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

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14 ELECTRONIC SUPPLEMENTARY INFORMATION

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1 A Optimal decanter temperature

2 The objective function for the optimization of the decanter D1 reads:

$$f^{flash} = \phi^{II} \cdot x_1^{II} + (1 - \phi^{II}) \cdot x_2^{I}$$

with ϕ^{II} the aqueous phase consisting mainly of H₂O (1) and $(1 - \phi^{II})$ the organic phase consisting mainly of GVL (2). A higher value for f^{flash} is desireable, therefore the objective f^{flash} is maximized to find the optimal operating temperature. The resulting temperatures are fixed parameters for the following flowsheet calculation and optimization.

8 B Cost calculation and assumptions

The prices for heating and cooling are adapted from Seider *et al.*¹ and linearized to achieve the respective temperature levels. The heating costs (HC) and cooling costs (CC) are calculated as follows:

$$\begin{split} f^{HC} &= \begin{cases} \dot{Q} \cdot 2.56 \frac{\mathfrak{E}}{\text{GJ}} , & \text{for } T \leqslant 412.05 \,\text{K} \,, \\ \dot{Q} \cdot (0.044 \cdot \frac{T}{\text{K}} - 15.566) \frac{\mathfrak{E}}{\text{GJ}} \,, & \text{for } T > 412.05 \,\text{K} \,, \end{cases} \\ f^{CC} &= \begin{cases} \dot{Q} \cdot (-0.068 \cdot \frac{T}{\text{K}} + 22.411) \frac{\mathfrak{E}}{\text{GJ}} \,, & \text{for } T \leqslant 303.15 \,\text{K} \,, \\ \dot{Q} \cdot 0.31 \frac{\mathfrak{E}}{\text{GI}} \,, & \text{for } T > 303.15 \,\text{K} \,. \end{cases} \end{split}$$

To calculate the electricity costs (EC), the power of the adiabatic pump needs to be determined:

$$P = \dot{n} \cdot v_{\rm m} \cdot (p_{\rm out} - p_{\rm in}).$$

The electricity costs

$$f^{EC} = P \cdot 11.1 \frac{\notin}{\text{GJ}}$$

9 depend solely on the required power.¹ We assume a unified price of $4 \in /\text{kg}$ 10 solvent². Finally, the operating costs

$$f^{OC} = f^{HC} + f^{CC} + f^{EC} + f^{SC}$$

11 are used to rank of the feasible co-solvent candidates.

1 Table B.1 summarizes all important assumptions, variables subject to opti-2 mization and parameters for the computer-aided part of the co-solvent screening.

Table B.1: Summary of assumptions, variables subject to optimization and parameters inside the computational co-solvent screening.

Value	Assumption	Variable	Parameter	
	description	optimization	fix	
Co-solvent candidates				
molecules considered	only organic molecules		> 2000	
from COSMO-RS database	liquid at $(T,p)^{ambient}$		orig. (> 4600)	
EHS evaluated molecules			30	
co-solvent price	4 €/kg			
Thermodynamic				
vapor pressure,			COSMO-RS	
molar volume			prediction	
enthalpy of vaporization,				
activity coefficients				
Heat capacity			Group contribution method	
Process model				
extraction-	pinch-based	T^{E1}		
column (E1)	reduced-order model			
distillation-	pinch-based	p^{C1}		
column (C1)	reduced-order model			
decanter (D1)	LLE-flash model	T^{D1}		
reactor (R1)	reaction negleted		453K, 20.27 bar	
co-solvent in feed	Ū.	X _{co-solvent}		
recycle of organic phase	exiting stream		86.3%	
GVL concentration	$< 2 \mathrm{wt}$ %			
in raffinate				

1 C Experimental methods

2 C.1 Materials

Beechwood chips with sizes of 2 - 10 mm and a moisture content of 6% by weight (determined at 378 K over night according to Sluiter *et al.*³) are used in all experiments as representative lignocellulosic biomass. γ -valerolactone ($\geq 98\%$) is obtained from Acros Organics and ethylbenzene ($\geq 99\%$) is purchased from Alfa Aesar. Toluene ($\geq 99.5\%$) and sulfuric acid ($\geq 95-97\%$) are obtained from VWR Chemicals. Water is deionized (conductivity < 0.8 µS/cm at 298 K). All chemicals are used without further steps of purification.

10 C.2 Experimental validation of phase composition

- 11 Determination of the phase composition for the ternary solvent systems H_2O ,
- 12 GVL, co-solvent, samples according to Table C.2 are prepared in a separating funnel. After thoroughly mixing, the sealed separating funnel is placed in an

Table C.2: Overall sample composition given in mol-% and phase split temperature for determination of phase compositions.

co-solvent	$\mathbf{x}_{\mathrm{GVL}}$	$x_{\rm H_2O}$	$\mathbf{x}_{\mathrm{toluene}}$	$\mathbf{x}_{\mathrm{ethylbenzene}}$	$T_{\rm split}$
toluene	34.85	57.80	7.35	-	$310~{\rm K}$
ethylbenzene	34.85	58.80	-	6.35	$328 \mathrm{K}$

13

14~ oven, heated to the optimal phase split temperature to remain for 6 hours for

15 phase separation. The obtained liquid samples of the upper and the lower phases 16 are weighed and subsequently analyzed.

17 C.3 Experimental biomass conversion

A stainless steel batch autoclave (BR-300, Berghof Products + Instruments
GmbH, Eningen, Germany) equipped with PTFE inlay, stirrer, pressure sensor,
PT100 temperature sensor, BTC-3000 temperature controller and data logger
(ver. 2.1.3) is employed for all biomass conversion experiments.

22In the first stage, a solid to liquid mass ratio of approximately 1:4 together with 23a sulfuric acid concentration of 1.4% by weight with regard to the total liquid mass is adjusted. The first stage reaction temperature of 390 K in the preheated, 24 25sealed and stirred (150 rpm) autoclave is reached after 20 minutes and held for 60 minutes. Subsequently, the autoclave is cooled to room temperature and the 2627reaction mixture is weighed. Liquid and solid products are separated by a 2.5 28 μm filter paper (Whatman, 70 mm, grade 5) with vacuum filtration. A sample 29of the solid product is taken for moisture content analysis by weighing before and after drying at 313 K for 24 hours under vacuum. The remaining solid 30 residues of the first reaction stage are transferred to the second reaction stage. 31 As for the co-solvent toluene, Motagamwala et al.⁴ found the best conversion 3233 results for a system of $H_2O:GVL:co-solvent$ with mass ratios of 20:60:20 and 34 0.04% of sulfuric acid with regard to the liquid mass. We adjust the same mass ratios for the second reaction stage. The reaction temperature of 460 K of the 35 second reaction stage in the preheated, sealed and stirred autoclave is reached 36 after 30 minutes and held for 40 minutes. Thereafter, the autoclave is cooled to 37

1 room temperature and the reaction mixture is treated analogously to the first 2 stage. Samples of washed and dried solid residue after the first and the second 3 stage for both co-solvents ethylbenzene and toluene are treated according to 4 the NREL/TP-510-42618 protocol for determination of the residual content of 5 structural carbohydrates and lignin.⁵ Each solid sample is analyzed with one 6 replica.

7 C.4 Analytical methods

The sugar content in the liquid hydrolysate of the solid residues are determined 8 9 according to the NREL/TP-510-42618 protocol. The sugar analysis is performed with ion exchange chromatography (IC) (ICS-5000+, Thermo Scientific, 10 Waltham, MA, USA) equipped with a CarboPac PA100-column for species sep-11 aration (Thermo Scientific, Waltham, MA, USA) and the software Chromeleon 127.2 (Thermo Scientific, Waltham, MA, USA) for quantitative evaluation of the 13 14chromatogram. Liquid samples are analyzed by infrared (IR) spectroscopy employing a Matrix-MF Fourier-transform infrared (FT-IR) spectrometer equipped 1516 with a fiber-optic IN350-T diamond attenuated total reflection (ATR) probe with two reflections (Bruker Optic GmbH, Ettlingen, Germany). The spec-17trometer is cooled with liquid nitrogen and continuously purged with dry air. 18 19 Spectra are recorded in absorbance mode with OPUS ver. 7.5 (Bruker Optic GmbH, Ettlingen, Germany). A resolution of 4 cm^{-1} , 100 scans per spectrum 20and a total spectral range of $\tilde{\nu} = 600$ - 4000 cm⁻¹ are set. Background spectra 21 in air are taken before each measurement after cleaning the probe tip with iso-22propyl alcohol and compressed air. 2324Spectral analysis is performed in Peaxact (ver. 4.5, S-Pact, Aachen, Germany) 25applying PLS. Spectral data preprocessing includes selection of a spectral range of $\tilde{\nu} = 850 - 1900 \text{ cm}^{-1}$ for the upper and $\tilde{\nu} = 1015 - 1900 \text{ cm}^{-1}$ for the lower 26phase, a linear fit baseline subtraction, standard nominal variate (SNV) nor-2728malization and centering for standardization without any data smoothing. For 29the upper phase PLS models, each chemical species is calibrated with a PLS 30 rank of 3, whereas for the lower phase PLS models, a PLS rank of 1 is applied.

31 A leave-10%-out cross-validation is performed during calibration. The quality

of the calibration models with regard to each chemical species i is assessed by the coefficient of determination R_i^2 , the root mean square error of calibration

 $RMSEC_i$, and the root mean square error of cross validation $RMSECV_i$ (further

35 details on the figures of merit is provided by Conzen⁶).

1 D Model results

2 D.1 Co-solvent screening results: Ranking based on min-3 imal operating costs

Table D.1: 30 best co-solvent candidates with optimized process parameters and *Chem21* EHS score, ranked on operating costs (OC in \in / kmol water in raffinate). Red indicates hazardous, yellow problematic and green recommended.

	solvent	CAS	T_{D1}	p _{C1}	T_{E1}	OC	EHS
			К	bar	К	€/kmol WIR	
1	allylbenzene	300-57-2	322.59	0.42	309.11	0.187	14
2	ethylbenzene	100-41-4	328.47	0.10	310.15	0.189	10
3	3-methylstyrene	100-80-1	326.44	0.35	311.07	0.192	14
4	diphenylether	101-84-8	325.35	0.04	308.11	0.194	11
5	toluene	108 - 88 - 3	310.63	0.10	293.56	0.195	14
6	alpha-methylstyrene	98-83-9	322.44	0.10	308.99	0.196	13
7	(ethenyloxy)-benzene	766 - 94 - 9	311.85	0.10	291.19	0.197	15
8	dibenzofuran	132-64-9	329.36	0.04	303.00	0.198	15
9	cis-1-propenylbenzene	766 - 90 - 5	329.50	0.38	312.02	0.199	14
10	4-methylstyrene	622 - 97 - 9	323.31	0.10	308.21	0.199	14
11	1,2-dimethylbenzene	95-47-6	317.76	0.10	302.45	0.199	12
12	2-propylfuran	4229-91-8	309.49	0.10	288.18	0.201	14
13	2-methoxynaphthalene	93-04-9	313.78	0.04	299.96	0.203	12
14	2-vinyltoluene	611-15-4	322.96	0.10	313.17	0.206	14
15	1,3-dimethylbenzene	108 - 38 - 3	325.86	0.60	315.65	0.208	9
16	diphenylmethane	101 - 81 - 5	327.61	0.04	310.75	0.208	11
17	dibenzo-p-dioxin	262-12-4	330.92	0.04	308.70	0.211	15
18	naphthylethylether-beta	93-18-5	323.97	0.04	308.17	0.213	12
19	trans-1-propenylbenzene	873-66-5	330.95	0.32	332.13	0.214	14
20	cyclopropylbenzene	873-49-4	319.13	0.38	315.04	0.214	14
21	benzofuran	271 - 89 - 6	309.58	0.26	296.13	0.214	15
22	2-butylfuran	4466-24-4	327.37	0.10	306.49	0.215	14
23	4-methyl-1,3-pentadiene	926-56-7	305.46	0.19	288.13	0.216	20
24	isopropylbenzene	98-82-8	348.67	0.44	324.05	0.216	13
25	cycloheptatriene	544 - 25 - 2	306.17	0.39	287.92	0.217	15
26	3-methyl-1,4-pentadiene	1115-08-8	314.16	0.21	295.79	0.218	19
27	1,4-hexadiene	592 - 45 - 0	314.12	0.21	293.82	0.219	19
28	isobutylsalicylate	87-19-4	315.32	0.05	305.66	0.220	14
29	diantheme	4125-43-3	308.66	0.04	286.70	0.222	15
30	1,5-hexadiene	592 - 42 - 7	311.47	0.21	292.13	0.222	19

1 D.2 Process stream and heat integration res

Table D.2: Stream results for optimized flowsheet with the co-zene.



R

stream	flow	GVL	water	
	$\rm kmol/s$	m mol/mol	m mol/mol	11101/11101
1	1	0.3485	0.5880	0.0635
2	0.495	0.604	0.268	0.128
3	0.505	0.097	0.902	0.0004
4	0.068	0.604	0.268	0.128
5	0.105	0.467	0.036	0.498
6	0.173	0.52	0.127	0.353
7	0.083	1.7×10^{-16}	0.264	0.736
8	0.052	0	0	1
9	0.451	0	1	3.69×10^{-5}
10	0.090	1	0	0
11	0.428	0.604	0.268	0.128



Figure D.1: Heat exchanger network of optimized flowsheet with ethylbenzene. Red circles denote hot and blue circles cold process streams and grey dashed arrows the heat exchanger load (MW).

1 E Experimental results

2 E.1 PLS calibration and partition coefficients

Table E.1: Calibration results for the upper and the lower phase given in terms of R_i^2 / -, $RMSEC_i$ / mol mol⁻¹ and $RMSECV_i$ / mol mol⁻¹ for $i = \{GVL, H_2O, toluene, ethylbenzene\}$.

indicators	upper	phase for t	oluene	ne upper phase for ethylbenzene			
	GVL	H_2O	toluene	GVL	H_2O	ethylbenzene	
R_i^2	0.9995	0.9996	0.9988	0.9996	0.9999	0.9990	
$RMSEC_i$	$3.1 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$	$2.9 \cdot 10^{-3}$	$2.6 \cdot 10^{-3}$	$0.6 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$	
$RMSECV_i$	$5.6 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$	$4.3 \cdot 10^{-3}$	$4.4 \cdot 10^{-3}$	$0.9 \cdot 10^{-3}$	$3.4 \cdot 10^{-3}$	
indicators	lower	phase					
	GVL	H_2O					
R_i^2	0.9797	0.9797					
$RMSEC_i$	$2.8 \cdot 10^{-3}$	$2.8 \cdot 10^{-3}$					
$RMSECV_i$	$4.2 \cdot 10^{-3}$	$4.2 \cdot 10^{-3}$					

Partial least squares (PLS) calibration results for quantitative IR spectra evaluation are listed in Table E.1. R_i^2 values close to one are reached, thus the calibration explains the data well around its mean. The values for the $RMSECV_i$ are all one magnitude lower than the lowest mole fractions of chemical species during the experiments (0.025 mol mol⁻¹), which indicates a sufficiently precise calibration model.

10 E.2 Biomass hydrolysis experiments

Gravimetric analysis of the material streams (cf. Figure E.1 and Figure E.2) reveal a mass balance closure of 93% for the biomass hydrolysis with toluene as co-solvent, whereas 90% mass balance closure is achieved with ethylbenzene as co-solvent. For both co-solvents, beechwood conversion is very high with 96% in case of toluene and 98% in case of ethylbenzene.

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Figure E.1: Mass balance for two-stage conversion of beechwood with sulphuric acid, H_2O , GVL and co-solvent toluene. The mass balance is closed to an extend of 93%, whereas the total beechwood conversion accounts for 96%.



Figure E.2: Mass balance for two-stage conversion of beechwood with sulphuric acid, H_2O , GVL and co-solvent ethylbenzene. The mass balance is closed to an extend of 90%, whereas the total beechwood conversion accounts for 98%.



Figure E.3: IR spectrum of liquid reaction product after reaction stage one compared to IR spectrum of pure GVL. Both spectra are recorded at 298 K.

1 IR spectra of the first reaction stage (Figure E.3) and the upper and lower 2 phase resulting from the second reaction stage (Figure E.4) are recorded after phase split (at optimal split temperature) and at 298 K.



Figure E.4: IR spectra of upper and lower phases after reaction stage two employing toluene (**A** and **B**) and ethylbenzene (**C** and **D**) as co-solvent. Pure component spectra of GVL, toluene, ethylbenzene, xylose, and glucose are displayed for reference. Spectra are recorded after phase split (at optimum split temperature) and at 298 K.

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IR spectra after the second reaction stage do not show any co-solvent in

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Figure E.5: Results of IR measurements of the solvent system components inside the final hydrolysate. Corresponding phase compositions, given in mole fractions, for the upper phases (A) and for the lower phases (B) and their respective calculated partition coefficients (C).

the lower phase. This indicates that both co-solvents remain insoluble in the 1 2 lower phase (rich in water), but foster GVL partitioning in favor of the up-3 per phase. Partition coefficients of GVL and water in the liquid phases after 4 biomass conversion are calculated for both co-solvents based on the IR data of the respective chemical species, yielding values of $R_{\rm GVL} = 3.83$ and $R_{\rm H2O} = 0.49$ 5for toluene, and $R_{\rm GVL} = 2.48$ and $R_{\rm H2O} = 0.64$ for ethylbenzene, respectively 6 (cf. Figure E.5). The strong decrease in $R_{\rm GVL}$ and increase in $R_{\rm H2O}$ for both 78 co-solvents is attributed to dissolved wood components that change the crosssolubility of the two phases after biomass conversion.

Table E.2: Composition of raw material and solid residue after first and second conversion stage. Yield of dissolved C_6 and C_5 sugars after each stage via mass balance and referred to the respective raw material C_6 and C_5 sugar intake.

Species	Raw material	1 st stage	2 nd stage EB	2 nd stage TOL
	$/ \mathrm{wt}\%$	/ wt%	$/ \mathrm{wt}\%$	$/ \mathrm{wt}\%$
Lignin	19.04	46.87	66.52	68.31
Glucose	48.82	24.01	0.00	0.00
Xylose	19.59	9.15	0.00	0.00
Galactose	1.59	3.27	0.00	0.00
Rhamnose	0.27	0.00	0.00	0.00
Arabinose	0.62	0.00	0.00	0.00
Mannose	2.36	0.00	0.00	0.00
Cellobiose	0.00	1.17	1.45	0.00
Yield C _{6,dissolved}		64.3	99.9	100.0
Yield C _{5,dissolved}		69.8	100.0	100.0



Figure E.6: Composition of the raw material (beechwood) and the solid residues after the first and the second process stage for both toluene and ethylbenzene biomass conversion experiments. Pictures in upper row show the analyzed material samples, respectively. The respective numerical values are summarized in Table E.2

1 The compositions of the raw material beechwood and the solid residues after 2 the first and the second process stage for both biomass conversion experiments 3 using toluene and ethylbenzene are shown in Figure E.6. The respective numer-4 ical values are summarized in Table E.2. All compositions are determined according to the NREL/TP-510-42618 protocol with IC for the liquid hydrolysate 56 analysis. The IC results confirm that the sugars are extracted from the solid 7biomass into the liquid phase completely after the second stage for co-solvents 8 as only lignin (and a few cellobiose traces) are detected in the solid residue. Not 9 all biomass fractions could be recovered for the second stage as indicated by the 10 lack of about 30 wt%. Besides potentially remaining moisture, also minerals and 11ash can account for this part in the very small remaining solid fraction. The content of lignin in the solid residues after each process stage increases, whereas 1213the glucose content decreases compared to the initial raw material composition. 14This confirms biomass hydrolysis reactions in each process step and validates 15the assumption of full sugar solubilization after the second process stage for 16 both co-solvents.

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