SUPPORTING INFORMATION

Chemical recovery of γ-valerolactone/water biorefinery

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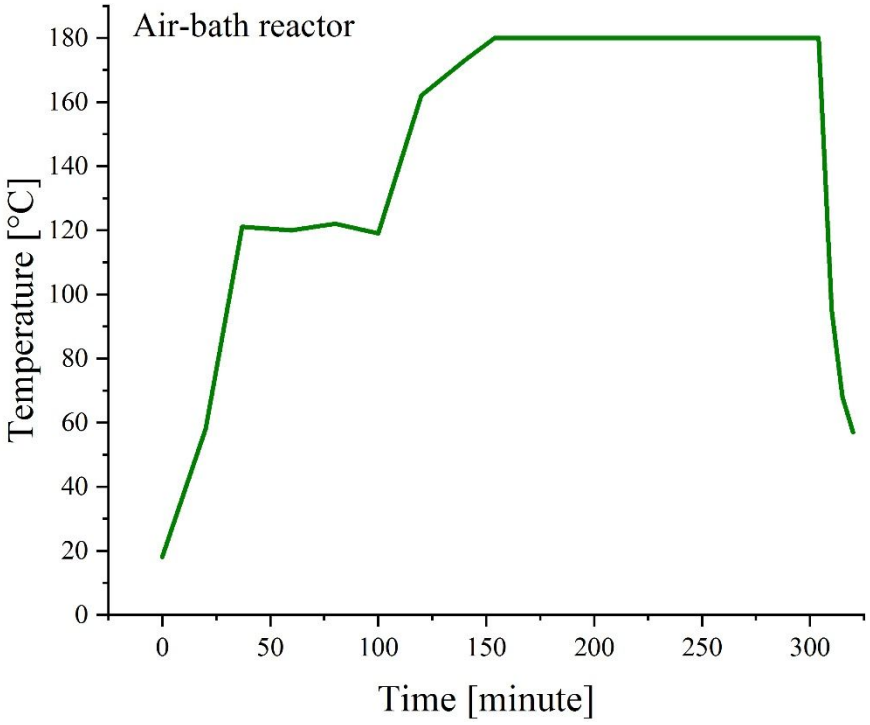
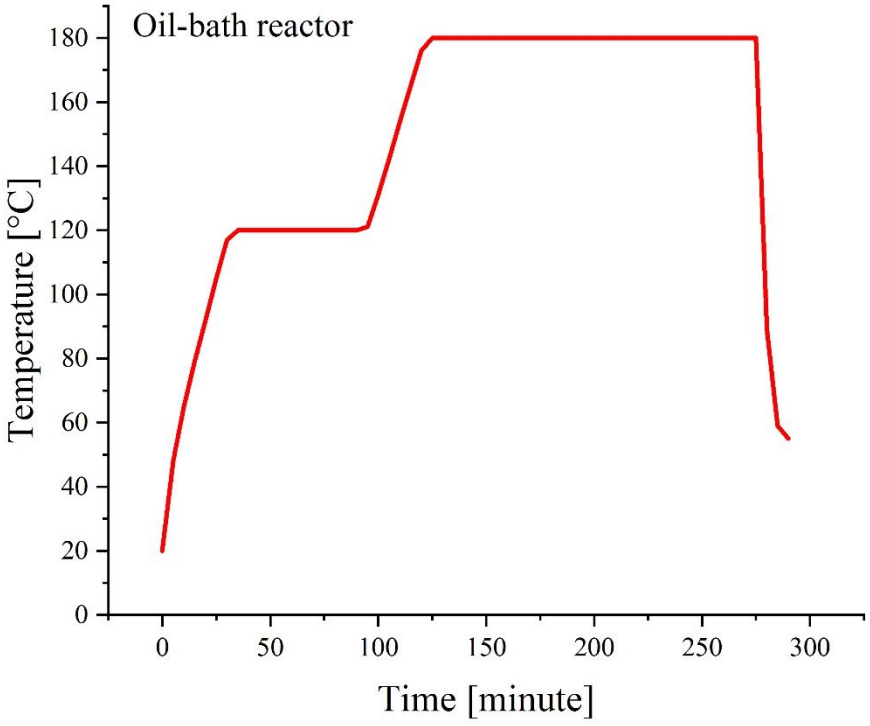
SUPPORTING MATERIAL 1

Temperature profiles of the GVL fractionation in oil-bath and air-bath reactors





SUPPORTING MATERIAL 2

Experiment protocol for investigating the recyclability of GVL recovered from spent liquor by liquid CO_2 extraction

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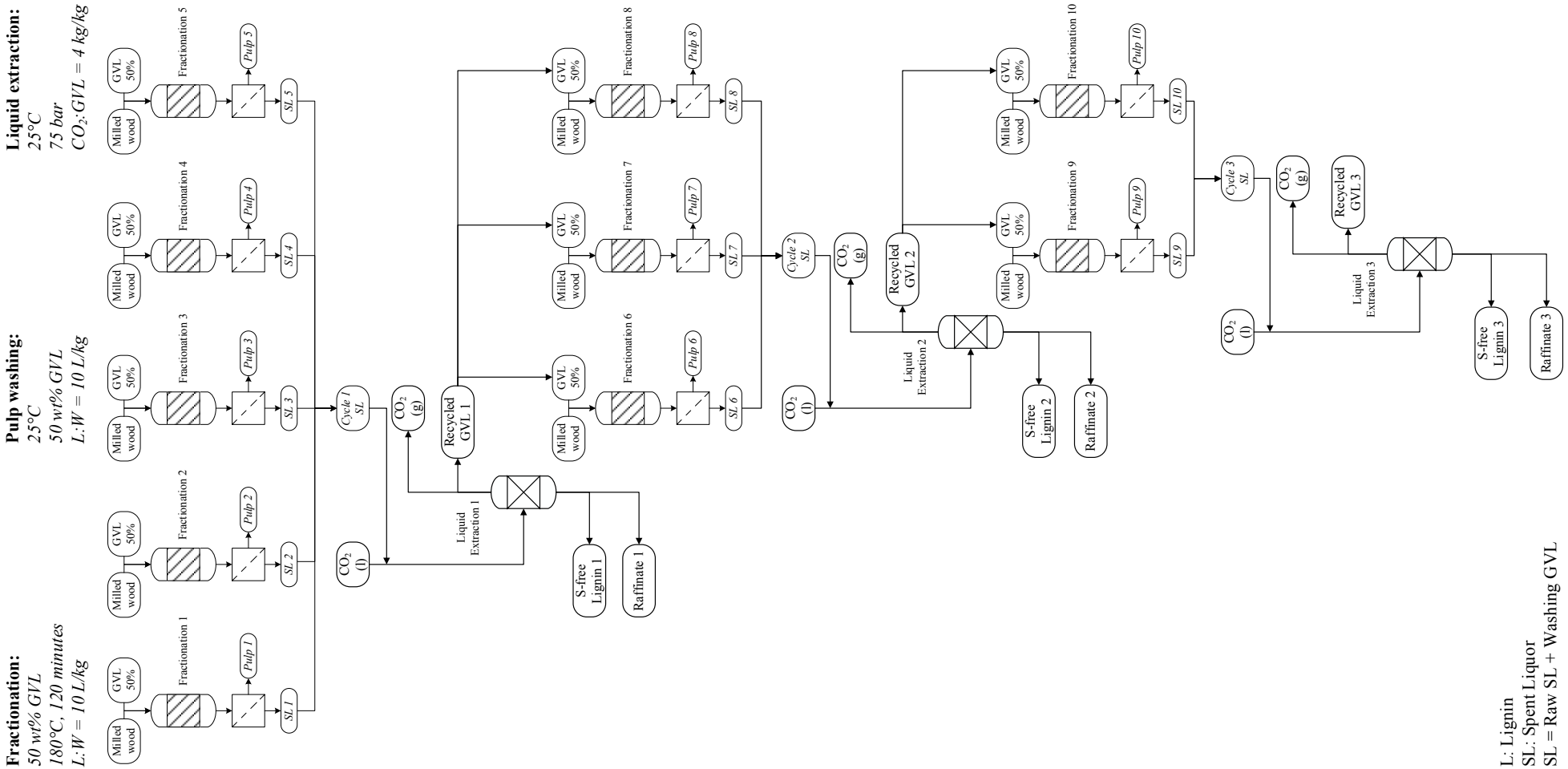


L: Lignin
SL: Spent Liquor
SL = Raw SL + Washing GVL

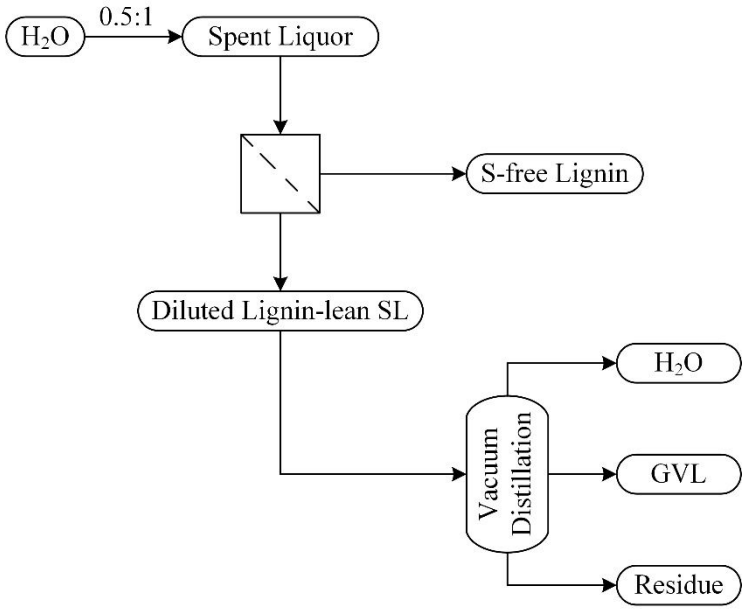
GVL mass balances in 3 consecutive fractionation cycles

Cycle	Sample	GVL in g	GVL spent liquor g	GVL washing water g	GVL out g	GVLout %
1	1	15.00	12.68	1.79	14.47	96.49
	2	15.00	12.94	1.63	14.57	97.11
	3	15.00	12.69	1.85	14.54	96.93
	4	15.00	13.00	1.55	14.55	96.98
	5	15.01	12.63	1.94	14.57	97.11
	AVERAGE-1	***15.00***	***12.79***	***1.75***	***14.54***	***96.92***
2	6	14.80	12.67	1.72	14.38	97.21
	7	14.80	12.59	1.69	14.28	96.49
	8	14.80	12.52	1.89	14.41	97.39
	AVERAGE-2	***14.80***	***12.59***	***1.77***	***14.36***	***97.03***
3	9	14.78	12.69	1.81	14.50	98.14
	10	14.78	12.74	1.85	14.59	98.70
	AVERAGE-3	***14.78***	***12.71***	***1.83***	***14.55***	***98.42***

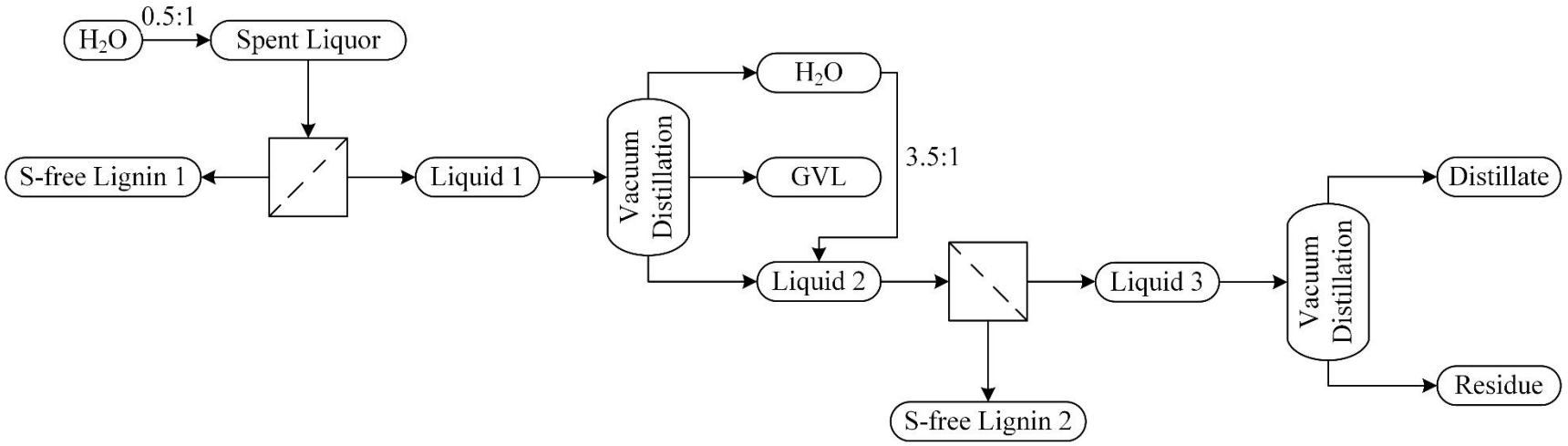
GVL content in the liquid samples were determined by GC

SUPPORTING MATERIAL 3

Experiment protocols for GVL recovery from spent liquor by vacuum distillation



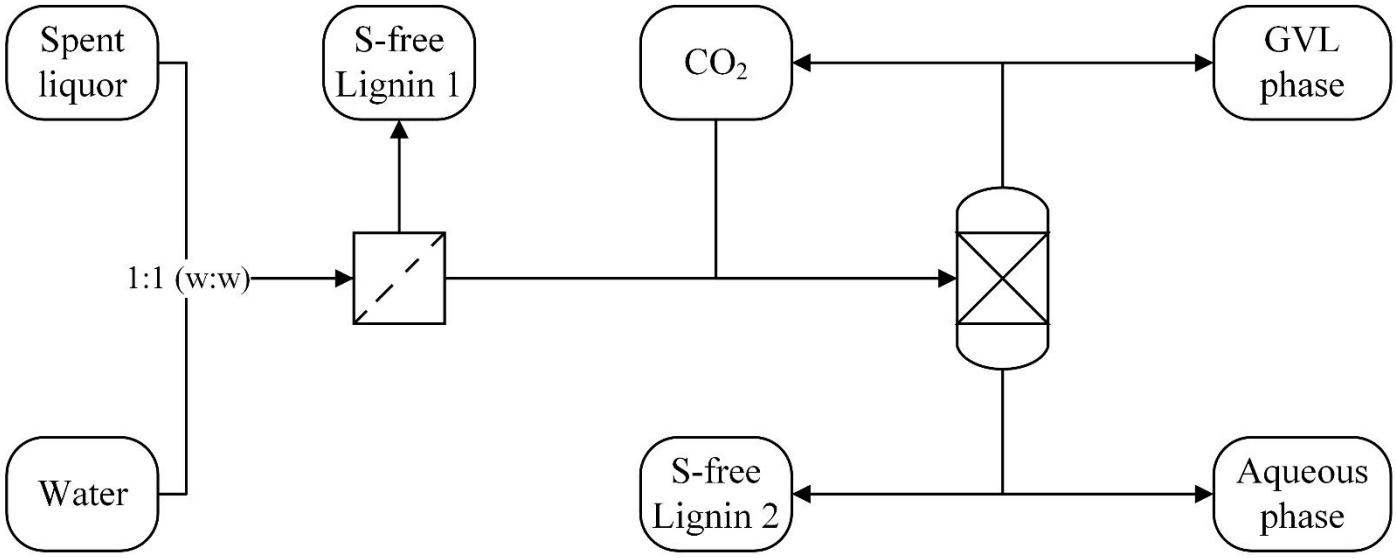
Scheme 1. One-staged (lignin removal + vacuum distillation) to recover GVL from the spent liquor.



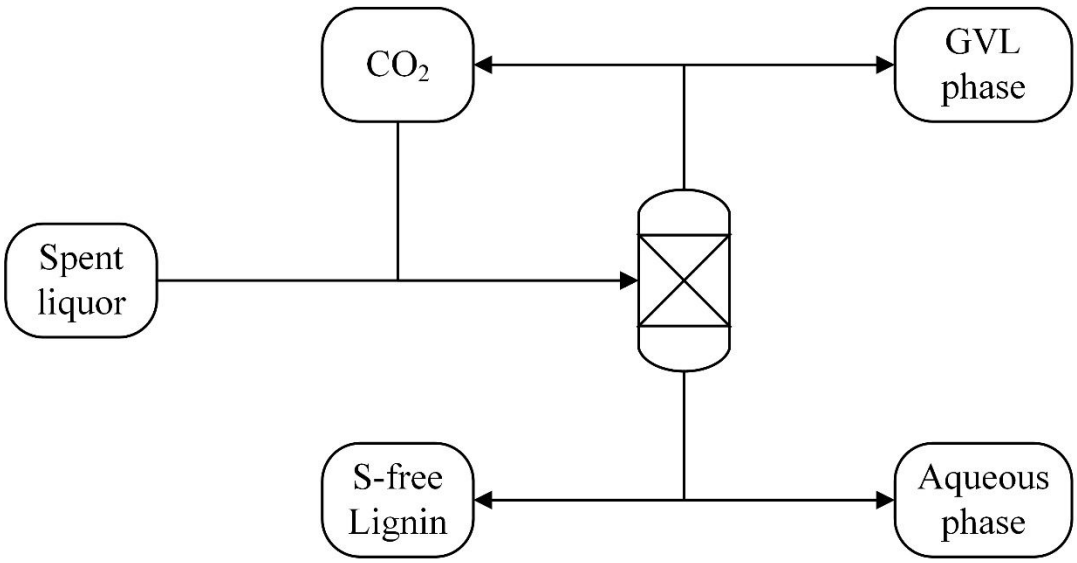
Scheme 2. Two-staged (lignin removal + vacuum distillation) to recover GVL from the spent liquor.

SUPPORTING MATERIAL 4

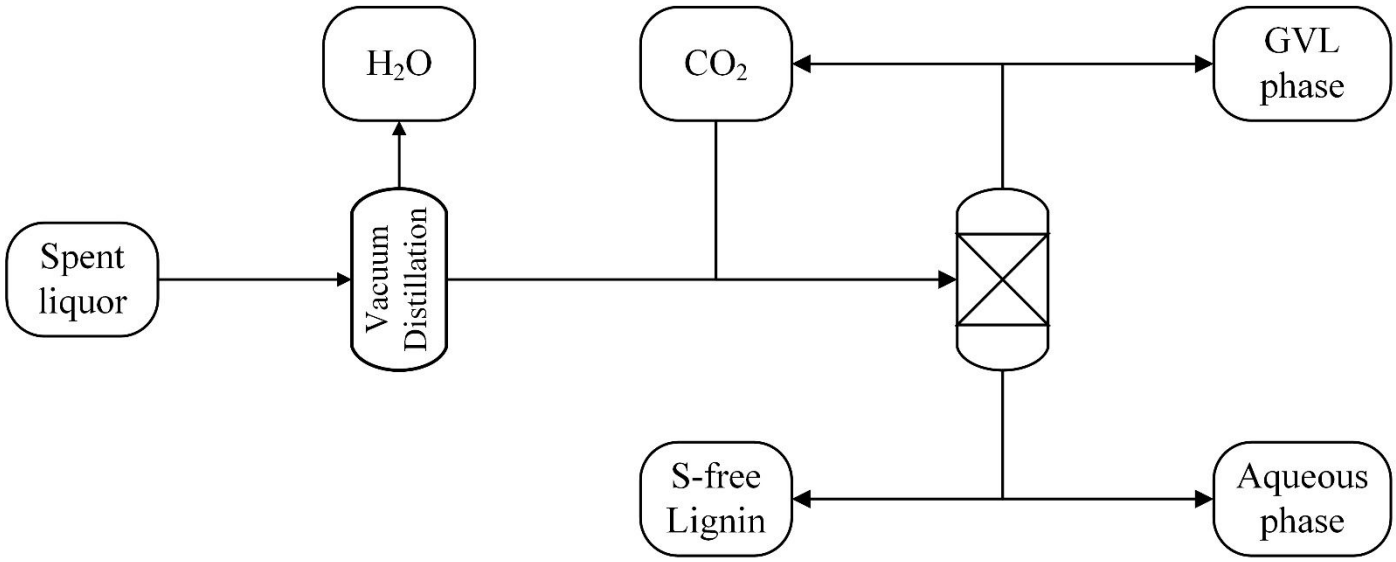
Experiment protocols for GVL recovery from spent liquor by liquid CO_2 extraction



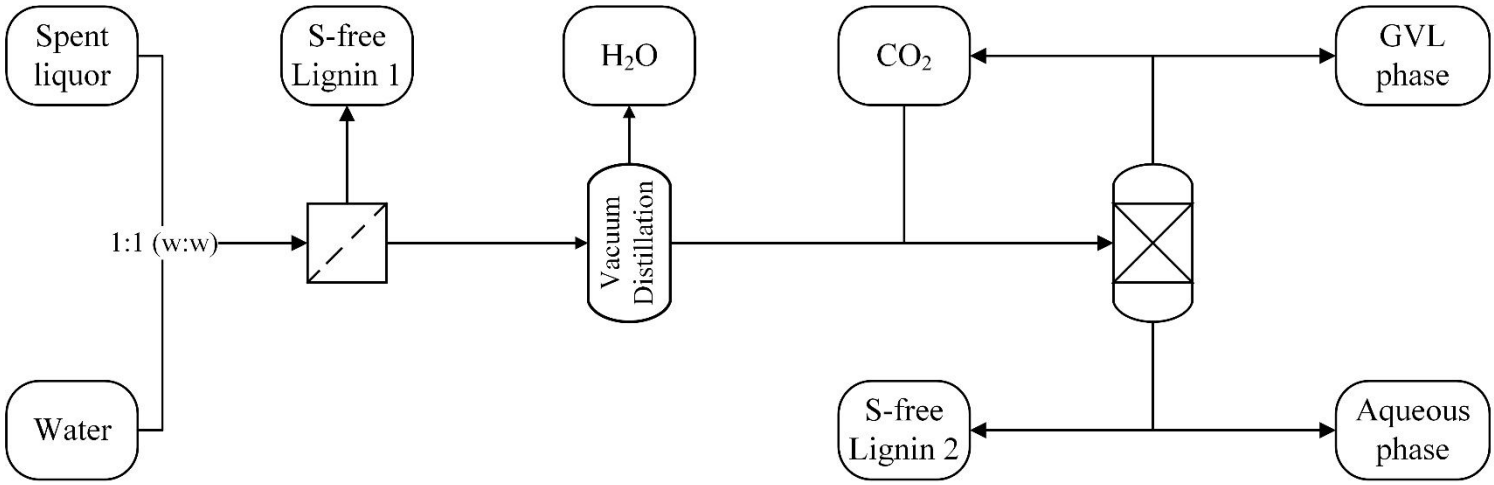
Scheme 3. Lignin was partly removed from the spent liquor before the extraction.



Scheme 4. Spent liquor was not treated before the extraction.

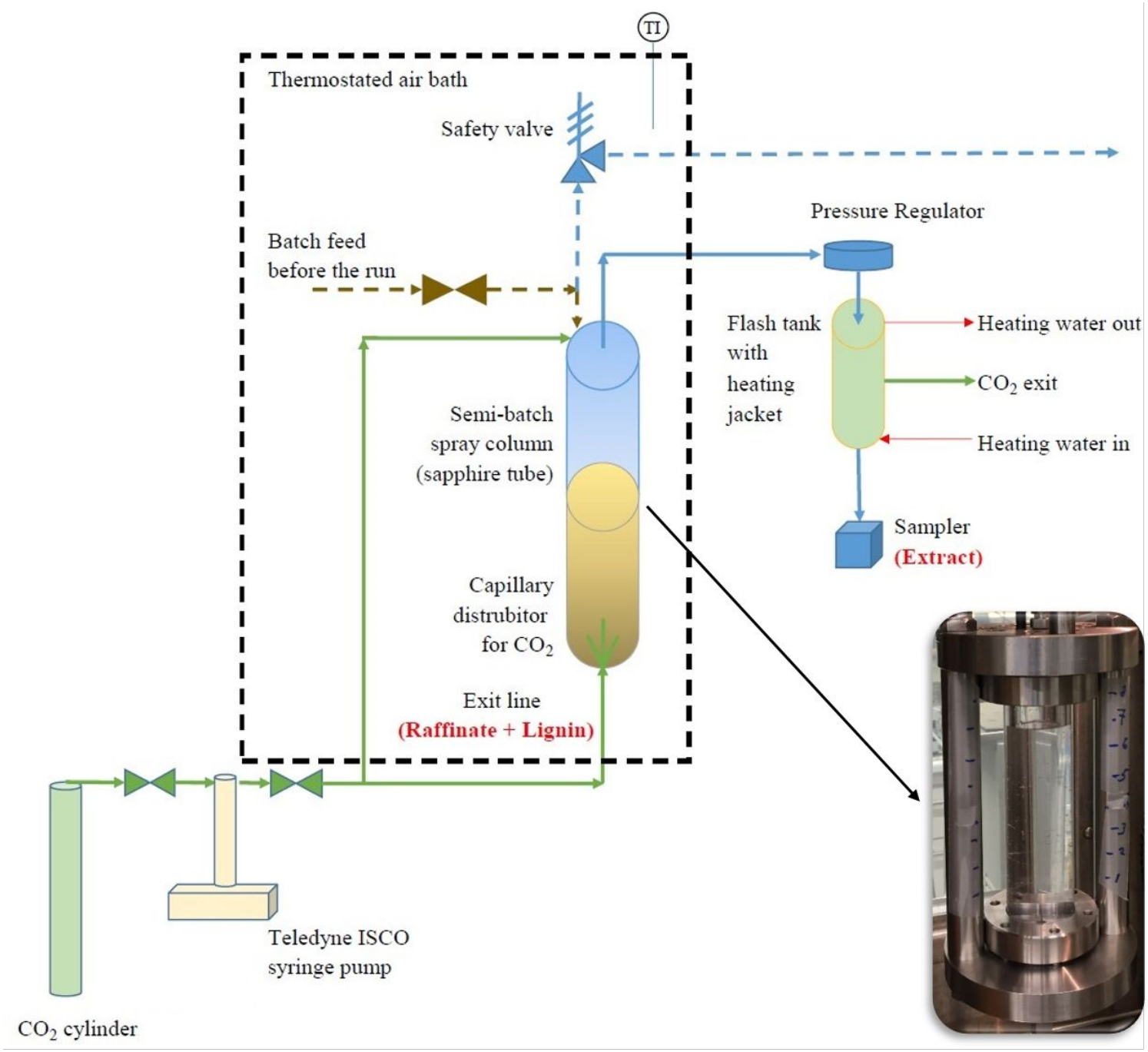


Scheme 5. Water was partly removed from the spent liquor before extraction.



Scheme 6. Lignin and water was partly removed from the spent liquor before extraction.

Schematic of the extraction unit



SUPPORTING MATERIAL 5

Analyses of pulp, lignin and liquids samples

1. Carbohydrate, lignin, furanic compounds and organic acids analyses of solid and liquid samples

The carbohydrate and lignin contents in the pulp and lignin samples were analyzed in accordance to the 2-step hydrolysis method described in the NREL/TP-510-42618 standard. The pulp was firstly hydrolyzed in 72% H_2SO_4, with an acid-to-pulp ratio of 10 mL/g, at 30°C, for 60 minutes. The hydrolyzed suspension was subjected to the second hydrolysis in 4% H_2SO_4, with an acid-to-material ratio of 300 mL/g, at 121°C, for 60 minutes. The hydrolyzed suspension was then filtered through a Robu® glass crucible (porosity 4). The monosaccharide content in the filtrate was determined by high performance anion-exchange chromatography (HPAEC) in a Dionex™ ICS-3000 device. The HPAEC system was equipped with an amperometry cell detector and a CarboPac™ PA20 column (3.0 mm × 150 mm). The column and detector were at 22ºC. The eluent was water with the flow of 0.37 mL/min. The samples were filtered through a 0.45 μm syringe filter before the analysis. From the amount of neutral monosaccharides, the cellulose and hemicelluloses content in wood and pulp samples was estimated with the Janson formula [1]. Acid insoluble (Klason) lignin, which was retained on the Robu® crucible was determined gravimetrically while acid soluble lignin (ASL) in the filtrate was quantified by measuring the absorbance at 25°C at the wavelength of 205 nm (Shimadzu UV-2550 spectrophotometer). An extinction coefficient of 148 L/(g.cm) was used for quantification of ASL [2]. The pulps were analyzed for intrinsic viscosity in accordance to the SCAN-CM 15:88 standard.

The carbohydrate content in the liquid samples were analyzed in accordance to the method described in the NREL/TP-510-42623 standard. The monomeric sugar content was determined by direct injection in the HPAEC, while the total sugars content were determined by HPAEC after hydrolysis at 121±1°C for 60 minutes, with sulfuric acid concentration of 4%. The lignin content in the spent and washing liquors was determined by UV-Vis spectrophotometry (Shimadzu UV-2550) at 25°C by diluting the liquor in ethanol 50 wt% and measuring the absorption at a wavelength of 205 nm, with the extinction coefficient of 148 L/(g.cm).

The content of furanic compounds (furfural and HMF) and organic acids (formic acid, acetic and levulinic acid) in the liquid samples was determined by high performance liquid chromatography (HPLC) in a Dionex UltiMate 3000 device. The HPLC system was equipped with a UV diode array detector and

a Rezex™ ROA-Organic Acid H+ (8%) LC column (7.8 mm × 300 mm). The UV detection wavelength was 210 nm and 280 nm for organic acids and furanic compounds, respectively. The column and detectors were at 55ºC. The eluent was 0.0025 mol/L sulfuric acid with the flow of 0.5 mL/min. The samples were filtered through a 0.45 μm syringe filter before the analysis.

2. Molecular mass determination for lignin samples

The molecular mass distributions, the number and weight average molecular masses (M_n, M_w, respectively) of the lignin samples were determined by gel permeation chromatography (GPC) in an Agilent 1100 HPLC/VWD device. The GPC system was equipped with a UV detector, a Phenogel™ pre-column (7.8 mm × 50 mm, particle size 5 μm) and two Phenogel™ size exclusion columns of styrene-divinylbenzene with pore sizes 50 and 1000 Å (7.8 mm × 300 mm, particle size 5 μm). The UV detection wavelength was 260 nm and 280 nm for the standards and samples, respectively. The column and detector were at 35ºC. The eluent, also the lignin solvent, was LiChrosol®-grade tetrahydrofuran (THF) with the flow of 1 mL/min. Lignin was not acetylated before the GPC analysis. The samples were prepared in THF with a concentration of about 2 mg/mL and filtered through a 0.45 μm syringe filter before the analysis. Calibration was performed with two standard solutions, one containing toluene, syringol, 2,2'-dihydroxybiphenyl, PS474, PS3470 and PS76600, and the other one containing toluene, polystyrene dimer PS208, PS1270, PS7000 and PS18200. The standard PS474 was divided by the columns to several oligomer peaks, of which polystyrene trimer PS312, tetramer PS417 and pentamer PS521 were included in the actual calibration. A molecular weight cut-off at 201 g/mol (one assumed phenylpropane unit in the eucalyptus GVL lignin) [3] was used in processing the results.

3. GVL/water ratio determination for liquid samples

The GVL/water mass ratio in the liquid samples was determined by gas chromatography (GC) in an Agilent 6890N device coupled with 7683 Series liquid injector. The GC system was equipped with a thermal conductivity detector (TCD) and a polar capillary Agilent DB-WAXetr column (0.32 mm × 30 000 mm, film thickness of 1 μm). Solid particles (mostly lignin) were separated from the analyzed mixture by the glass wool liner at the GC inlet. The GC inlet temperature and the split ratio was 250°C and 10:1, respectively. Helium was the carrier gas with an initial average velocity of 29 cm/s at constant flow mode. The GC oven temperature started at 80°C for 5 minutes, then it was raised with a rate of 60°C/min to 140°C and held for 2 minutes; after that, the temperature was raised with a rate of 60°C/min

to 200°C and held for 6 minutes. The detector temperature was at 250°C. The method can quantify water, GVL, acetic acid, formic acid and furfural in the liquid samples. However, due to the closeness of their retention time on the chromatogram, furanic compounds and organic acids were analyzed by HPLC as described earlier, while the GVL/water mass ratio was determined by the GC method.

The gravimetric samples were prepared to calibrate the response factors with acetone as the internal standard. The response factors of TCD were calculated as in equation (1).

$$F_i = F_{std} \times \frac{A_{std}}{A_i} \times \frac{m_i}{m_{std}} \qquad (1)$$

Where F is the response factor
A is the area of the peak
m is the mass of the sample/standard
std is the internal standard (acetone)
i is the component

The response factor of internal standard was set to 1. The response factors of GVL and water were 0.972 and 0.809, respectively. Prior to the analysis, the liquid sample was dissolved in acetone and injected to the GC sampling bottles. The masses of the sample and acetone were recorded. The mass of each individual component was deduced from equation (1) and the corresponding mass fraction was calculated as in equation (2).

$$w_i = \frac{m_i}{\sum_{i=1}^{N} m_i} \qquad (2)$$

Where w_i is the mass fraction of component i
N is the total number of components.

REFERENCES

1. Janson, J. Calculation of the polysaccharide composition of wood and pulp. *Paperi ja Puu* **1970**, *52*, 323-329.

2. Lê, H. Q.; Ma, Y.; Borrega, M.; Sixta, H. Wood biorefinery based on gamma-valerolactone/water fractionation. *Green Chem.* **2016**, *18*, 5466-5476.

3. Lê, H. Q.; Zaitseva, A.; Pokki, J.; Ståhl, M.; Alopaeus, V.; Sixta, H. Solubility of Organosolv Lignin in Gamma-Valerolactone/Water Binary Mixtures. *ChemSusChem* **2016**, *9*, 2939-2947.

SUPPORTING MATERIAL 6

Mass Balance (with Janson calculation)

Effect of time on fractionation of eucalyptus wood chips in 50wt % GVL solution at 180°C, with L:W = 3 or 4 L/kg in the oil-bath digester

Sample[a]	Pulp yield %odw[b]	Intrinsic viscosity mL/g	Wood components (%odw)									
			Pulp			Spent liquor[d]						***Total***
			Cellulose	Hemicellulose	Lignin[c]	Cellulose	Hemicellulose	Lignin[c]	Furfural	HMF	Organic acids[e]	
Wood	**100**	**-**	**46.4**	**22.1**	**29.3**	**-**	**-**	**-**	**-**	**-**	**-**	***97.8***[f]
4-90	50.7	846	44.3	4.1	2.2	0.5	9.4	25.7	2.4	0.2	7.2	96.1
4-120	48.8	769	43.2	3.8	1.8	0.5	7.5	25.7	3.9	0.4	8.1	94.9
4-150	47.1	562	42.6	3.2	1.3	0.7	4.9	26.2	6.0	0.6	7.7	93.4
3-90	48.9	773	43.1	3.7	2.1	0.5	7.3	25.5	3.8	0.3	7.1	93.5
3-120	47.0	597	41.9	3.2	1.9	0.6	5.6	26.0	5.2	0.5	7.5	92.3
3-150	45.6	493	40.9	3.1	1.5	0.5	4.9	26.6	5.9	0.6	8.0	92.0

(a) The sample is named as: fractionation L:W (in L/kg)-fractionation time (in minutes)
(b) odw: oven-dried wood
(c) As the raw material is unextracted wood, extractive are shown as lignin in analysis
(d) Component content in SL is the sum of that in free SL and washing liquids
(e) Organic acids: formic acid, acetic acid and levulinic acid
(f) Uronic acid, which is not bound to xylan (about 2.6 % odw), is not taken into account (Janson, J., *Paperi ja Puu* **1970**, 52, p. 323)

SUPPORTING MATERIAL 7

Molecular weight of lignin fractions isolated during GVL recovery processes

(The lignin samples are named according to the recovery scheme in supporting material 1 and 2)

Process	Sample	Mw[(a)] g/mol	Mn[(b)] g/mol	PDI[(c)]
Scheme 2 (2-staged distillation)	Lignin 1	2437	915	2.66
	Lignin 2	1177	601	1.96
	Lignin in residue	1469	460	3.20
Scheme 3	Lignin 1	1959	834	2.35
	Lignin 2	993	534	1.86
Scheme 4	Lignin	1962	780	2.52
Scheme 6	Lignin 1	2060	862	2.39
	Lignin 2	1057	632	1.67

(a) weight-average molecular weight
(b) number-average molecular weight
(c) poly dispersity index

SUPPORTING MATERIAL 8

Preliminary energy assessment for GVL recovery by vacuum distillation and liquid CO_2 extraction

The energy consumption for the recovery of GVL by distillation at reduced pressure and liquid CO_2 extraction was estimated by simulation models constructed in the ASPEN PLUS v.10 environment. For simplification, only the main components (GVL-water-CO2 for extraction and GVL-water for distillation) were included. Dissolved compounds (lignin, carbohydrates and furanic compounds) were not considered. For comparability purpose, similar separation capacity was targeted in both models, which are >98 wt% purity of GVL in the organic phase and >99 wt% purity of water in the aqueous phase. Spent liquor containing 50 wt% GVL and 50 wt% water was continuously feed at a rate of 1 kg/s. UNIQUAC and SRK thermodynamic models were used for the liquid and vapor phase, respectively, in the distillation column, flash tanks and compressor. Fixed K-factors obtained from the experimental data were used in the extraction unit.

1. Distillation at reduced pressure

The spent liquor was firstly evaporated at reduced pressure. In a real process, this step prevents the lignin from entering the distillation column. A standard black liquor evaporator for kraft process can handle this process. The feed was preheated to 100°C before the evaporation. The evaporator was modelled as a flash tank operating at fixed pressure and heating duty so that about 7 – 8 % of the original GVL was left as residue (resembling the residual liquid containing all the non-volatile extracted components discussed in section 3.2.1 and 3.2.2). The vapor was directed to the 15th stage of a 20-staged distillation column where water and GVL were separated with the specified purity. The modelling of distillation column included the vapor-liquid equilibrium (VLE), mass balance and energy balance for each ideal stage. The distillation stages were assumed ideal but the phase equilibrium was not ideal because of the UNIQUAC model. The total energy requirement of the process was:

- Heating
  - Preheater: 259.9 kW
  - Evaporator: 1275.0 kW
  - Reboiler: 909.4 kW
- Cooling
  - Condenser: -2355.6 kW
  - Coolers: -78.0 kW

The energy consumption was evaluated with the ideal operation of the process where refrigerating and heating efficiency was not considered. Heat integration should be considered to utilize the energy of hot streams (hot distillate, hot bottom and vapor entering the condenser) for pre-heating the feed streams.

ASPEN model of GVL recovery by vacuum distillation

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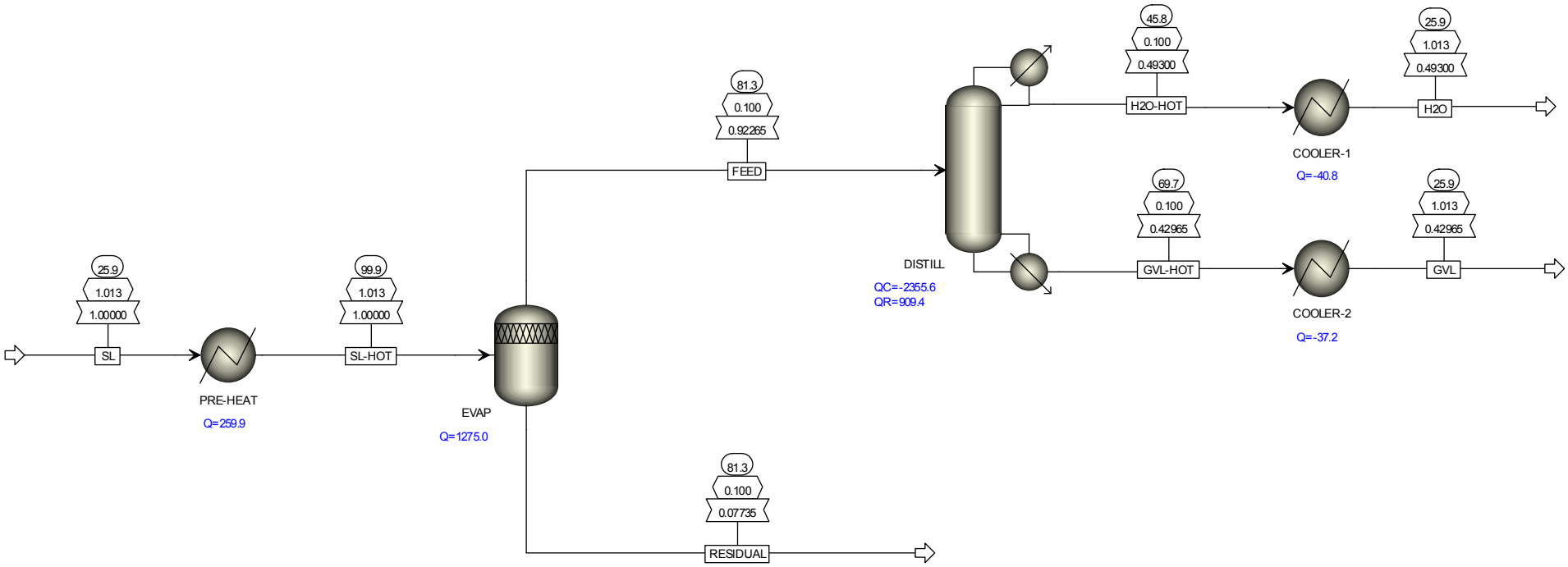

2. Liquid CO_2 extraction

The spent liquor was extracted with CO_2 (solvent-to-feed ratio of 0.45 : 1, i.e. twice the minimum ratio which is obtained by the modified McCabe-Thiele graphical method) in a three-staged extraction unit. The extractor was modelled as three decanters with ideal phase equilibrium stages, operating isothermally and connected in counter-current mode. The distribution coefficients of the components ($K_i = x_{i,\ extract} / x_{i,\ raffinate}$) were fixed for each component within each ideal phase equilibrium. The K-values were calculated from the measured phase equilibrium [1]. The simulation model took into account the mole balance, phase equilibrium and energy balance.

CO_2 was recovered from the extract by a 4-staged decompression-recompression at the pressure level of 1 – 2.9 – 8.6 – 25.4 – 75 bar (ca. 2.9x step). The depressurization of extract was modelled as flash units with UNIQUAC VLE model where the parameters were optimized based on literature and measured data. The distribution coefficient ($Ki = y_{i,\ vapor} / x_{i,\ liquid}$) was included in the thermodynamic model. The flash units were VLE stages operating isothermally at specified pressure. The decompression of CO_2 absorbed heat, requiring the flask tanks to be heated in order to avoid icing. The 4-staged compressor was operating isentropically. The gas from the last flash tank was the inlet of the compressor and the gas from the first flash tank was the inlet of the last stage of compressor. There was an optional liquid knockout stream after each compression stage in case of condensation. The total energy requirement of the process was:

- Heating
  - Extractor: 8.6 kW
  - Flash tanks: 76.7 kW
- Cooling
  - Compressor: -60.8 kW
- Compressing 51.2 kW

The operation of the compressor generated heat, which could be directed to the extractor and flash tanks to avoid freezing during operation.

Reference

1. Pokki, J.; Lê, H. Q.; Petri, U.; Sixta, H.; Alopaeus, V. Isobaric vapor-liquid equilibrium of furfural + γ-valerolactone at 30 kPa and isothermal liquid-liquid equilibrium of carbon dioxide + γ-valerolactone + water at 298 K. *Submitted* **2018**.

ASPEN model of GVL recovery by liquid CO_2 extraction

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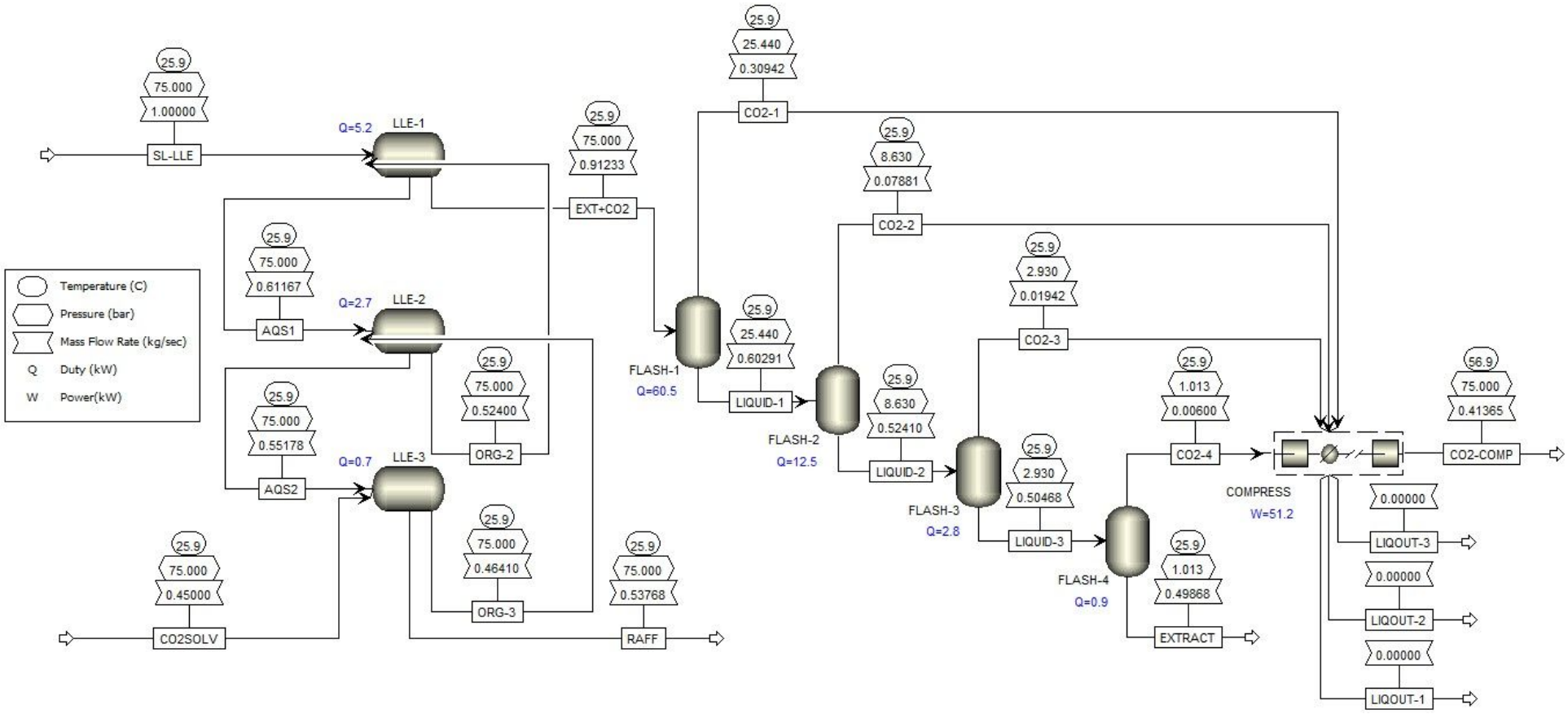

SUPPORTING MATERIAL 9

NMR analysis of GVL recycled by liquid CO_2 extraction in the 3-fractionation cycle investigation

Liquid-state NMR experiments were performed in $CDCl_3$ at 22°C in a Bruker Avance III spectrometer operating at 400.13 MHz for ^1H nucleus. NMR data was processed with TopSpin 3.0 software. The ^1H chemical shifts were referenced to Tetramethylsilane (TMS) with the chemical shift of 0 ppm at 22°C.