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Optimally Designed Solvent System for Lignocellulosic Biomass Conversion Supported by Property Predictions

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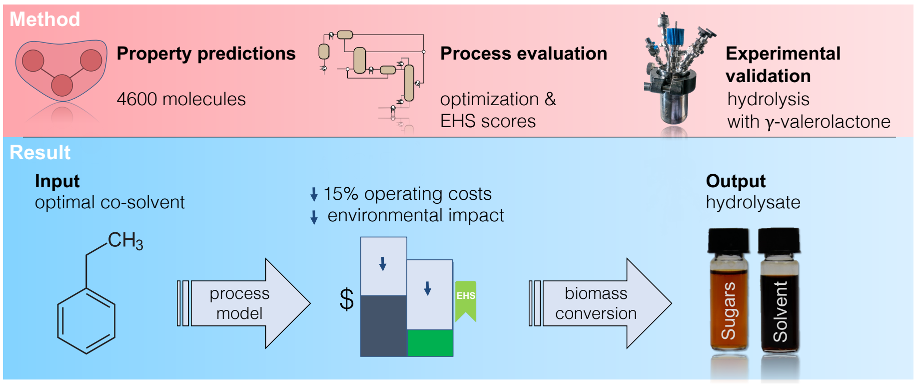
Abstract:



The conversion of biomass with high sugar yields is enabled by a process using the solvent γ-valerolactone. There, the lactone dissolves the organic species, and a co-solvent is used to switch the solvent system's number of phases for efficient separation of the sugars in the aqueous phase. However, selecting the right co-solvent, a key economic driver for this process, currently involves several material-intensive and labor-intensive steps, from selecting candidates by experts to extensive experimental evaluation, and can lead to suboptimal choices. Here, we report a cost-optimal solvent-based biorefinery by combining process-based co-solvent screening and experimental validation of the best co-solvent candidate found. Assisted by property predictions, the solvent system we propose results from screening a broad range of molecules while reducing the manual effort compared to conventional solvent selection. The integration of reduced-order models embedded in process optimization allows identifying a cost-optimal co-solvent systematically. Additionally, environmental, health, and safety (EHS) evaluations assist in excluding hazardous co-solvents. The best candidate is validated experimentally inside the co-solvent hydrolysis reaction. Our findings show that through process optimization and the use of ethylbenzene as a co-solvent, we can enable 15% savings in operating costs and

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achieve a better EHS score than the reported benchmark toluene. Ethylbenzene shows lower performance than toluene in the analysis of phase partitioning and, therefore, would not be a leading co-solvent based on a laboratory-based evaluation alone. Here, we demonstrate that we can improve the final co-solvent choice, and a process-based co-solvent selection is needed.

1 Introduction

1.1 Biomass conversion using γ-valerolactone

To achieve a carbon-neutral economy, the sustainable production of fuels and chemicals to replace their fossil counterparts is critical, and plant-based biomass as a feedstock is a prime candidate due to its abundance.[1] A promising avenue for bio-based production of commodities is often seen in the selective conversion of biomass through the intermediate products xylose and glucose.[2] The conversion reactions involve the cleavage of β-1,4 glycosidic bonds into hemicellulose and cellulose with either enzymes or acid catalysts. In the case of acids, high concentrations or high temperatures cause the rapid breakdown of sugars into undesirable side-products.[3] Such high acid concentrations are no longer necessary when a solvent is introduced to decouple the residence times of solid biomass polymers and their soluble compounds. This can be achieved by flowing the solvent through a heated packed bed of biomass. In this way, low sugar degradation and high economic efficiency can be achieved.[4]

One solvent, γ-valerolactone (GVL), has been reported to promote this conversion reaction by preventing the re-precipitation of the by-product lignin on the reactive cellulose surface.[3,5] GVL enhances reaction selectivity toward desired products[6] compared to biomass conversion processes using only water as a solvent. The economic analysis of this process shows that the separation and recycling of the GVL solvent is essential for profitability.[3] Efficient separation can be achieved by introducing a co-solvent, which allows for a temperature-induced change of the number of phases, forming a switchable miscible solvent system (SMSS). The co-solvent promotes the formation of two phases when cooled to ambient temperature, inducing an organic phase rich in GVL and co-solvent and a second one rich in water, dissolved sugars, and the acid catalyst.[7] Therefore, selecting this co-solvent is a crucial step in designing the GVL separation process.

The original attempt to select a suitable co-solvent for such a SMSS was an experimental evaluation of known candidate co-solvents conducted by Motagamwala *et al.*[7] Their approach included manual testing of the ability for temperature-induced phase switching at reaction and separation temperatures. Of the 16 candidates considered, 11 were then evaluated on their extraction efficiency and environmental, health, and safety (EHS) scores.[8] Each candidate co-solvent was used inside the biomass conversion reaction, and its influence on the respective sugar yield was measured. Among the 16 well-known co-solvents tested, toluene was selected as it offered the best trade-off between extraction efficiency and EHS-score[7] and was later assessed for its techno-economic performance in a bio-ethanol production process.[9]

However, the selection of co-solvents based on extraction efficiency can generally lead to sub-optimal process performance, as such performance indicators do not capture potential trade-offs in the process.[10] These trade-offs are present inside the proposed recovery[9] of the co-solvent. This includes the extraction of GVL from water in an extraction column and the regeneration of the co-solvent in a distillation column. A high affinity of the solvent to the solute is advantageous for efficient extraction, while a low affinity is preferred for solvent recovery by distillation. Capturing this trade-off motivates assessment at the process level instead of the co-solvent level. Moreover, manual screening of co-solvents in an experimental setup has apparent disadvantages. First, the pre-selection of candidates relies on the intuition and experience of a small number of people. Second, it is not scalable-exhaustive laboratory automation would be necessary to test a co-solvent scope that covers a broad range of molecules. Third, the mentioned process trade-offs could only be captured in a plant setup. This work aims to find a cost-optimal co-solvent on the process level. Computer-aided solvent screening methods, using a wide range of molecules, allow defining a cost-optimal candidate for this process.[11]

1.2 Computer-aided solvent screening

Although neglecting the process during solvent selection can cause suboptimal choices, the evaluation of performance indicators such as phase distribution coefficients[12–17] is often used to estimate downstream process efficiency and, in some cases, also validated in rigorous simulations or experiments.[18,19] Such performance indicators have been used to evaluate a large number of molecules using thermodynamic property predictions calculated with COSMO-RS.[20] An overview of performance evaluation for predicted molecular properties is given in Gertig *et al.*[21] They differentiate between evaluation with simple performance indicators, in-silico assessment inside a process simulation, and additional process optimization. Only the latter two approaches can take trade-offs inside the process into account. To that end, simple shortcut models for the unit operations can be used.[10,22,23] But these models can cause inaccuracies, especially with nonideal separations.[24] These inaccuracies are avoided by using sophisticated pinch-based reduced-order unit operation models.[25,26] Previous studies have shown that the automated in-silico assessment of molecular properties based on COSMO-RS predictions inside such unit operation models is possible and improves the final solvent selection.[11,27–29] Scheffczyk *et al.*[11] automatically select solvents from the COSMO-RS database for a process using reduced-order separation models. In more recent studies, Scheffczyk *et al.*[29] and Fleitmann *et al.*[27] perform process optimization for the reduced-order models. However, they do not apply heat integration for the process and lack the evaluation of EHS for the selected solvents. While these studies show how much effort has been placed toward automating the screening of solvent systems for separation processes, only a few articles have been published that perform solvent screening for SMSSs.[17,30,31] Despite the advances in solvent screening on the process level, these studies use performance indicators for their selection.

We showed that the concept of computer-aided solvent selection had been deployed successfully on several applications. Still, existing computer-aided methods are not applicable to the complexity of SMSS design for biomass conversion. The influence of a co-solvent on the sugar yield can only be evaluated experimentally. In contrast to the manual co-solvent selection for the biomass conversion using GVL[7], our approach combines computational solvent screening, process optimization, and experimental biomass conversion to define a cost-optimal co-solvent. We demonstrate that we can engineer a solvent system that enhances biomass conversion due to the positive effects of using GVL as a solvent while being cost-optimal inside the process. Specifically, we report the following contributions: (1) an evaluation of over 2000 molecules in the COSMO-RS database within a process model using reduced-order unit operation models embedded in a process optimization; (2) an additional evaluation of calculated EHS scores for the 30 best candidate co-solvents ranked on their operating costs; (3) the successful application of the best co-solvent found in an experimental setup to convert beechwood to sugars; (4) the comparison of the resulting phase compositions from the conversion reaction with ternary model mixtures and the COSMO-RS predictions; (5) an experimental evaluation of the sugar concentration inside the residual biomass after the conversion reaction for the best candidate and the benchmark co-solvent. Our results show that process-based selection of co-solvents is required and that the reference toluene performs better when simple performance indicators such as partition coefficients are the basis for selection but would perform worse in the process than the best co-solvent found in this work.

2 Methods

We perform solvent selection in a series of discrete stages. We first present the process model for a given GVL separation, then the prediction of thermodynamic properties in COSMO-RS, process optimization, and experimental validation. We perform an automated evaluation on the process level for a list of > 2000 co-solvents from the COSMO-RS database and establish a ranking based on minimum operating costs. A summary of all important assumptions, variables subject to optimization and parameters for the computer-aided co-solvent screening can be found in the ESI† (Table B.1, Section B).

2.1 Process model: γ-valerolactone separation

The process structure for the GVL recovery of the co-solvent hydrolysis is adapted from Won *et al.*[9] No structural changes compared to the original separation section are made, except that we do not depict solids removal for simplicity. Figure 1 illustrates the process, starting with reactor R1, which is operated at 453 K and 20.67 bar. R1 is fed with water, GVL, and the co-solvent toluene ($z_F = 0.578, 0.349, 0.074$ on molar basis). This solvent system is single-phased at the reaction temperature. After the reaction at 453 K, the mixture is cooled below the mixture's upper critical solution temperature. Inside the reactor, the biomass is converted to soluble carbohydrates by the catalyst sulfuric acid. Additionally, GVL and water form two liquid phases due to the co-solvent. The resulting two phases are immediately separated in decanter D1, and 86.3% of the organic phase is recycled to R1 and contains most of the GVL. This value is maintained throughout the screening. The aqueous phase of decanter D1 contains the sugars resulting from the hydrolysis of the biomass and small amounts of GVL. However, this GVL concentration is too high for further fermentation of the sugars to fuels and chemicals. Most microorganisms tolerate up to about 2 wt% of GVL in the fermentation medium.[32] Therefore, the aqueous stream of D1 is further purified in an extraction column E1 to achieve this concentration. The GVL concentration is reduced below 2 wt% of GVL by the co-solvent $X_{\text{co-solvent}}$ inside extraction column E1. The raffinate of E1 constitutes the feed for the fermentation. The fermentation is not part of our model. The extract phase of the extraction, consisting of GVL and the co-solvent $X_{\text{co-solvent}}$, is transferred to distillation column C1, where both are separated, and the co-solvent is reused for extraction. The heavy boiling product of C1 consists mainly of GVL

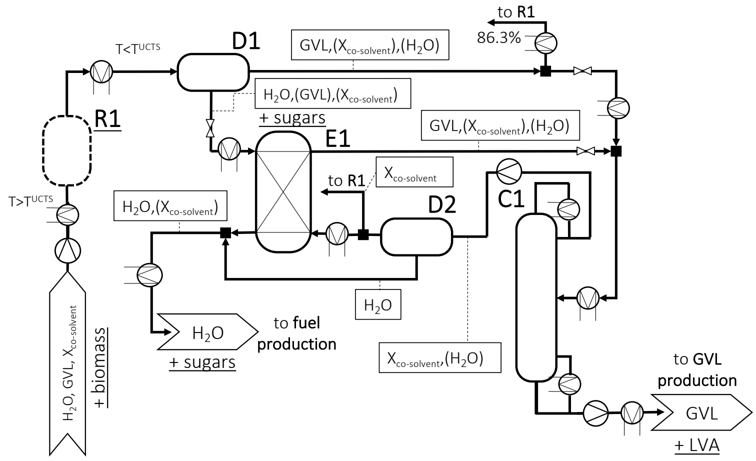

Figure 1: Process flowsheet consisting of a decanter D1 and a hybrid extraction-distillation E1 and C1. Feed stream to reactor R1 contains the solute GVL, carrier H_2O and co-solvent $X_{\text{co-solvent}}$. R1 is not part of the model and is therefore, illustrated in dashed lines. Biomass and the resulting sugars are assumed to be inert substances. Bracketed components are solutes.

and the side product levulinic acid (LVA) from the hydrolysis reaction in R1. The LVA at the bottom of C1 is further hydrogenated to GVL (not considered in the model) and then recycled back to R1 to compensate for the GVL losses in the raffinate stream.

2.2 Model assumptions and implementation

The process model in this work aims to consider all the effects of a co-solvent on the operating costs of GVL separation. The biomass conversion reaction, including the acid catalyst, is neglected, and the resulting products are assumed to be inert.

The process model consists of a liquid-liquid equilibrium (LLE) flash model D1 at constant temperature and pressure , pinch-based reduced-order models for extraction column E1 and distillation column C1, and all heat exchangers and pumps. Decanter D2 is assumed to be an ideal separation of co-solvent and water. The recycles from D1 and D2 to R1 are not closed to reduce computing time. Therefore both constitute exiting streams in the process model. Only the co-solvent lost in the aqueous stream, leaving extraction E1, is accounted for and priced as a solvent loss.

We apply a pinch-based design method for heat integration.[33] The specific energy costs (€ J $^{-1}$) are assumed to be piecewise-affine-linear functions of the temperature.[34] The co-solvent price is kept constant for each candidate.[35] This allows evaluating a large number of co-solvents, even the more uncommon ones, without causing a price disadvantage in this early stage of the process design. This is particularly important because the amount of co-solvent in the screening is variable to determine optimal compositions. Detailed information on the cost functions can be found in the ESI† (Section B).

2.3 Co-solvent screening methodology

2.3.1 Thermodynamic property prediction

We divide the screening process for co-solvent molecules into four explicit stages, including 1) property prediction (COSMO-RS database search, pure component and mixture prediction, regression of the pure and mixture property models), 2) evaluation at the process level (heat integration and optimization), 3) manual EHS and chemical stability evaluation (Figure 2A) and 4) experimental execution (beechwood conversion, analysis of resulting liquid phases) (Figure 2B). We

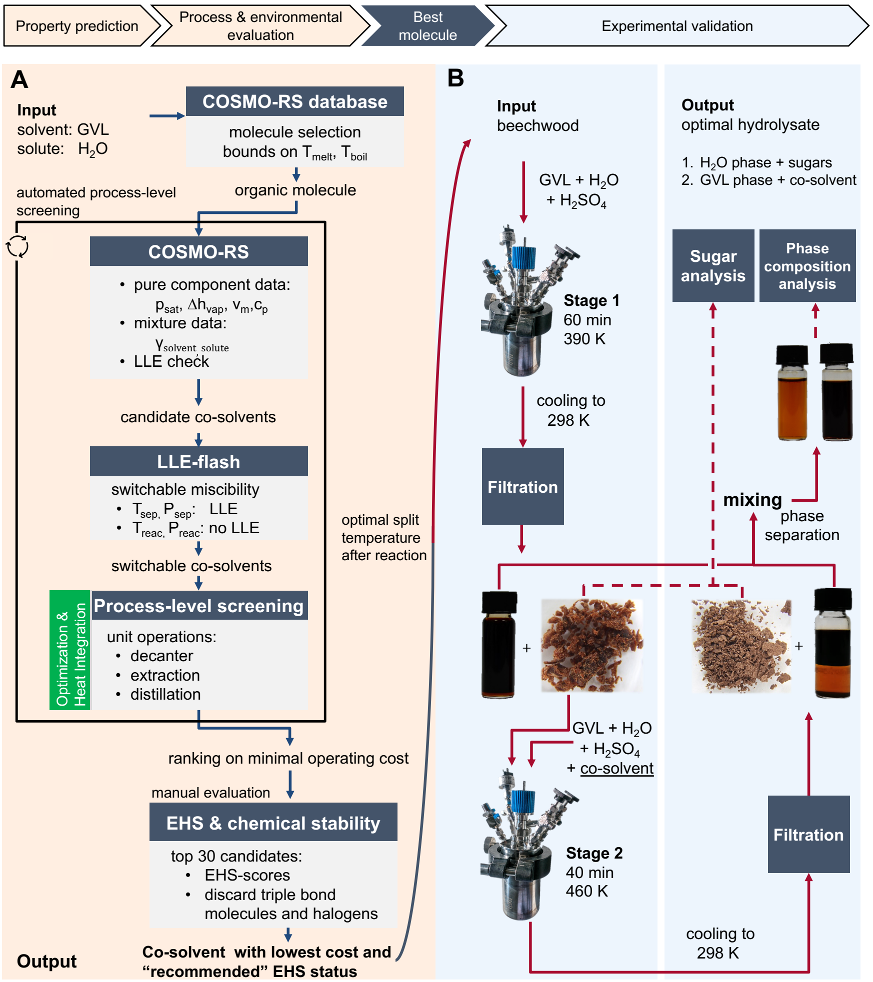

Figure 2: Workflow of (**A**) the computational solvent screening using COSMO-RS on process level with EHS evaluation of the top 30 candidates and (**B**) the experimental procedure of two-stage beechwood conversion and subsequent phase composition analysis of the liquid product and residual sugar analysis of the solid product. Stage 1: single-phased. Stage 2: single-phased at reaction temperature and two-phased below 460 K.

choose a manual EHS evaluation for the 30 best candidates after process optimization using a numerical procedure[36] to reduce model complexity. However, this step can also be automated using predictive EHS models[31], which would allow evaluating all candidates.

The first stage in the co-solvent selection is to narrow down the available molecules (> 4600) in the COSMO-RS database by setting bounds on the melting and boiling points so that all molecules meet the requirement to be liquid at ambient conditions, with a safety margin of 15 K (313.15 K). The boiling point of the co-solvent candidate $X_{\text{co-solvent}}$ needs to be lower than that of LVA ($T_b = 519$ K), since LVA is used for further GVL production and must, therefore, form the bottom product of the distillation column. Next, we select a subset of molecules from the COSMO-RS database based on design constraints, i.e., we consider only organic molecules and exclude halogens, which results in 2000 molecules.

The following stages are automatically repeated for each molecule (black box in Figure 2A): The existence of an LLE with water is checked using the binary LLE calculation in COSMOtherm.[37] It is not clear from the COSMOtherm manual[38] whether this check satisfies the necessary and sufficient condition of thermodynamic phase stability. Therefore it is not possible to state if there is a guarantee that the LLE check results in a correct phase split. This analysis should be performed in a later design stage. The compositions of the phases are not yet constrained at this point. For each resulting candidate co-solvent $X_{\text{co-solvent}}$, pure component properties (vapor pressure, enthalpy of vaporization, and molar volume) are predicted in COSMO-RS. Only for the calculation of heat capacities the group contribution method of Benson and Buss[39] is used, which combines low computational time with reasonable accuracy compared to other methods for the estimation of heat capacities.[40] The calculation of heat capacities in COSMO-RS is possible but computationally too demanding for this study.

Isothermal activity coefficients are calculated directly in COSMO-RS for both the liquid-liquid and the vapor-liquid equilibrium. All predictions are performed in COSMOtherm 17 on the TZVPD-fine accuracy level. Nonrandom two-liquid (NRTL)[41] parameters are fitted to the binary subsystems and used to predict ternary phase behavior. The NRTL activity coefficient model is well suited to represent highly nonideal mixtures. Still, for pressures above 10 bar, predictive equation-of-state models are preferable because they consider the pressure dependence of mutual solubility. Here we assume the pressure dependence to be negligible to reduce the computational cost at this stage. This effect should be analyzed in a later design stage. Furthermore, false miscibility gaps could potentially rise from the regression of NRTL parameters using COSMO-RS activity coefficients since only the necessary condition of phase stability is enforced.[42] We choose not to enforce both necessary and sufficient conditions of phase stability, to reduce the computational effort when fitting a large number of molecules.

The number of phases of the solvent systems must be switchable to recycle most of the organic stream exiting the reactor R1. This is checked for the following temperatures using an LLE flash routine: 453 K (conversion temperature, one phase required), ambient temperature (a surrogate for separation temperature, two phases desired). We discard non-switchable systems for the evaluation at the process level. The fraction of $X_{\text{co-solvent}}$ in z_F is variable at this stage, as it affects the ability and temperature range of phase switching. We first check the switchability for a feasible feed composition. Suppose the mixture forms two phases at the reaction temperature. In that case, we lower $x_{\text{co-solvent}}$ while keeping the ratio of GVL and water constant to identify the lowest co-solvent concentration possible while ensuring switchability.

2.3.2 Process optimization and EHS evaluation

The decanter temperature T_{D1} is optimized separately from the remaining separation process. This is because of the model simplification that the recycles from D1 and D2 to R1 in the original separation process[9] are exiting streams in our process model. This decomposed approach can lead to suboptimal results compared to an optimization where all unit operations are subject to the same cost function. However, such a rigorous approach would require the inclusion of biomass conversion in the process model. The objective function for the flash optimization (cf. Section A, ESI†) aims to maximize the partition of GVL and water in the respective phases. The resulting temperatures are fixed for the flowsheet calculation and optimization.

The process model consists of two reduced-order column models (extraction and distillation), heat exchangers, and pumps. We minimize the operating costs resulting from the reduced-order process model, considering heating, cooling, electricity, and co-solvent loss. In addition, we use temperature-dependent NRTL parameters in the unit operation models and can thus perform process optimization. To determine the parameters in this work, we use an equally-spaced temperature grid in the range of 398.15 K to 473.15 K with ten temperature grid points. Overall we perform 11 evaluations of the activity coefficients on each of the temperature grid points.

The reduced-order column models yield a pure product (sharp separation). Simultaneously, they operate at minimum solvent (extraction) and energy (distillation) demand, so there is no need to define purity requirements. We solve the optimization problem with the derivative-free solver *Pattern Search*[43] in MATLAB® V7.10, which proved to be an error-prone solver in this work. The resulting co-solvents with their respective cost-optimal process operating points are ranked toward minimum operating costs. Whereas pinch-based reduced-order models allow a systematic screening with rapid calculations of minimum energy and solvent demand while being thermodynamically accurate, they do not replace a rigorous distillation or extraction model. These models assume an infinite number of separation stages and therefore operate at a point of minimum reflux or minimum solvent demand. Therefore, the screening results can only be considered as a possible lower estimate on the operating costs of the actual process.

Another important measure that must be considered while selecting a co-solvent is its impact on the environment and human life. Therefore, the top 30 candidates are evaluated further on their EHS scores. This step can also be automated using predictive models.[44] These models would then allow for complete automation of the computational selection procedure and would also enable evaluating molecules not listed in databases. However, in this work, we choose a manual selection to reduce model complexity. In particular, we apply the method *CHEM21*[36], which was introduced to evaluate less classical solvents by the Global Harmonized System and European regulations. This method allows us to classify all solvents in the categories *recommended* (solvents that can be tested in a first screening within processes), *problematic* (solvents whose implementation on the pilot or production scale requires specific measures) and *hazardous* (scale-up constraints are significant and the substitution of these solvents during process development is a priority).[36] We exclude problematic and hazardous co-solvents. The co-solvent candidate with the lowest operating costs and a *recommended* EHS status is manually chosen for experimental validation.

2.3.3 Experimental validation

Our approach to the automated screening of co-solvent candidates for co-solvent hydrolysis includes selection criteria that cannot be quantified on a model-based basis: First, the co-solvent candidate should not hinder the production of sugars from the biomass. It should also promote the formation of two phases upon cooling, such that one organic phase is rich in GVL and co-solvent and the other is rich in sugars and water. Finally, the co-solvent candidate should render lignin insoluble in both phases.[7] To consider these effects inside our process model, a detailed representation of the biomass conversion reaction would be needed, which would significantly increase the computational time. Therefore, we chose an experimental validation of the best co-solvent candidate after the computational screening.

We convert beechwood into soluble carbohydrates using the best co-solvent found in a laboratory setup to ensure that we meet these criteria. The next best-ranked candidate is tested if the best-ranked co-solvent fails inside the validation experiments. The biomass is processed in a two-step approach,[7,9] as outlined in Figure 2B. Besides impregnation and contacting the biomass with the catalyst, the mild conditions in the first step allow the release of lignin and hemicellulose fractions while further degradation of the resulting monosaccharides is avoided. The increased temperature in the second step enables complete biomass disintegration and cellulose hydrolysis. The separation of both temperature levels in a two-step approach, thus, supports the maximum release of monosaccharides from the biomass with avoidance of temperature-induced degradation reactions. We calculate partition coefficients for the resulting two liquid phases using IR spectroscopy for concentration measurement. The feasibility of sugar quantification within the solvent system by IR spectroscopy is evaluated. After the beechwood conversion reaction, the mixture is filtered, and the dried residue is weighted to close the mass balance. Differences in the solid content would indicate changes in the amount of lignin insoluble in the mixture. To determine the amount of unreacted sugars in the solid residues, washed and dried solid samples from the first and second conversion stages are hydrolyzed with an aqueous sulfuric acid solution following the NREL protocol.[45] The insoluble lignin content is determined from the remaining solid fraction gravimetrically, whereas the resulting hydrolysate is analyzed with ion-exchange chromatography (IC) for C_5- and C_6-sugars. Details of the experimental procedure are summarized in the ESI† (Section C).

3 Results

3.1 Process optimization results

We apply the proposed method to compile a list of the 30 best co-solvents ranked on minimal operating costs (cf. Table D.1, ESI†). Since the biomass conversion reaction is not part of the model and the main resulting products are sugar molecules dissolved in the aqueous phase of the extraction column E1, we indicate operating costs in € per kmol water in raffinate (WIR) instead of kmol product. The majority of the 30 evaluated co-solvents are aromatic hydrocarbons (cf. Table D.1, ESI†). Out of the top five molecules ranked on their operating costs (cf. Figure 3), ethylbenzene and toluene were already listed among 16 other co-solvents in the solvent selection of Motagamwala *et al.*[7] Toluene was selected on the basis of experimental extraction efficiency measurements and EHS assessment.

In our analysis, the performance in the process significantly changes through process optimization (Figure 3A). Of the five best candidates, the most significant improvement in operating costs is achieved for diphenylether with 35% reduction, followed by 3-methylstyrene (25%), allylbenzene (21%), ethylbenzene (15%) and toluene (12%). Before process optimization, toluene is the leading candidate among the five. After optimization the co-solvent with the lowest operating costs is allylbenzene with €0.187 WIR $^{-1}$.

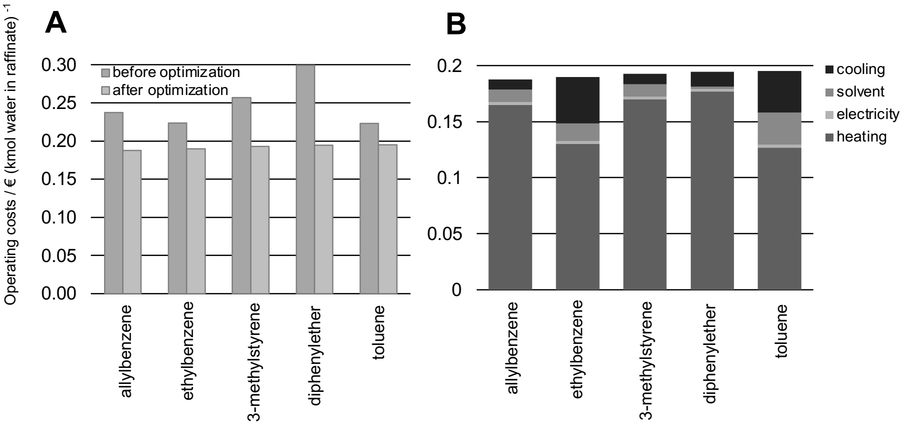

Figure 3: (**A**) Operating costs of the five best performing co-solvent candidates with heat integration, before (dark gray) and after optimization (light gray). (**B**) Cost structure of co-solvent candidates after heat integration and process optimization.

The top 30 candidates differ in terms of their cost composition; they are, however, very similar in their final optimal operating costs (Figure 3B). A high share of total operating costs is attributed to heating costs. Ethylbenzene and toluene have the lowest shares of 68% and 64%, respectively, indicating good performance of the molecule in the distillation. Similarly, a low share of costs caused by solvent loss indicates efficient extraction within the process. Solvent prices are assumed to be constant in our study. Therefore, the amount of solvent lost in the process can significantly impact the operating costs, particularly when market prices are used. The highest share in costs caused by solvent loss is observed for toluene (15%).

3.2 Ranking of best co-solvents and EHS results

Our screening yields three Pareto dominant co-solvent candidates (see Figure 4, in black circles) in the considered set of molecules selected from the COSMO-RS database in the objectives operating costs and EHS scores. The EHS score is calculated by a numerical procedure[36], and as such, is a metric. A low score indicates an environmentally favorable solvent. Two (ethylbenzene and 1,3-dimethylbenzene) out of the 30 best-ranked candidates achieve an EHS score low enough to be recommended. Among the top 30 molecules, 1,3-dimethylbenzene achieves the lowest EHS score of 9 but is only ranked 15th in operating costs. The co-solvent with the lowest operating costs (€0.187 kmol WIR $^{-1}$), allylbenzene, is classified as problematic with an EHS score of 14. The third Pareto dominant candidate, ethylbenzene, yields an EHS score of 10 and a *recommended* status. Furthermore, ethylbenzene is economically more favorable than 1,3-dimethylbenzene, with operating costs of €0.19 kmol WIR $^{-1}$. Here, the benchmark co-solvent toluene is ranked fifth with operating costs of €0.195 kmol WIR $^{-1}$ and is classified *problematic* with a total EHS score of 14. It is important to note that the differences in operating costs among the top candidates after optimization are quite small, indicating that only a detailed comparison between the best co-solvents within the final process can give certainty about the best candidate. However, the differences in the EHS scores among the 30 best-performing co-solvents is significant since the depicted range in Figure 4 can result in a co-solvent being *recommended* (lower end of the scale) or *hazardous* (upper end of the scale) according to the *CHEM21* system. Ethylbenzene is the only co-solvent candidate that exceeds the benchmark toluene proposed by Won *et al.*[9] with about 15% improvement in operating costs achieved through solvent screening and process optimization in this work,

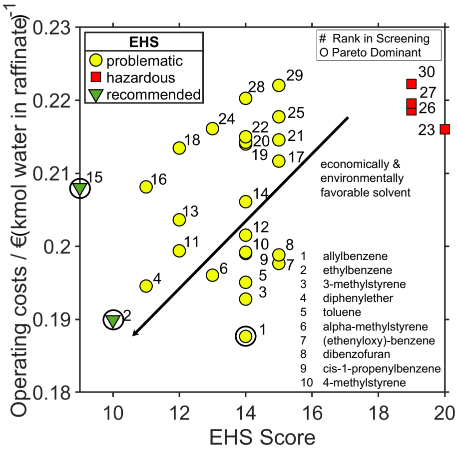

Figure 4: Operating costs per kmol water in raffinate with respect to environment, health and safety scores using the CHEM21 method. The economically and environmentally most favorable co-solvent is located at the lower left corner. Pareto dominant points are highlighted in black circles (1 = allybenzene, 2 = ethylbenzene, 15 = 1,3-dimethylbenzene). Toluene and ethylbenzene were already considered by Motagamwala *et al.*[7]

as well as in its EHS rating (from 14/*problematic* for toluene to 10/*recommended* for ethylbenzene). We, therefore, conclude that ethylbenzene is the most promising candidate for co-solvent hydrolysis. Recently, Teixeira *et al.*[46] showed that ethylbenzene could be obtained from biomass-derived furan using a zeolite catalyst with a high yield and selectivity under mild conditions. This additionally supports further investigation of ethylbenzene since unlike toluene, it can be sourced renewably.

The optimization and heat integration results for the best candidate ethylbenzene are summarized in Figure 5. The reaction temperature and pressure are adapted from Won *et al.*[9], while all other design variables such as temperature and pressure of the unit operations are optimization variables. In this SMSS,

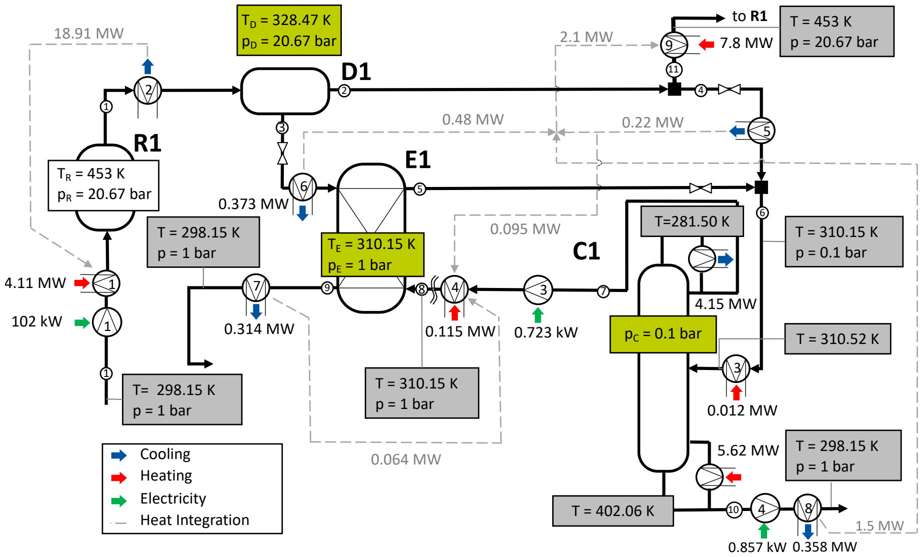

Figure 5: Flowsheet optimization and heat integration results for the co-solvent ethylbenzene with 1 kmol s^{-1} feed stream, optimization variables given in green boxes and stream conditions in gray boxes. Utility streams are illustrated with entering/exiting arrows; cooling (blue), heating (red) and electricity (green). Both extraction and distillation columns are modeled using reduced-order models. A stream table can be found in the ESI[†] (Section D.2).

in which ethylbenzene constitutes the co-solvent, decanter D1 is optimal at 328.47 K, while the extraction column is cost-optimal at 310.14 K. The heating of the feed constitutes the second-highest power consumption of the heat exchanger after the recycle stream to R1. The optimum distillation pressure is 0.1 bar. A stream table and the results of heat integration are summarized in the ESI[†] (Table D.2, Figure D.1).

3.3 Experimental results

The method's accuracy is tested by validating the SMSS, consisting of water, GVL, and the co-solvent, at the computationally determined optimal feed compositions and temperatures (cf. Table D.1, ESI†) for decanter D1 in the following. IR spectra of the organic (top) and aqueous (bottom) phases after phase separation at optimal split temperature for the co-solvents ethylbenzene and toluene are shown in Figure 6.

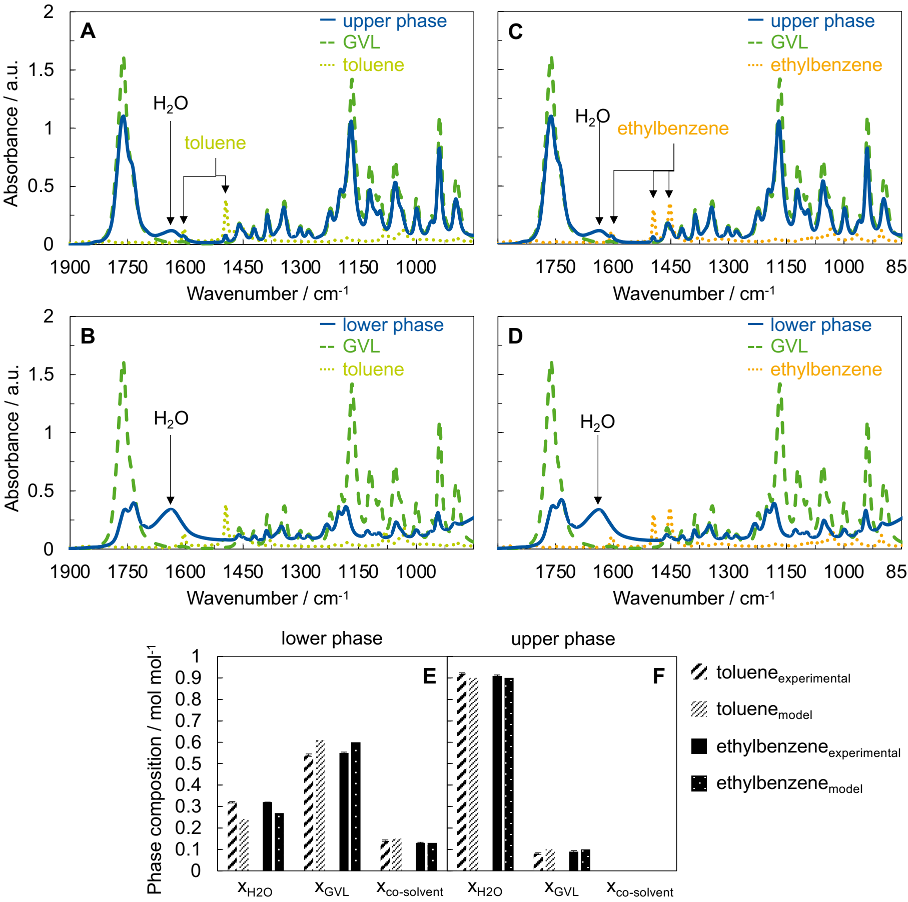

Figure 6: IR spectra of the pure chemical species GVL, toluene, and ethylbenzene together with spectra of the upper (**A**, **C**) and lower (**B**, **D**) phases of the ternary solvent systems after phase separation at optimum split temperature (toluene: 310 K, ethylbenzene: 328 K). Corresponding phase composition, given in mole fractions, for the upper phases (**E**) and for the lower phases (**F**) are compared to model results from COSMO-RS.

GVL dominates the spectra of the upper phases for both co-solvents. However, toluene and ethylbenzene peaks can be also detected at wavenumber of $1\,450\ \text{cm}^{-1}$, $1\,496\ \text{cm}^{-1}$, and $\tilde{\nu} = 1\,604\ \text{cm}^{-1}$ in the upper phase, respectively. No such peaks are found in the lower phase leading to the conclusion that the toluene and ethylbenzene content is insignificant in the lower (aqueous) phase, and both species are only present in the upper phase, as expected (cf. Figure 6A,C). Quantitative analysis of the IR spectra for the upper and lower phases is done applying partial least squares regression (PLS). Calibration accuracies between $0.9{\cdot}10^{-3}$ to $5.2{\cdot}10^{-3}$ mol per mol for the respective chemical species are reached (cf. Table E.1, ESI†). Mole fractions for the upper and lower phase are shown in Figure 6E-F. The phase composition does not change substantially by using ethylbenzene instead of toluene as a co-solvent, which is expected due to the strong similarity of both co-solvents' molecular structures. Partition coefficients of GVL and water are calculated from experimental data as ratios of the respective species mole fraction in the upper phase divided by the species mole fraction in the lower phase, yielding $R_{\mathrm{GVL}} = 6.75$ for toluene and $R_{\mathrm{GVL}} = 6.11$ for ethylbenzene. Consequently, toluene yields slightly better results in GVL extraction compared to ethylbenzene, whereas H_2O distributes equally for both co-solvents ($R_{\mathrm{H2O}} = 0.35$). The COSMO-RS model predictions in Figure 6E-F show good agreement with experimental data of both phases. We observe a systematic underestimation of the species water and a systematic overestimation of species GVL in both phases by COSMO-RS. The deviations (about 0.1 mol per mol) for the upper phase still support valid COSMO-RS model results that enable a permissible co-solvent ranking.

In the next step, beechwood hydrolysis experiments are performed with both co-solvents according to Figure 2 (cf. Section C, ESI†). The total beechwood conversion is very high and reaches comparable values of 96% for toluene and 98% for ethylbenzene, indicating no negative influence on the biomass conversion process for both co-solvents. Partition coefficients for GVL after biomass conversion decrease by 40-60% (cf. Figure E5, ESI†) compared to the artificial ternary mixtures (c.f. Figure 6A-D), which is attributed to sulfuric acid or dissolved wood components that change the cross-solubility of the two phases. We use the resulting phase compositions of the ternary system inside our reduced-order process model to calculate how that would affect the process performance. The analysis indicates an increase in operating costs by a factor of 2.2-2.4.

IR spectroscopy does not resolve the sugar species signals in the organic and aqueous phases due to the abundance of signals from the very IR-active GVL molecule. However, IC analysis of the hydrolysate from samples of the solid residues show that the residues after the second process step for both toluene and ethylbenzene consist of almost only lignin with only minor traces of sugar species in case of ethylbenzene (cf. Figure E.6, ESI†). Thus, the results indicate effective sugar extraction from the solid biomass for ethylbenzene and toluene. Similar results were observed by Motagamwala *et al.*[7], where co-solvents similar in molecular structure showed comparable influence on the sugar yield.

4 Conclusions

Solvent-enabled disintegration and conversion of biomass to produce biorenewable fuels and chemicals require a cost-efficient process such that the production is competitive with their petroleum-derived equivalents. To achieve this target, the efficient separation of the solvent is seen as a key success indicator. Here we aimed to define a cost-optimal co-solvent for the GVL-based co-solvent hydrolysis. By combining computer-aided solvent screening with the insights gained through experimental biomass conversion experiments, we could find an optimal co-solvent molecule for this process. We replaced the manual miscibility analysis and extraction experiments with computer-aided process evaluations to achieve this. We implemented a wide range of co-solvent candidates from the COSMO-RS database into a process model and optimized the operating costs while ensuring environmental compatibility in an EHS study. In combination with process optimization, process-level evaluation has proven necessary, as it is the only way to capture process trade-offs.

We identify ethylbenzene as a promising co-solvent for the switchable GVL-based biomass hydrolysis process. Using ethylbenzene and considering only the solvent system, we reduced the operating costs of a process model using reduced-order unit operation models by about 15%, in contrast to the benchmark co-solvent toluene in a non-optimal process. This result would not be expected based on the analysis of partition coefficients alone and underlines the process-based approach.

By IR spectroscopy analysis of the phase compositions inside the ternary model mixture, the partition coefficients are determined and related to COSMO-RS predictions. We demonstrate that COSMO-RS predictions are reasonable estimates of the experimental partition coefficients with a maximum deviation of about 0.1 mol per mol. We confirm that the co-solvent we recommend does not hinder the biomass dissolution and the formation of two phases. Following the NREL protocol, we hydrolyze the solid residues which result from the co-solvent-based biomass conversion for toluene and ethylbenzene to determine the amount of unconverted sugars. Through IC analysis of the hydrolysate, we show that the residues consist almost entirely of lignin and contain only minor traces of sugar species in the case of ethylbenzene. We perform the decanter step after the biomass conversion experimentally with ethylbenzene and toluene. Additional analysis of the partition inside the hydrolysate indicates a decrease in the partition coefficients by 40-60%, which would increase the operating costs in the final process by a factor of 2.2-2.4.

Using our approach, we assessed a large number of molecules at the process level and defined a cost-optimal co-solvent for the GVL separation. Unlocking the full potential of such co-solvent-based biomass conversion processes will help to make biomass-derived fuels and chemicals competitive and environmentally friendly.

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Author Contributions

KK: Conception and organization of the manuscript; Design of the computational procedure; Computational modelling and optimization; Environment, health and safety evaluation; Preparation of the computational part of the manuscript

AE: Design of experimental procedure; Experimental evaluation of the partition coefficients and biomass hydrolysis; Calibration, application and evaluation of IR spectroscopy; Analysis of solid residues; Preparation of the experimental part of the manuscript

CK: Assistance in the implementation of process models

JS: Generation of COSMO-RS data; Estimation NRTL-parameters

AB: Discussion of the COSMO-RS calculations

JV: Design of the project; Definition of the work; Scientific support; Guidance and discussion on the experimental, analytical and computational method; Preparation of parts of the manuscript; Advice on structure and presentation of this work

AM: Design of the project; Definition of the work; Scientific support; Preparation of parts of the manuscript; Guidance and discussion on the computational method; Advice on structure and presentation of this work

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Supporting information

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Conflicting interests declaration

There are no conflicts to declare.

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