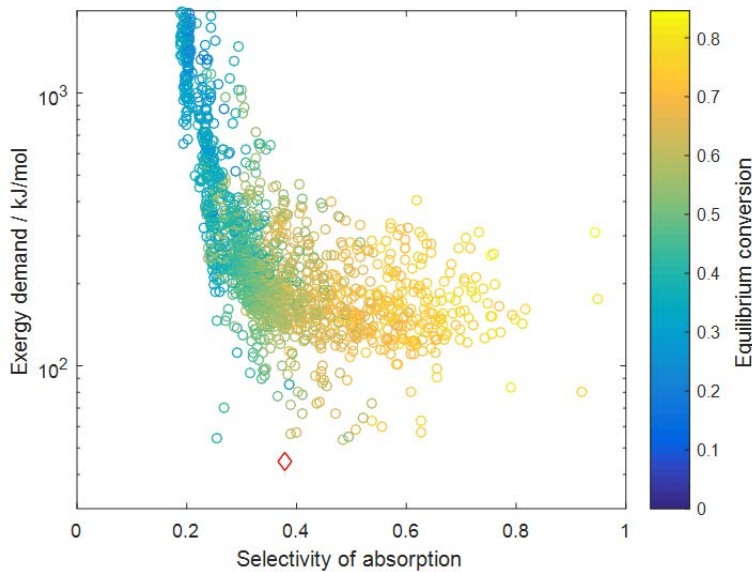


Figure 4: Exergy demand of process versus selectivity of absorption for each solvent. The red diamond marks the solvent with the lowest exergy demand.

Notably, the results indicate that ranking using single property targets is not sufficient to capture process-level trade-offs in molecular properties. The top two solvents with the lowest total exergy demand have low boiling points compared to all evaluated solvents (Table 1), suggesting that a low boiling point is desirable for this process. However, a ranking only based on the boiling points of the solvents is not sufficient, e.g., the solvent 3-methyl-pentane is ranked fifth regarding boiling points, but on rank 1478 regarding the total exergy demand of the process (see Table 1). The comparison highlights the need for full process evaluation for optimal results instead of heuristic evaluation of thermodynamic properties.

For practical purpose, additional constraints need to be applied such as availability or chemical stability, which are currently not evaluated in the screening framework. Our design approach therefore provides a ranked list of several solvent candidates and not only one promising solvent. This ranking can serve as an input for decision-making and further refinement by a process engineer.

Table 1: Top two solvents with the lowest exergy demand E of the process ^(a) compared to the solvents with highest selectivity of absorption S_{Abs} ^(b), equilibrium conversion ξ ^(c) and benchmark solvent for heuristic evaluation of boiling point T_{boil} ^(d). The exergy demand of each solvent E_i is given in multiples of the exergy demand of the top solvent E_1 .

Rank	Solvent	S_{Abs}	ξ	T_{boil} / K	E_i / E_1
1	1-trans-3-pentadiene ^a	0.38	0.38	306	1
2	1-penten-3-yne ^a	0.48	0.61	330	1.2
504	phenoxyacetaldehyde ^b	0.95	0.80	535	3.9
1195	4-ethenyl-1,3-dioxolan-2-one ^c	0.94	0.85	570	6.9
1478	3-methylpentane ^d	0.19	0.26	319	14.4

4. Conclusion

A method for integrated solvent and process design is presented. The method combines predictive thermodynamics and process optimization for optimal selection of solvents and processes. All unit operations are modeled by advanced pinch-based process models allowing for accurate but still efficient process optimization of complete flowsheets. All pinch-based process models consistently use the same thermodynamic models for equilibrium properties, which are predicted by COSMO-RS for each solvent candidate. Thus, the presented method avoids extensive experiments for thermodynamic parameters by predictive assessment of several thousand solvents.

The method is applied for optimal solvent selection in a complex flowsheet for the integrated capture and conversion of CO₂. In this case study, CO₂ is absorbed from natural gas and subsequently converted to CO via liquid energy storage using dimethylformamide. More than 4000 solvent candidates are evaluated regarding the overall exergy demand of the process. For each solvent, the operating conditions of the process flowsheet are optimized to find the optimal solvent-process combination. The results show a close interaction between absorption, reaction and distillation requiring a solvent with balanced molecular properties. The results thus highlight the need for process evaluation based on a complete flowsheet. Evaluation of single process units or heuristic property targets would lead to different, suboptimal results. The presented integrated design approach is shown to capture complex interaction while still being computationally efficient. Based on the predictive evaluation with the presented method, a ranked list of solvents is obtained, in which 1-trans-3-pentadiene is identified as the best solvent for integrated capture and conversion of CO₂. The results of the presented case study serve as an input for further rigorous and experimental validation.

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