Electronic Supplementary Information

Stepping away from purified solvents in reductive catalytic fractionation: a step forward towards a disruptive wood biorefinery process

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1. Experimental Procedures

1.1. Chemicals and Materials

All commercial chemicals were analytic reagents and were used without further purifications. 5 % Pd on Carbon (Pd/C), tetrahydrofuran (>99%, stabilized with 250 ppm BHT), N-methyl-N-(trimethylsilyl)trifluoroacetamide (>98.5%), anhydrous pyridine (99.8%), 2-isopropylphenol (>98%), ammonium hydroxide chloride, $NaBH_4$, 2-octanol, allose (β-D-allose), myo-inositol, glucose (D-(+)-glucose), mannose (D-(+)-mannose), galactose (D-(+)-galactose), xylose (D-(+)-xylose), arabinose (L-(+)-arabinose) were purchased from Sigma Aldrich. Ethyl acetate (99.5%), methanol (99.9%), methyl acetate (99%), 1-methylimidazol (99%) and bromophenol blue were purchased from Acros organics. Ammonium solution (25%), acetic anhydride (>98%), KOH pellets, Na_2SO_4 and acetic acid (glacial) were purchased from Avantor. Benzoic acid was purchased from Merck. A 72 wt% solution of H_2SO_4 was purchased from ChemLab. Birch and Spruce were milled and sieved to obtain a sawdust fraction with a size of 250-500 µm and 500 - 1000 µm.

1.2. Reductive Catalytic Fractionation

1.2.1. 100 ml reactor

RCF reactions with birch were performed in a 100 ml stainless steel batch reactor (Parr Instruments & Co.). 4 g of birch sawdust (250-500 µm) was loaded into the reactor with 4.0 g Pd/C and 40 ml of the solvent mixture. A comprehensive list of the solvent compositions used in the experiments is provided in **Table S2**. After sealing and a threefold flushing of the reactor with N_2 (at 10 bar), the reactor was pressurized with H_2 (30 bar at RT). Then, the reaction mixture was stirred (750 rpm) and simultaneously heated to 220 °C (~15 min. heating time), unless mentioned otherwise. After the reaction, lasting 2 h (unless mentioned otherwise) the reactor was cooled with water and depressurized at RT. For reaction liquor analysis, 1 ml of sample was then taken and filtered with a 0.2 µm PTFE membrane to remove any particulate matter before analysis. The reactor content was quantitatively collected by washing the reactor with acetone, and the pulp was thoroughly washed with acetone and ethanol. After removal of the volatile solvents by rotary evaporation, a brownish crude lignin oil was obtained which was subject to a threefold extraction with ethyl acetate and water to obtain a refined lignin oil used in further analyses. The pulp was dried in an oven overnight before used in further analyses.

1.2.2. 2 L reactor

Spruce crude lignin oil was obtained with a RCF reaction in a 2 L stainless steel batch reactor (Parr Instruments & Co.). 150 g of spruce sawdust (500 - 1000 µm) was loaded into the reactor with 15.0 g Pd/C and 800 ml methanol. After sealing and a threefold flushing of the reactor with N_2 (at 10 bar), the reactor was pressurized with H_2 (30 bar at RT). Then, the reaction mixture was stirred (750 rpm) and simultaneously heated to 235 °C (~30 min. heating time). After the reaction which lasted 3 h, the reactor was cooled and depressurized at RT. The reactor content was quantitatively collected by washing the reactor with methanol. The resulting filtrate, obtained after removal of the solid pulp, was diluted with methanol before being used in the 100 ml RCF reactions.

1.3. Biomass/Pulp Compositional Analysis

1.3.1. Carbohydrates

The carbohydrate content and composition in the wood feedstocks as well as in the carbohydrate pulps obtained after RCF reaction were determined using a standard total sugar determination procedure, adapted with hydrolysis conditions for cellulose-rich materials.[1–3] Samples of 10 mg were pre-hydrolysed in a 13 M H_2SO_4-solution (1 ml) at RT for 2 h and subsequently hydrolysed in a diluted 2 M H_2SO_4-solution (6.5 ml) at 373 K for 2 h. The resulting monosaccharides were reduced to alditols and acetylated to increase their volatility for gas chromatography (GC) analysis. First, internal standard (1 ml of a 1 mg/ml β-D-allose solution of 1:1 benzoic acid:water) was added to 3 ml of the hydrolysed sample. NH_3 25% in water (1.5 ml) was added, as well as droplets of 2-octanol to avoid excessive foaming. The reduction was completed by addition of $NaBH_4$ (0.2 mL of a 200 mg $NaBH_4$/ml 2 M NH_3 solution) for 30 min at 313 K and the reaction was stopped by adding 0.4 mL acetic acid. 1-methylimidazole (0.5 ml) was added to 0.5 ml of the resulting sample to catalyse the formation of alditol acetates with acetic acid anhydride (5 ml). After 10 min, 1 ml of ethanol was added to react with the remaining acetic acid anhydride and 5 minutes later, the reaction was quenched by adding 10 ml of water. The reaction vials were then placed in an ice bath and bromophenol blue (0.5 ml of a 0.4 g/l water solution) as well as KOH (2 x 5 ml of a 7.5 M solution) were added to colour the aqueous phase blue. The yellow ethyl acetate phase, containing the acetylated alditols, could then easily be separated with a Pasteur pipette and was dried with anhydrous Na_2SO_4 before being put in a vial. GC analysis was performed on a Hewlett Packard HP 6890 gas chromatograph with a split injection system (split ratio 59:1) and H_2 as carrier gas. A 100 m CP-Sil 88 column with an internal diameter of 0.25 mm and a film thickness of 0.2 µm was used for separation, and detection was done with a flame ionization detector (FID). The column temperature was set to 60 °C and was immediately heated to 120 °C (8.8 $°C.min^{-1}$). After 0.95 min. the column was heated to 180 °C (4.2 $°C.min^{-1}$). This temperature was maintained for 1.05 min. after which the column was heated to 220 °C (6.2 $°C.min^{-1}$). This temperature was maintained for 7.4 min. The final column temperature was set to 225 °C which was reached using a 22.3 $°C.min^{-1}$ heating rate. This temperature was maintained for 63 min. The FID-detector was kept constant at a temperature of 300 °C. Calibration samples (glucose, galactose, mannose, xylose, and arabinose), containing known amounts of the expected monosaccharides were included in the analyses. To calculate the carbohydrate content in the analysed samples, a correction factor (*viz.*, 0.88 for C5 sugars and 0.9 for C6 sugars) was used to compensate for the addition of water during hydrolysis. Each substrate was analysed in threefold, and the average values were used in the calculations of the carbohydrate retention.

1.3.2. Lignin

The determination of the lignin content of lignocellulose samples (feedstock and pulp), was based on a procedure from Lin & Dence.[4] The lignocellulose samples were sieved and the fraction of 250- 500 µm was used for analysis. A Soxhlet extraction in an ethanol/toluene (1/2) mixture for 3 h was done first to remove any extractives like fats, waxes, resins and terpenoids/steroids, that can influence the lignin determination, from the lignocellulose samples. Triplicate samples of extracted substrate (0.33 g) were transferred to 20 ml vials after which 5 ml of a 72 wt% H_2SO_4-solution was added. The mixture was left at room temperature for 2 h while continuously stirred with a magnetic rod. Afterwards the content of each beaker was transferred to a round-bottom-flask which already contained 50 to 100 ml of water. The vials were rinsed, and extra water was added until a H_2SO_4 concentration of 3 wt% was reached (approximate volume of 195.6 ml). The diluted solution was heated to 95 °C for 20 h in a water bath. After filtration of the hot solution, a brown lignin precipitate was retained. The precipitate was washed with hot water to remove any leftover acid and the obtained residue was dried in an oven at 353 K overnight. To determine the acid soluble lignin, the UV-absorbance of the hydrolysate was measured with a UV spectrophotometer (UV-1800, Shimadzu) at 240 nm. The Lambert-Beer's law was used to determine the acid soluble lignin concentration in the hydrolysate, using a absorptivity of 25 l/g.cm.[5] The lignin content of the sample was calculated by the sum of the Klason and acid-soluble lignin.

1.3.3. Acetyl

The acetyl content of the lignocellulose samples was determined by analysis of the hydrolysate, obtained for lignin analysis, with HPLC. The hydrolysate was filtered with a 0.2 µm PES filter to remove any particulate matter before analysis. 25 µl of sample was injected in an Agilent 1200 series HPLC equipped with a Metacarb 67H column (300 x 6.5 mm), using 3 wt% H_2SO_4 as eluent at a flowrate of 0.6 ml/min. A refractive index detector was coupled to the column for detection of acetic acid that is formed in the hydrolysis reaction. Column and detector temperature were set to 40 °C. A calibration curve of acetic acid in 3 wt% H_2SO_4 was created to determine the acetic acid concentration in the hydrolysate, which was subsequently reverse calculated to an acetyl-content of the sample using the hydrolysate volume (195.6 ml) and acetyl and acetic acid molecular weights.

1.3.4. Water

The water content of the lignocellulose samples was determined by a moisture analyser (Halogen Moisture Analyzer HC103, Mettler Toledo). 0.5 g of sample was loaded on a tray which was heated to 150 °C by a halogen lamp. The removal of water was detected gravimetrically. The continuous analysis was stopped when the detected change in mass was below 1 mg in 90 seconds. Analyses were repeated in triplicate.

1.3.5. Ash

The ash content of the lignocellulose samples was determined using a muffle oven for which a ramping program was used to reach a fixed temperature for 575 °C that was hold for 3 hours.[6] Samples were weighed before and after the oven-program for ash determination.

1.4. Reaction Liquor Analysis

1.4.1. Methyl Acetate

The formation of methyl acetate in RCF was quantitatively analysed by GC analysis of the reaction liquor. Prior to injection, the reaction liquor was filtered using a 0.2 µm PTFE filter to remove any particulate matter. The sample was analysed on an Agilent 6890 N GC equipped with a DB-17 column (Agilent) and an FID-detector. The column temperature was set to 50 °C for 2 min. after which it was heated to 140 °C at a heating rate of 5 $°C.min^{-1}$, and to 280 °C at a heating rate of 30 $°C.min^{-1}$. The sensitivity factor of methyl acetate was determined from a calibration curve with methyl acetate solutions in methanol at various concentrations (**Fig. S4a**). Deacetylation degree based on the methyl acetate formation was reverse calculated based on the methyl acetate concentration of the reaction liquor, which was assumed to have a liquid volume of 40 ml for the 100 ml reactions.

1.4.2. Water

The release of water into the reaction liquor was analysed by coulometric Karl-Fischer titration (Titrator Compact, Mettler Toledo) in triplicate. A few droplets of reaction liquor with known weight were titrated to determine the water concentration in solution. This concentration was corrected for the water originally present in the solvent methanol. The water released from the biomass was subsequently determined by assuming a liquid volume of 40 ml.

1.5. Lignin Oil Analysis

1.5.1. GC Analysis

The phenolic monomers of the refined lignin oils were quantitatively analysed by GC. A weighed amount (±20 mg) of internal standard - 2-isopropylphenol - was added to a GC-vial containing a weighed amount of lignin (~40 mg) in 0.2 ml of tetrahydrofuran. 0.6 ml of pyridine and 0.15 ml of N-methyl-N- (trimethylsilyl)trifluoroacetamide were added. The vial was sealed and put in an oven at 80 °C for 20 min to induce derivatization by trimethylsilylation. The samples were analysed on a GC (Agilent 6890 series) equipped with a HP5-column. The following operating conditions were used: injection temperature of 300 °C, column temperature program: 50 °C (2 min), 15 °C min^{-1} to 150 °C, 10 °C min^{-1} to 220 °C and 20 °C min^{-1} to 290 °C (12 min), with a detection temperature of 300 °C. The sensitivity factors of most of the monomers were obtained by calibration with commercial standards. Identification of the monomer signals was performed with GC-MS using an Agilent 6890 series GC equipped with a HP1-MS capillary column and an Agilent 5973 series mass spectroscopy detector. The scanning range of the MS was set between 150 and 800 g/mol.

1.5.2. GPC Analysis

The distribution of the molar mass of the lignin oil products was investigated using gel permeation chromatography – size exclusion (GPC-SEC). A lignin sample was solubilized in THF (5 mg.ml^{-1}) and subsequently filtered with a 0.2 µm PTFE membrane to remove any particulate matter to prevent plugging of the column. GPC-SEC analyses were performed at 40 °C on a Waters E2695 equipped with a PL-Gel 3 µm Mixed-E column with at length of 300 mm, using THF as a solvent with a flow of 1 ml min^{-1}. The detection was UV based at a wavelength of 280 nm. Calibration was done with commercial polystyrene standards of Agilent.

1.6. Analysis of the Aqueous Phase

1.6.1. GC Analysis

The water-soluble carbohydrate monomers of were analysed by GC. An amount (±6 mg) of internal standard - myoinositol - was added using 0.2 ml of an aqueous solution containing 0.0287 g $\text{myoinositol.ml}^{-1}$ to a GC-vial containing a weighed amount of water-soluble oil products (~40 mg). 0.4 ml of pyridine containing 50 ppm $NH_2OH.HCl$ was added. The vial was sealed and put in an oven at 80 °C for 20 min. Then, 0.3 ml of N-methyl-N-(trimethylsilyl)trifluoroacetamide was added. Again, the vial was sealed and put in an oven at 80 °C for 20 min. The derivatized sample was analysed in the same way as the lignin monomers (*see 'Lignin Oil Analysis'*). Identification of the signals was performed with GC-MS using an Agilent 6890 series GC equipped with a HP1-MS capillary column and an Agilent 5973 series mass spectroscopy detector. The scanning range of the MS was set between 150 and 800 g/mol.

1.7. Gas Phase Analysis

GC analysis of the gaseous products in the headspace was performed on an Interscience Trace GC equipped with HayeSep. Q and RTX-1 columns and an FID and TCD detector. Commercial standards were used for identification and quantification.

2. Figures

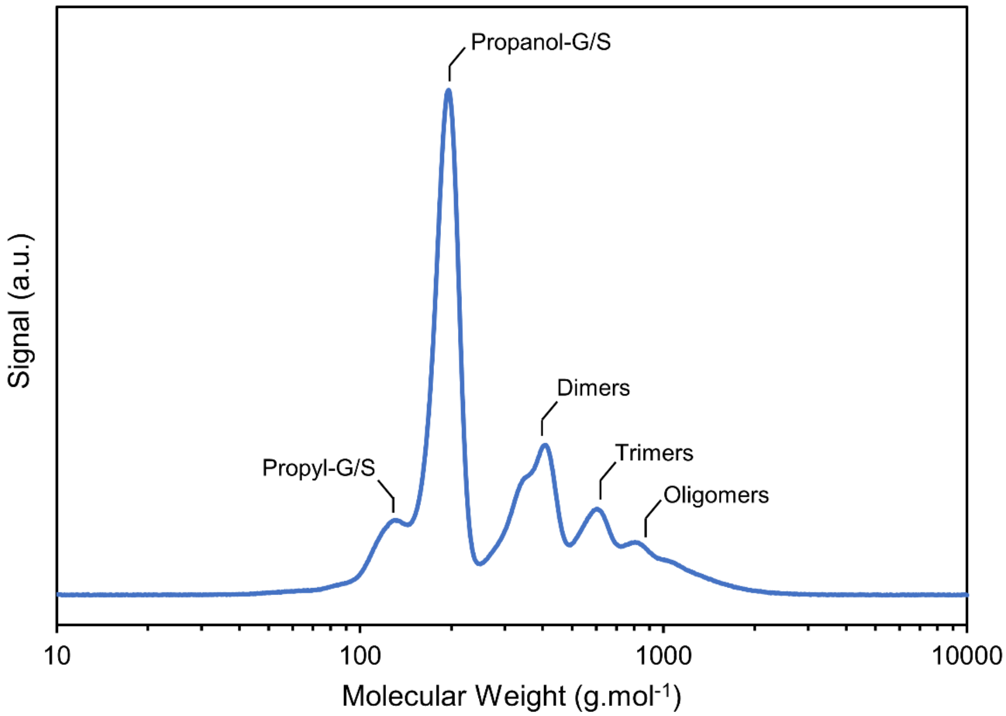

Fig. S1 Gel permeation chromatography (GPC) of the birch lignin oil obtained with a standard RCF reaction in methanol. Reaction conditions: 4 g birch sawdust (250 – 500 µm), 0.4 g Pd/C, 40 ml methanol, 30 bar H_2 (at RT), 220°C, 2 h.

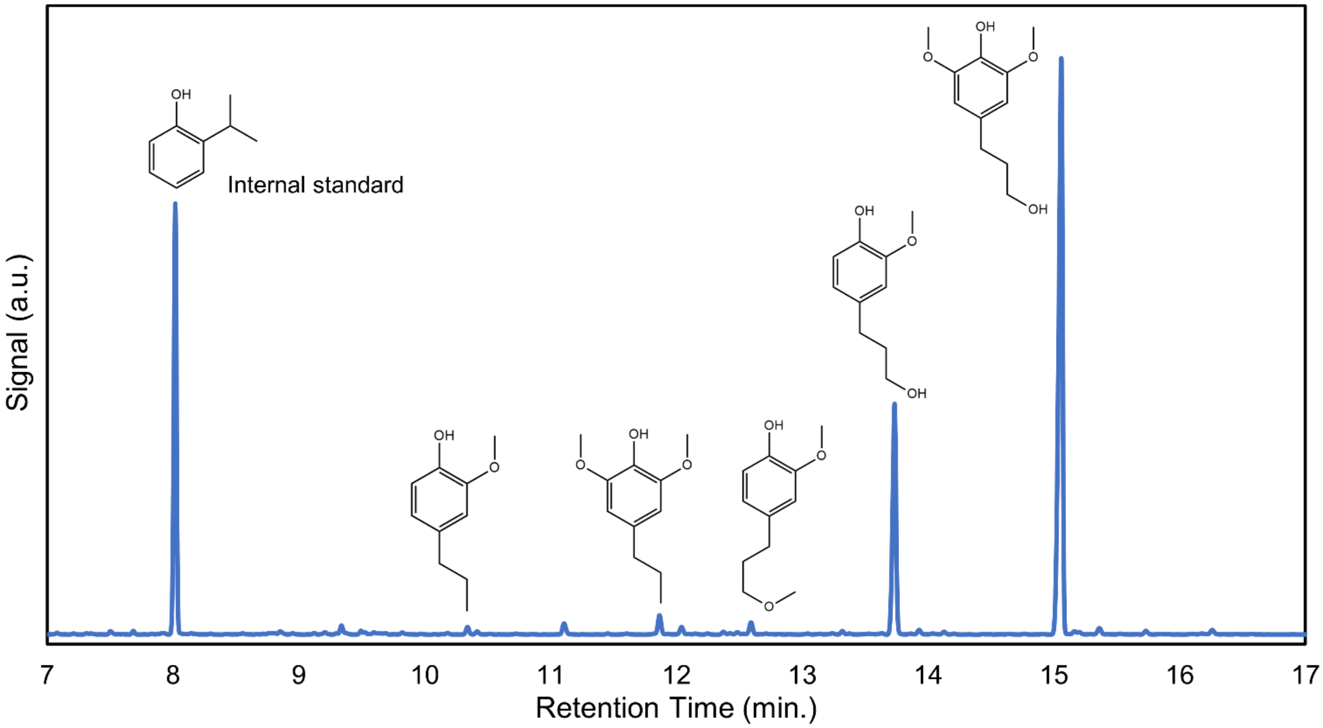

Fig. S2 GC-chromatogram of the birch lignin oil obtained with a standard RCF reaction in methanol.

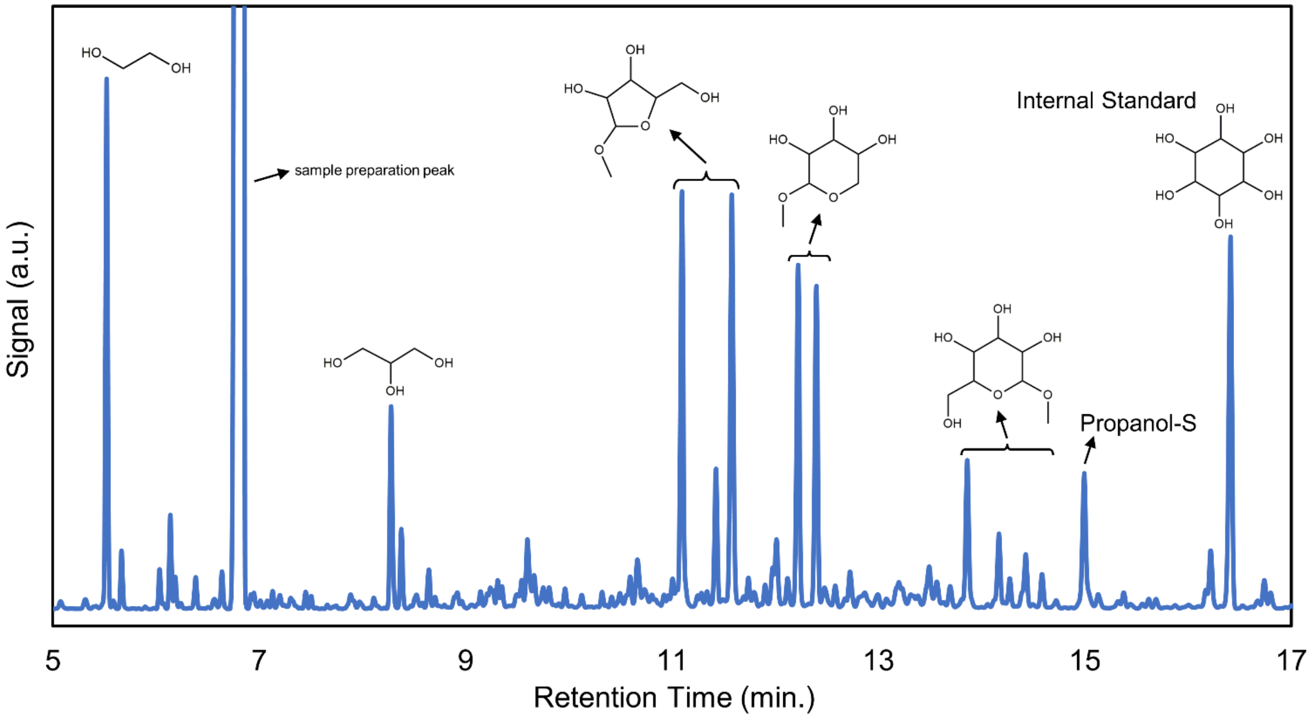

Fig. S3 GC-chromatogram of the aqueous phase obtained with a standard RCF reaction of birch in methanol. The major peaks of the sugar monomers and polyol products (ethylene glycol, glycerol) are assigned on the chromatogram.

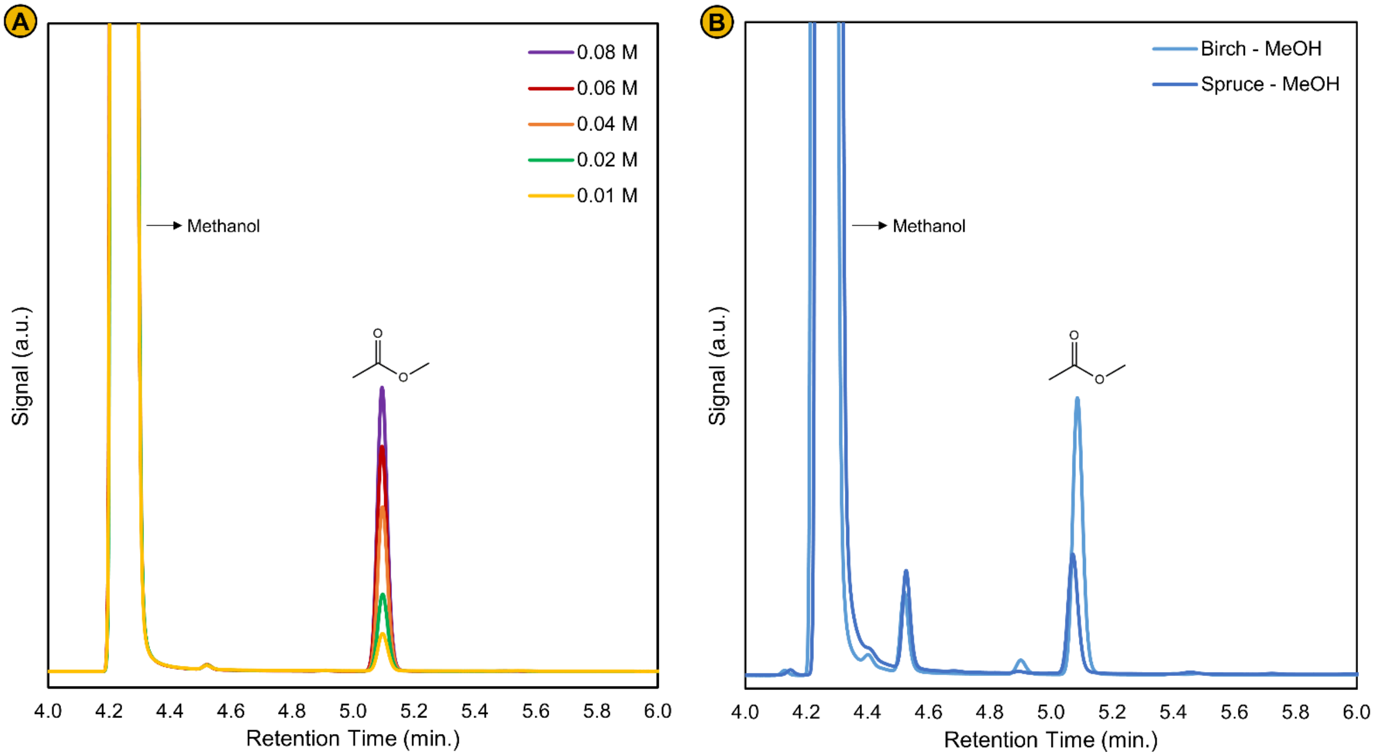

Fig. S4 a) GC-chromatogram of a methyl acetate solution in methanol at varying concentrations and **b)** GC-chromatogram of the reaction liquor following a standard RCF reaction of birch (Birch - MeOH) and spruce (Spruce - MeOH) in methanol.

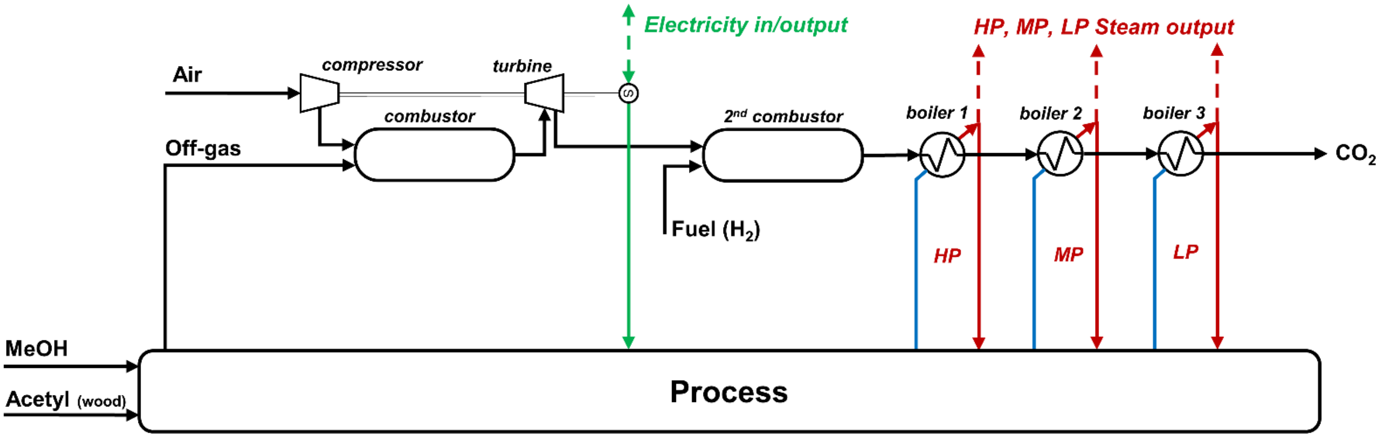

Fig. S5 Schematic overview of the combined heat and power plant (CHP) and its interaction with the process. The cooling water pump around is not shown but consumes part of the electricity that is produced by the gas turbine. The net electricity and steam requirements are calculated by pinch-point analysis of the heat exchanger network. Typical efficiencies used in the modelling of this CHP are shown in **Table S4**.

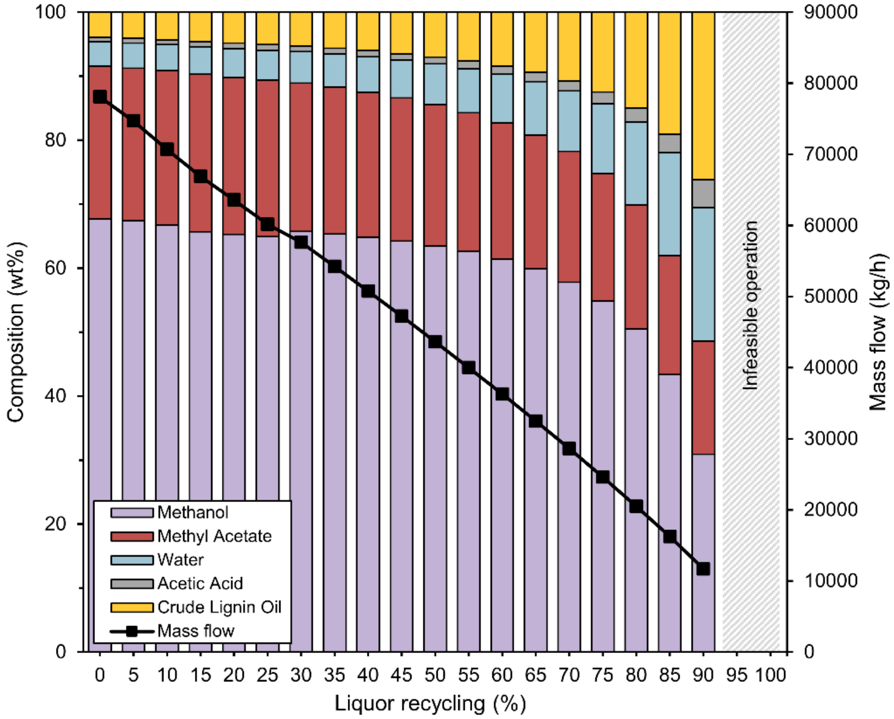

Fig. S6 Composition of the liquid stream entering the crude distillation column (left axis) and the mass flow rate (right axis) in function of the liquor recycling (%).

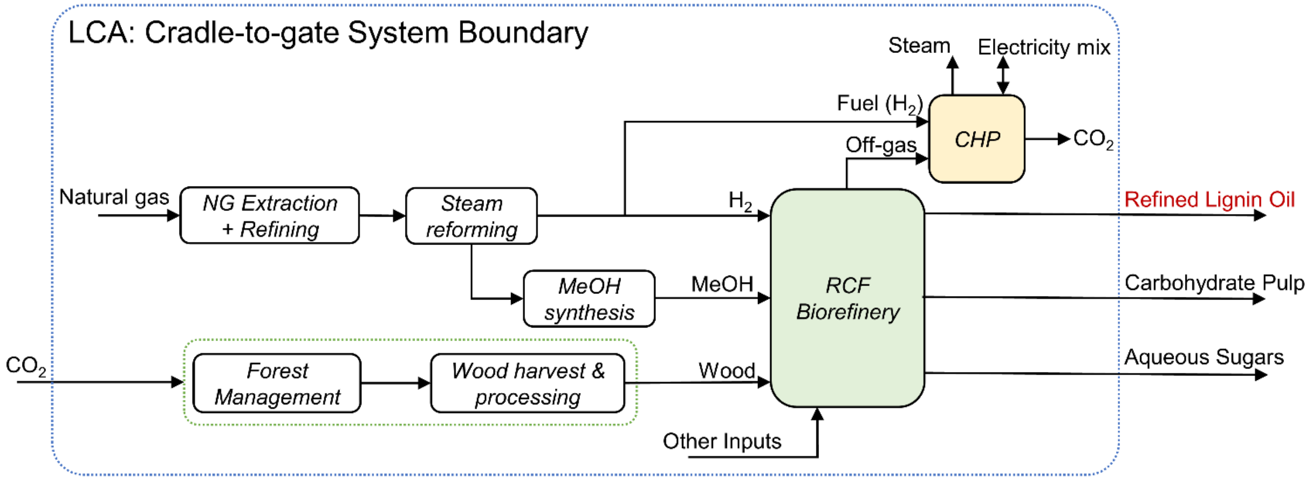

Fig. S7 System boundary of the LCA with grey hydrogen produced from natural gas stream reforming as fuel source and a regular electricity mix as the power resource. **Table S7** provides a complete overview of the GWP values of the process in- and outputs.

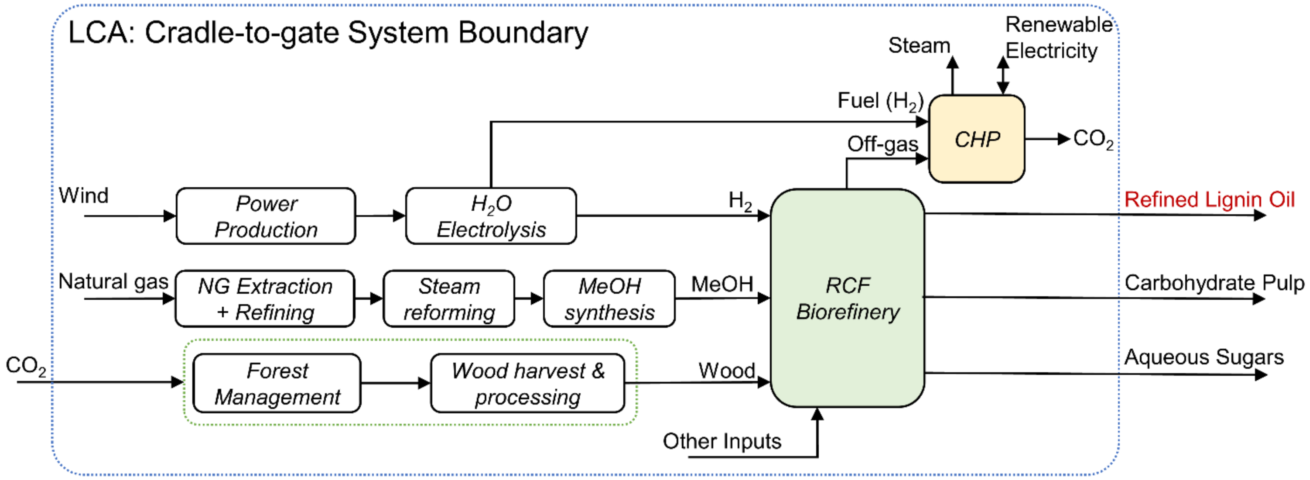

Fig. S8 System boundary of the LCA with green hydrogen produced from wind-based electrolysis as fuel source and renewable electricity as the power resource. **Table S7** provides a complete overview of the GWP values of the process in- and outputs.

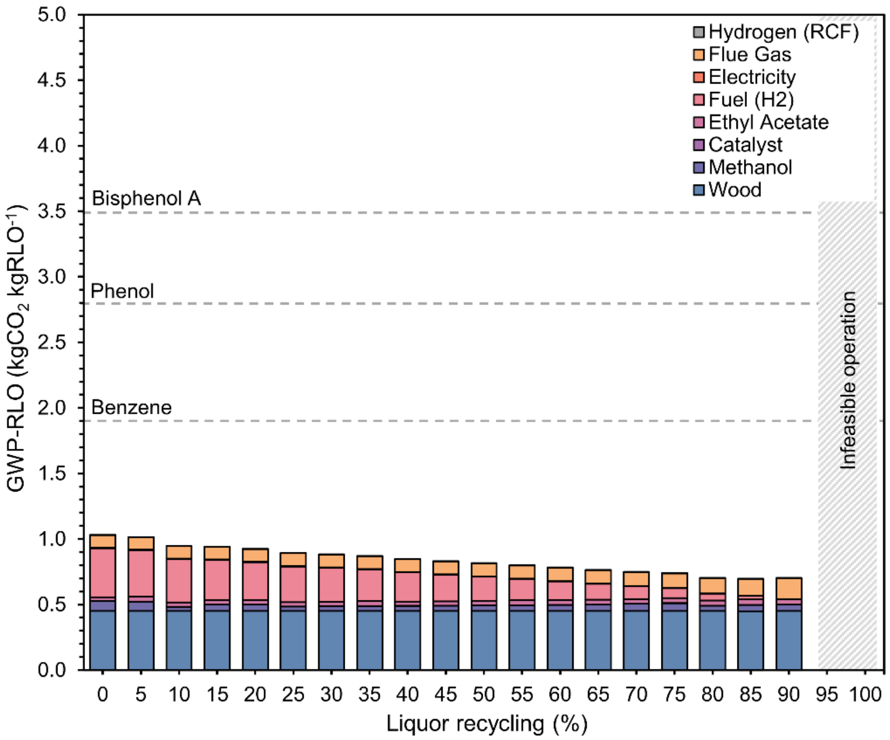

Fig. S9 Share of process in- and outputs to the global warming potential of the refined lignin oil (GWP-RLO) in function of the liquor recycling, compared to the GWP of benzene, phenol, and bisphenol A when renewable electricity and green hydrogen (as fuel) are used. The system boundaries of these GWP-RLO calculations are shown in **Fig. S8**. The GWP parameters of the in- and outputs are shown in **Table S7**.

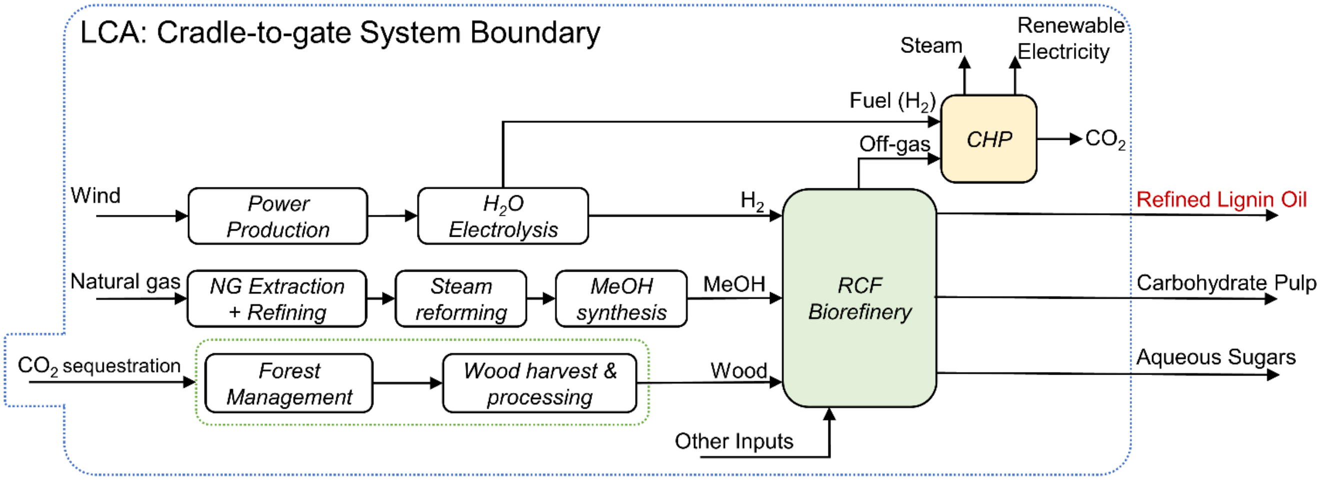

Fig. S10 System boundary of the LCA with green hydrogen produced from wind-based electrolysis as fuel source and renewable electricity as the power resource. This system boundary includes the biogenic carbon sequestration by plant photosynthesis. **Table S7** provides a complete overview of the GWP values of the process in- and outputs. The GWP drops by 4.9 $kgCO_2.kgRLO^{-1}$ by including biogenic carbon uptake by plant photosynthesis within the system boundary.

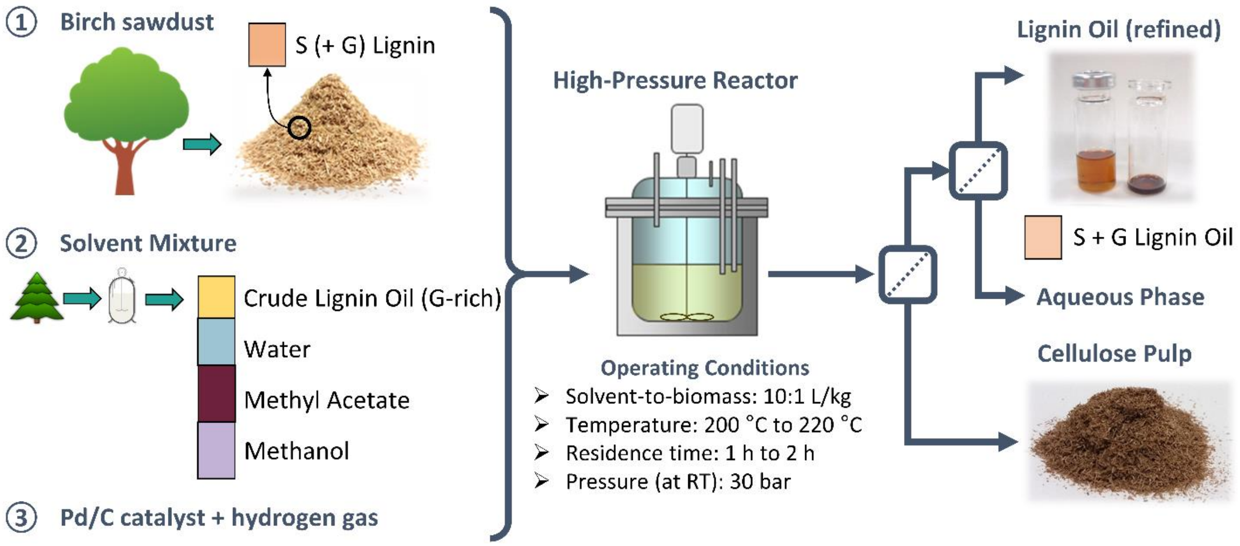

Fig. S11 Scheme of the experimental RCF reactions with solvent mixture which contains spruce crude lignin oil. Spruce crude lignin oil was obtained by a 2 L batch RCF. See **Table S2** for a complete overview of the experimental conditions used in the RCF reactions.

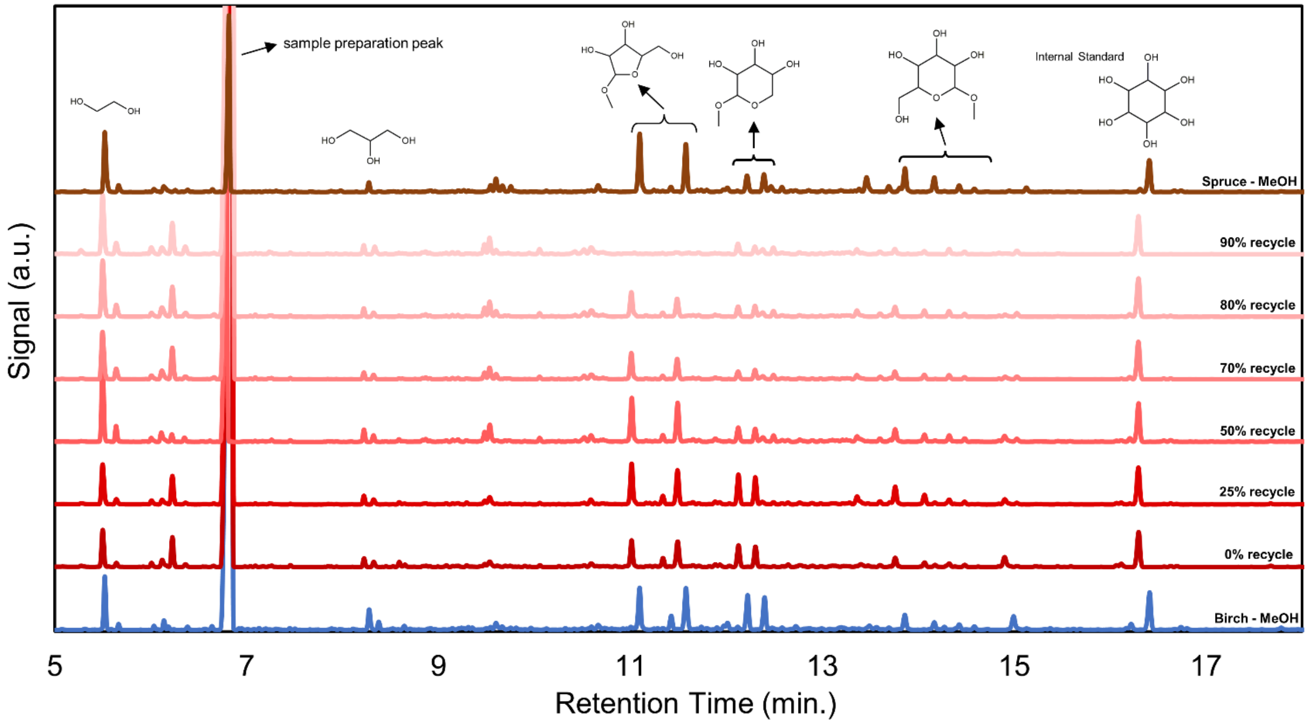

Fig. S12 GC-chromatograms of the aqueous phase for a standard RCF reaction using spruce (Spruce - MeOH) and for birch RCF reactions with pure methanol (Birch - MeOH) and with solvent compositions at liquor recycling between 0% and 90%. See **Table S2** for the solvent compositions and the reaction conditions.

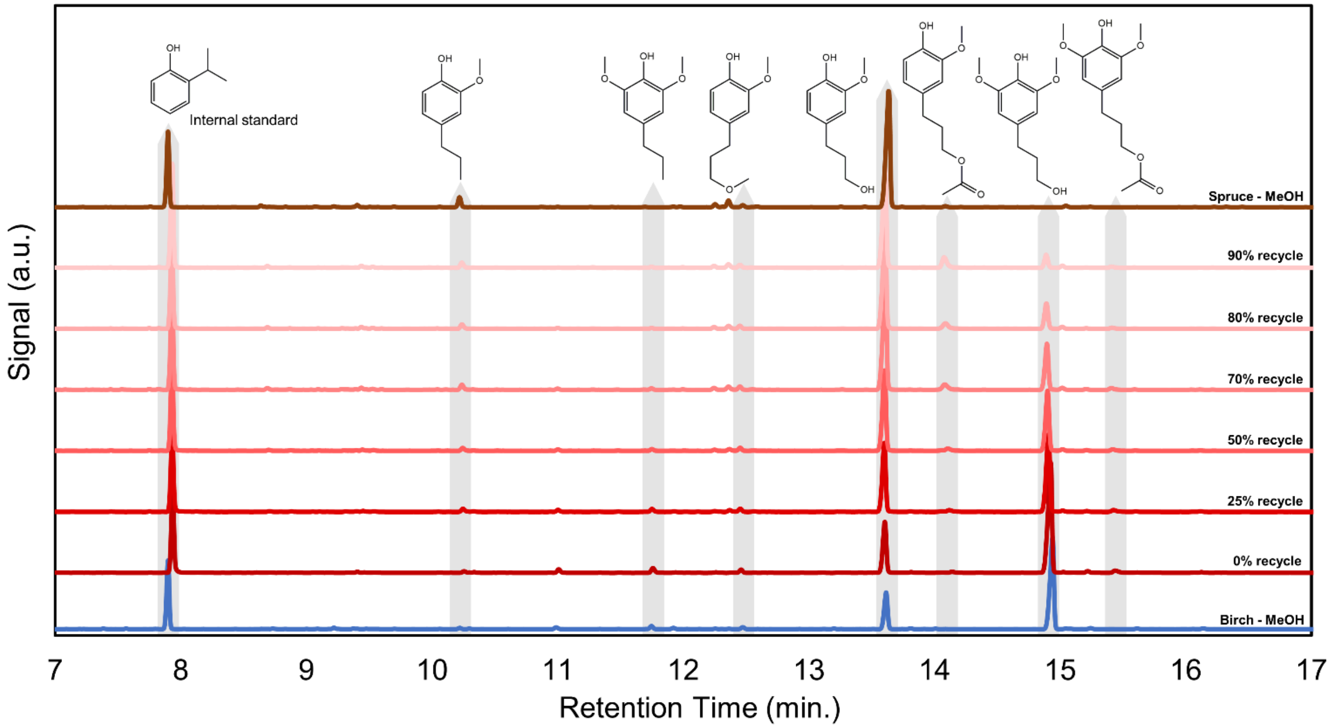

Fig. S13 GC-chromatograms of the refined lignin oil for a standard RCF reaction using spruce (Spruce - MeOH) and for birch RCF reactions with pure methanol (Birch - MeOH) and with solvent compositions at liquor recycling between 0% and 90%. See **Table S2** for the solvent compositions and the reaction conditions.

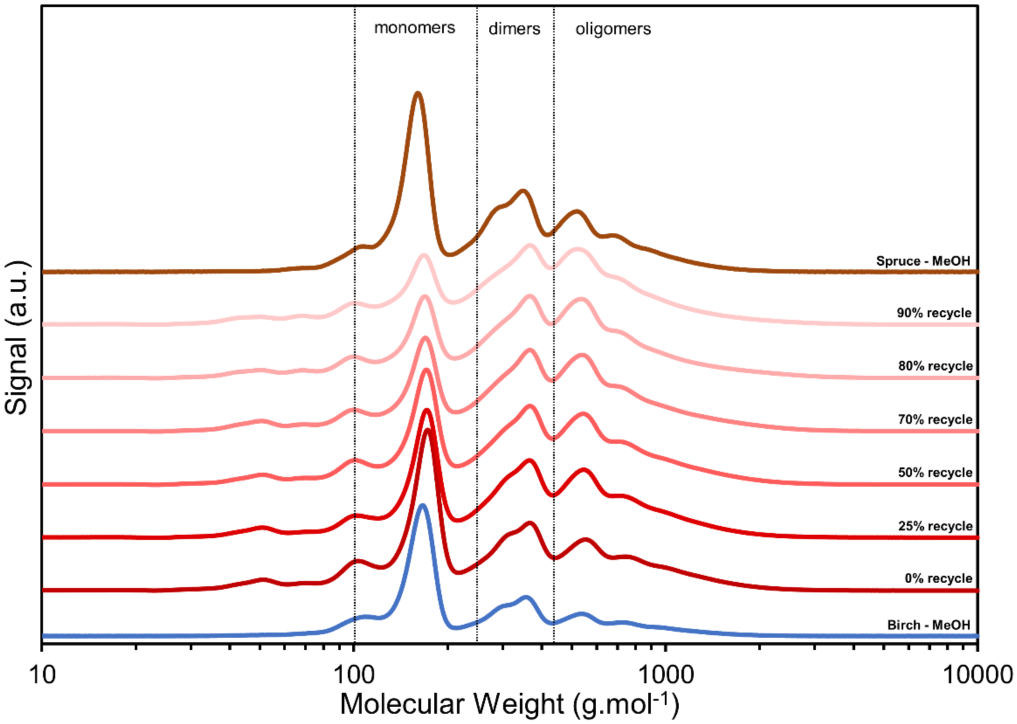

Fig. S14 GPC-chromatograms of the refined lignin oil for a standard RCF reaction using spruce (Spruce - MeOH) and for birch RCF reactions with pure methanol (Birch - MeOH) and with solvent compositions at liquor recycling between 0% and 90%. See **Table S2** for the solvent compositions and the reaction conditions.

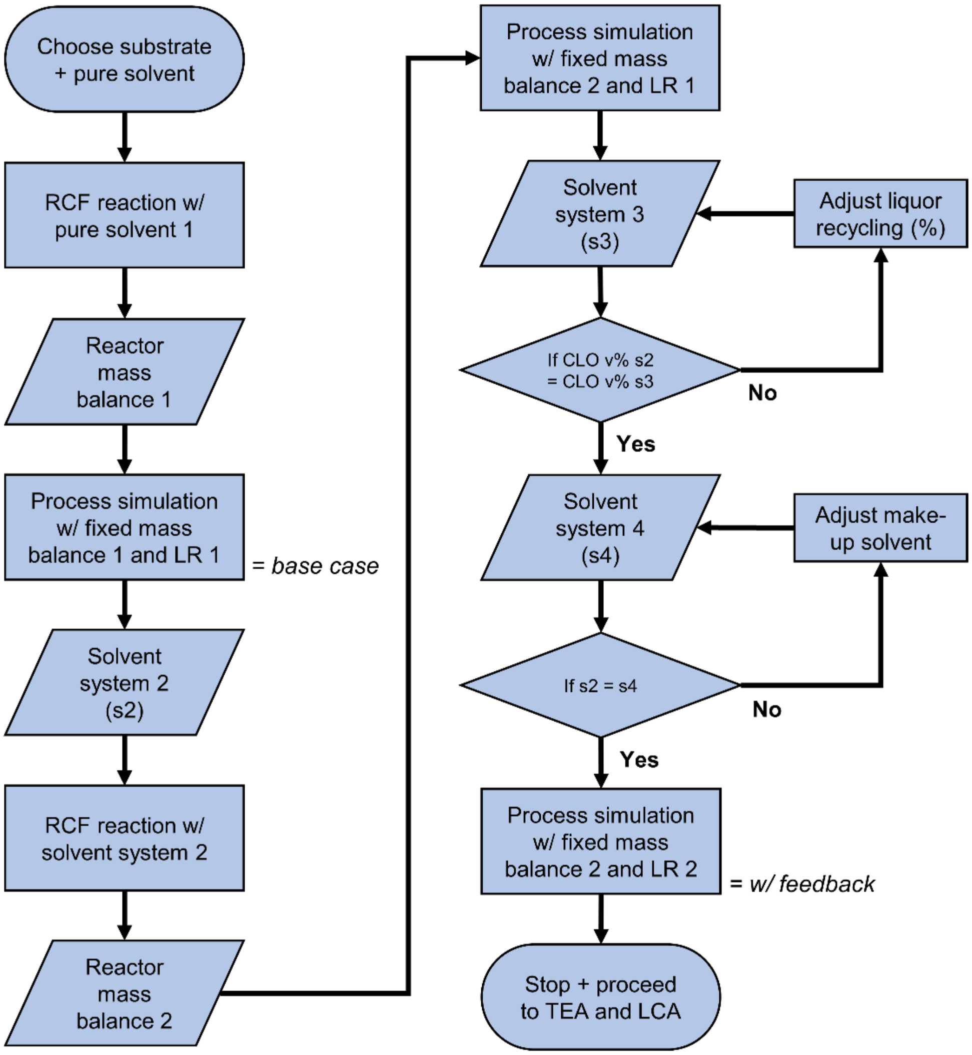

Fig. S15 Flow chart of methodology used to match the solvent mixture composition and volumetric flow rate in experimental RCF following a first process simulation based on standard RCF reaction with pure solvent and a fixed liquor recycling (*i.e.*, *base case*) with a new process simulation with an adjusted liquor recycling and make-up solvent composition (*i.e.*, *w/ feedback*).

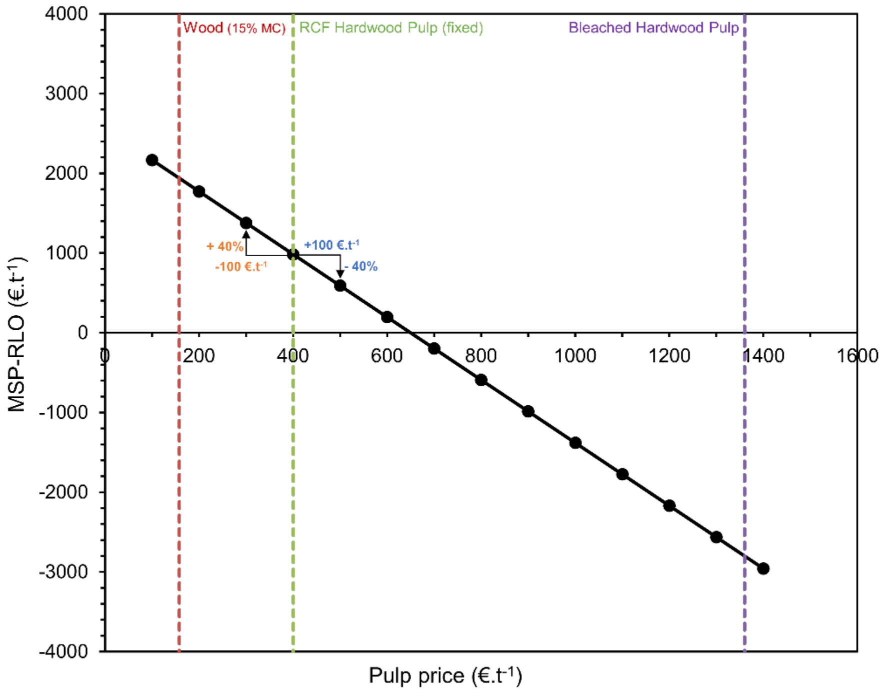

Fig. S16 Minimum selling price of the refined lignin oil (MSP-RLO) in function of the pulp selling price for an 80% liquor recycling case using birch feedstock. The pulp selling price was univariately changed whilst all technical variables and economic parameters were kept constant. The wood selling price and pulp prices used in this work amount 158 and 400 €.t^{-1}, respectively. The price for hardwood bleached pulp in Europe[7] amounts 1360 €.t^{-1}. The high sensitivity of the pulp price on the economics of the RCF biorefinery shows that a comparison of the economic analyses of various design cases would be cumbersome in case that pulp price is changed based on the lignin content.

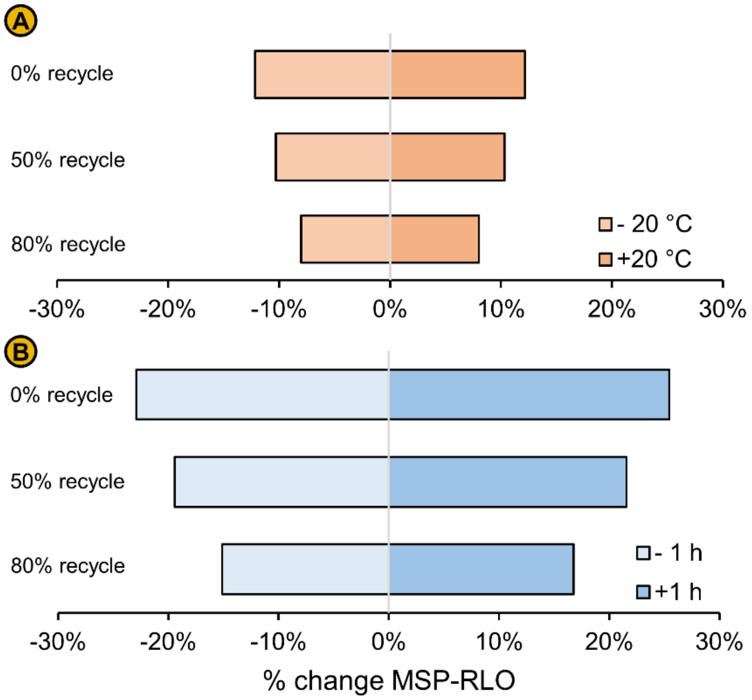

Fig. S17 % change of the MSP-RLO obtained by univariate analysis of the **a)** the reactor residence time for ±1 h and **b)** the reaction temperature for ±20°C at a liquor recycling of 0, 50 and 80%. Process simulations and economic calculations were done for a reactor residence time of 1, 2, and 3 h at a reaction temperature of 220°C, and for 200, 220 and 240°C at a reactor residence time of 2 h. Operational and capital expenses were re-evaluated and included in the MSP-RLO estimations.

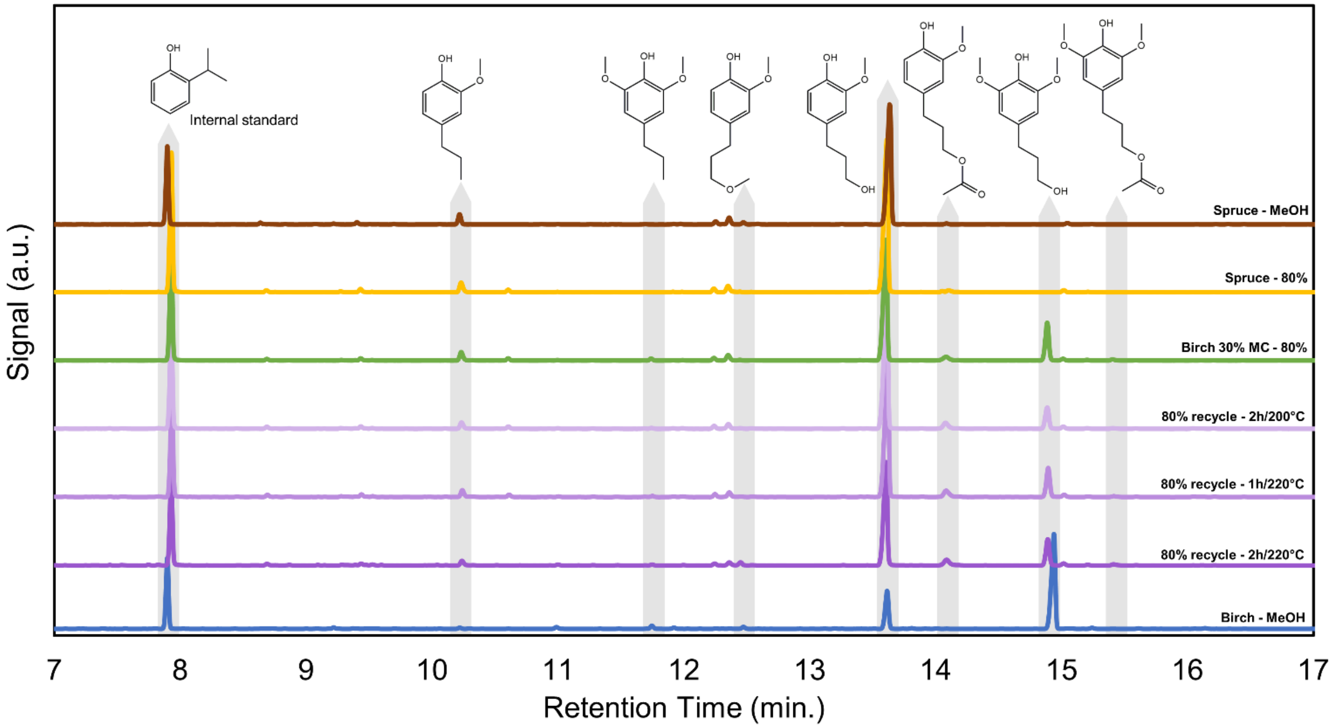

Fig. S18 GC-chromatograms of the refined lignin oil for standard spruce (Spruce - MeOH) and birch (Birch - MeOH) reaction and for the reactions used to optimize the reactor cost and to demonstrate the general applicability of the process design. See **Table S2** for the solvent compositions and the reaction conditions.

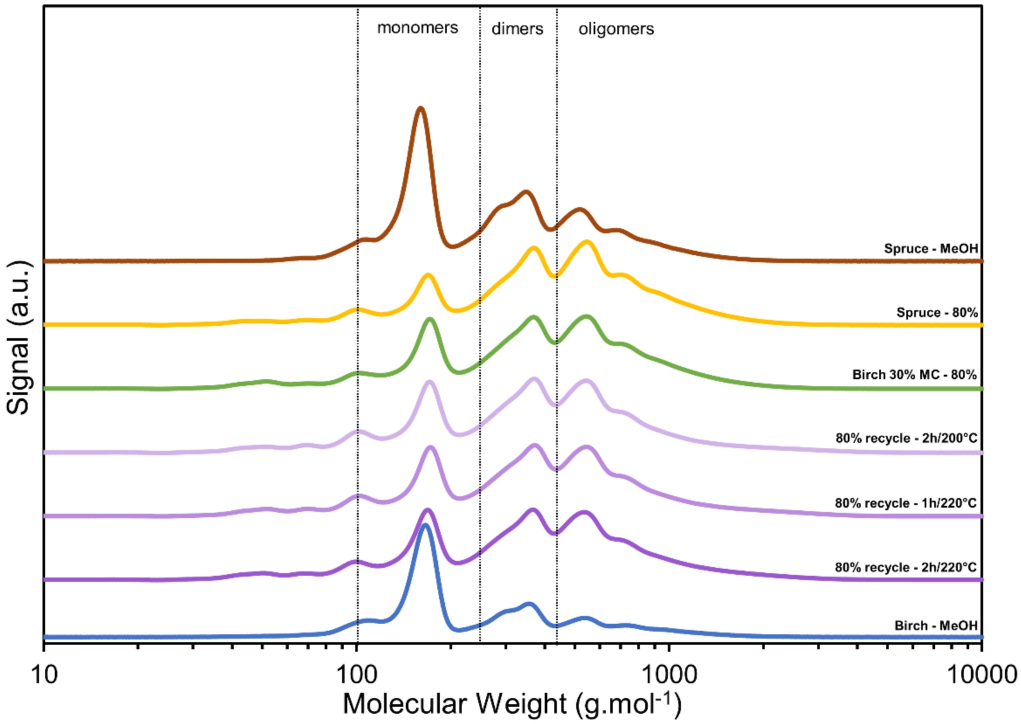

Fig. S19 GPC-chromatograms of the refined lignin oil for standard spruce (Spruce - MeOH) and birch (Birch - MeOH) reaction and for the reactions used to optimize the reactor cost and to demonstrate the general applicability of the process design. See **Table S2** for the solvent compositions and the reaction conditions.

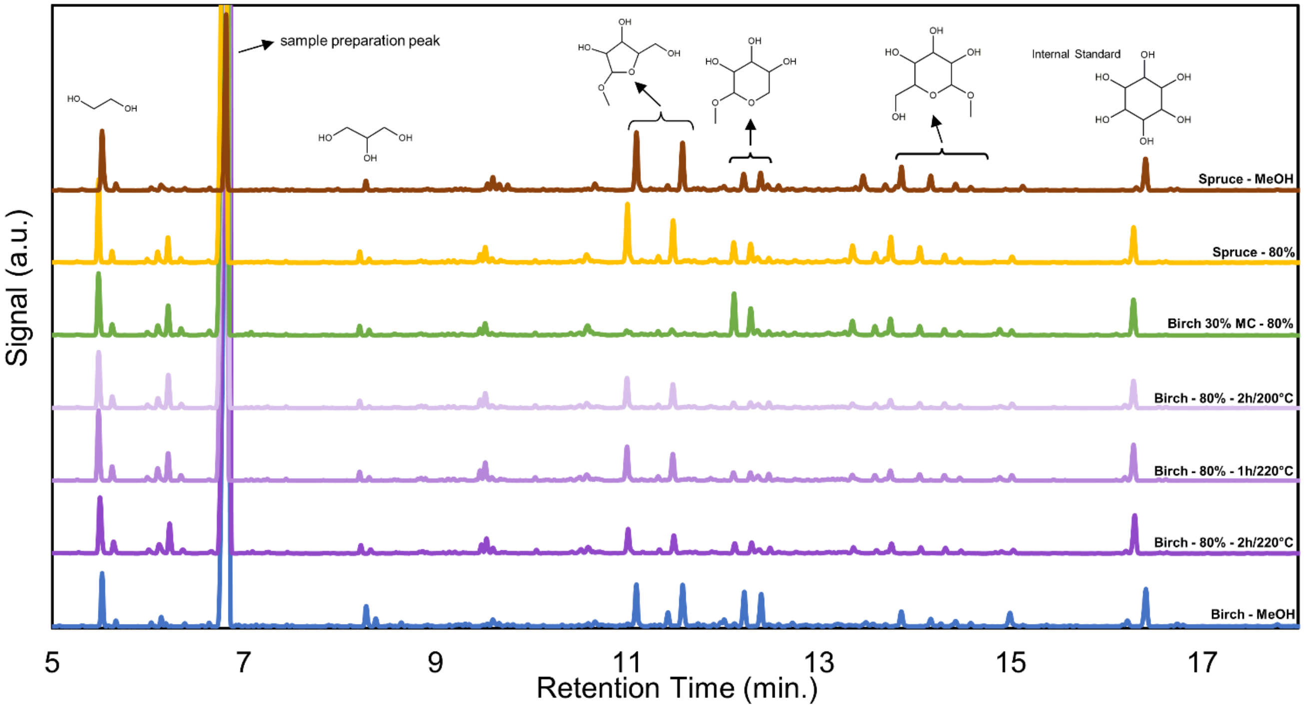

Fig. S20 GC-chromatograms of the aqueous phase for standard spruce (Spruce - MeOH) and birch (Birch - MeOH) reaction and for the reactions used to optimize the reactor cost and to demonstrate the general applicability of the process design. See **Table S2** for the solvent compositions and the reaction conditions.

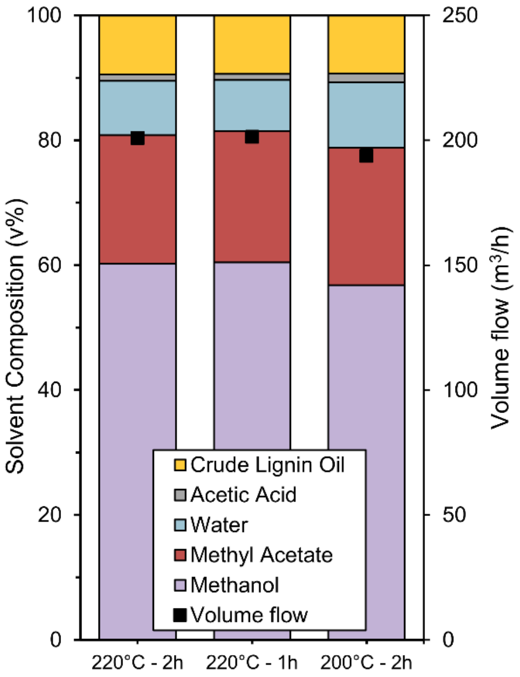

Fig. S21 Simulated solvent composition after implementation of the experimental results in the process simulation and readjustment of the liquor recycling and the make-up solvent composition for the RCF reactions at varying reaction time and temperature.

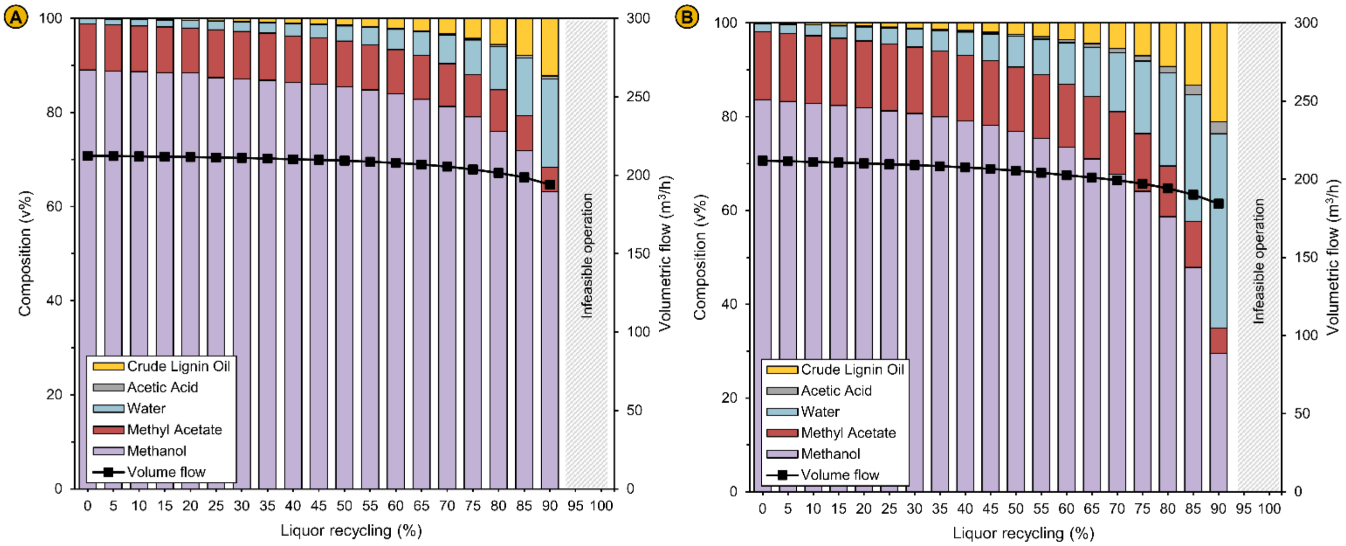

Fig. S22 The solvent composition at the reactor inlet (left axis) and inlet solvent volumetric flow rate at reaction conditions (right axis) in function of the liquor recycling (%) for the process simulation using the consumption and formation of mass in the RCF reactor according to **a)** a standard MeOH reaction with spruce containing 15% moisture and **b)** a standard MeOH reaction with birch containing 30% moisture.

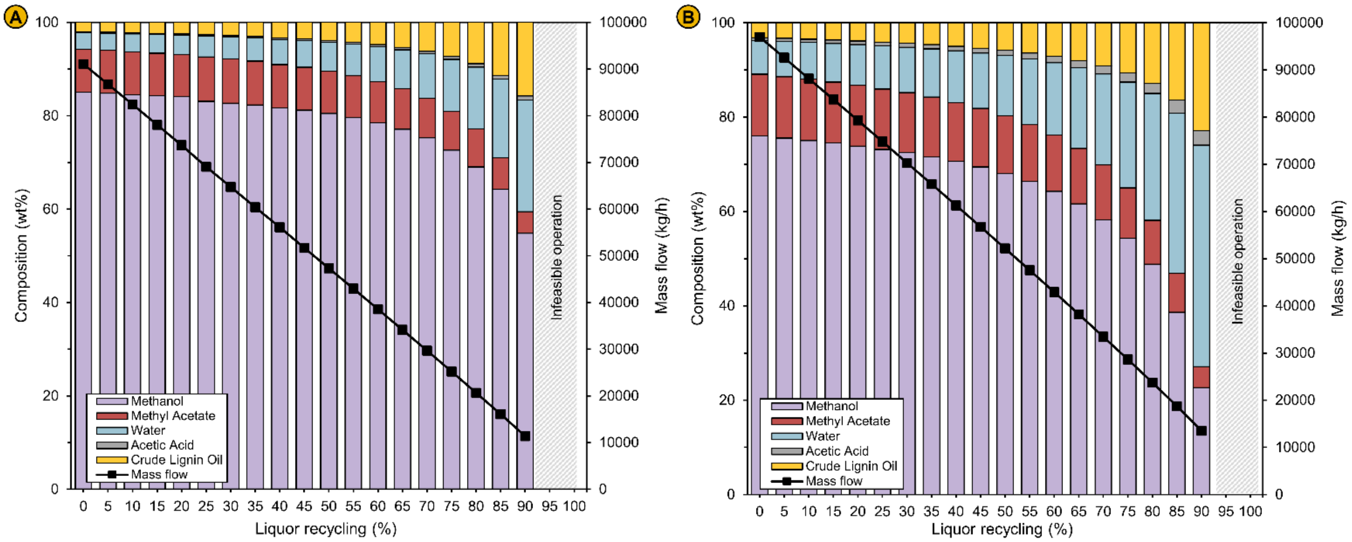

Fig. S23 The composition (left axis) and mass flow rate (right axis) of the liquid entering the crude distillation in function of the liquor recycling (%) for the process simulation using the consumption and formation of mass in the RCF reactor according to **a)** a standard MeOH reaction with spruce containing 15% moisture and **b)** a standard MeOH reaction with birch containing 30% moisture.

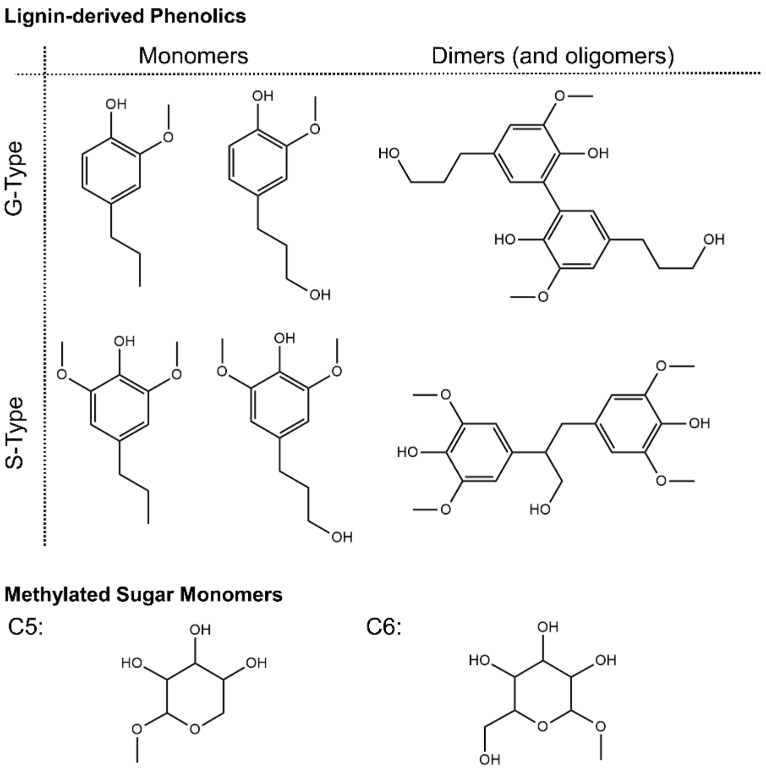

Fig. S24 Chemical structure of the model compounds used to represent the crude lignin oil components in Aspen HYSYS. Acetylated equivalents of the monomers, dimers and oligomers have been implemented in the simulations as well to verify their behaviour in the process. They behave similarly as the non-acetylated compounds.

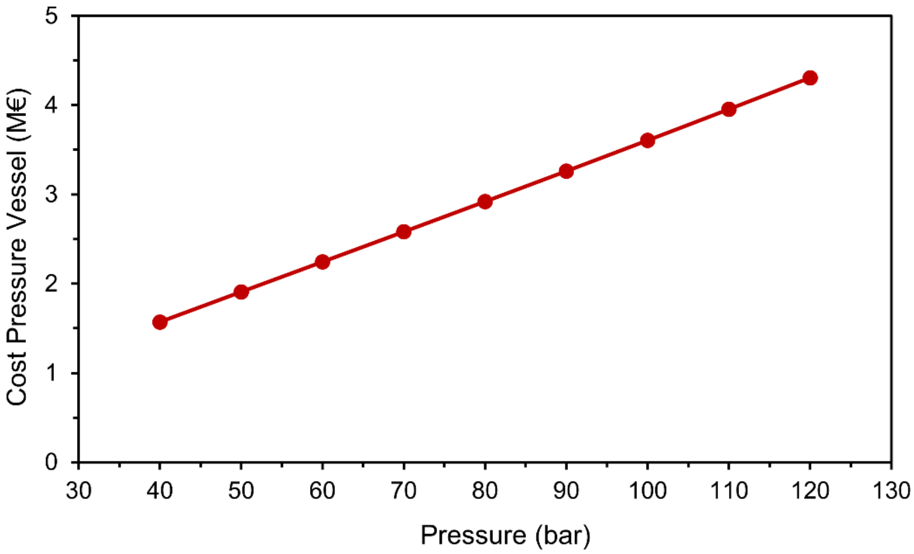

Fig. S25 Cost of a pressure vessel (without multiplication with the factorials) in function of the pressure. The prices were estimated using shell mass for a vertical pressure vessel with a volume of 300 m^3 that is able to withstand the corresponding pressure at a design temperature of 250 °C. The relative change in cost was used to scale the costs of the RCF reactors from 220 °C and 90 bar to 200 °C and 70 bar in the reactor cost optimization section.

3. Tables

Table S1 Composition of the gas phase after the RCF base reaction with pure methanol. Reaction conditions: 4 g birch sawdust (250 – 500 µm), 0.4 g Pd/C, 40 ml methanol, 30 bar H_2 (at RT), 220°C, 2 h.

Gas Phase Composition	
Component	Vol %
Hydrogen	94.20
Nitrogen	4.05
Carbonmonoxide	0.86
Carbondioxide	0.52
Methanol	0.12
Methane	0.22
Ethane	0.01

Table S2 Overview of the solvent composition and reaction conditions used in the RCF reactions. The labels used in this table correspond to labels used in the figures in each section of the main text. The crude lignin oil (CLO) used in the reactions originates from a 2L RCF reaction with softwood Spruce in methanol.

Overview Solvent Composition of RCF Reactions									
RCF Reaction	**Feedstock**	**Solvent**	**Volumetric share (v%)**					**Conditions**	
Label	**Type**	**Volume (ml)**	**MeOH**	**MeOAc**	**H_2O**	**HOAc**	**CLO**	**Time (h)**	**Temp. (°C)**
Section: ***Model-driven Experimental RCF***									
Birch - MeOH	birch	40	100%	0%	0%	0%	0%	2	220
0% recycling	birch	40	72%	26%	1%	0%	0%	2	220
25% recycling	birch	40	71%	26%	2%	0%	1%	2	220
50% recycling	birch	40	69%	24%	3%	0%	2%	2	220
70% recycling	birch	40	65%	23%	6%	1%	5%	2	220
80% recycling	birch	40	58%	22%	9%	1%	9%	2	220
90% recycling	birch	40	38%	20%	18%	3%	21%	2	220
Spruce - MeOH	spruce	40	100%	0%	0%	0%	0%	2	220
Section: ***Reducing the Reactor Capital Costs***									
220°C - 2h	birch	40	58%	22%	9%	1%	9%	2	220
220°C - 1h	birch	40	58%	22%	9%	1%	9%	1	220
200°C - 2h	birch	40	58%	22%	9%	1%	9%	2	200
Section: ***General applicability of the Process Design***									
Spruce - MeOH	spruce	40	100%	0%	0%	0%	0%	2	220
80% recycling	spruce	40	76%	9%	9%	0%	6%	2	220
Birch - MeOH	birch	40	100%	0%	0%	0%	0%	2	220
15% MC	birch	40	58%	22%	9%	1%	9%	2	220
30% MC	birch	40	59%	11%	20%	1%	9%	2	220

Table S3 Composition of the make-up solvent in function of the liquor recycle. The solvent composition was adjusted after implementation of the experimental results in the process simulation to match the inlet solvent composition in the process simulation with the solvent composition used in the experiments (see **Fig. S15** for a schematic overview of the procedure).

Make-up solvent composition				
Case	**LR (%)**	**MeOH (v%)**	**H_2O (v%)**	**Mass flow (kg.h^{-1})**
base	0	100	0	632
w/ feedback	0	100	0	632
base	25	100	0	274
w/ feedback	22.5	100	0	250
base	50	100	0	342
w/ feedback	40	50	50	525
base	70	100	0	448
w/ feedback	58	28	72	1057
base	80	100	0	333
w/ feedback	67	22	78	1717
base	90	100	0	403
w/ feedback	76	10	90	2501

Table S4 Efficiency of the boiler and steam turbine using in the CHP calculations. The condensate return equals the amount of high pressure, medium pressure and low-pressure condensate that is returned to the CHP boiler relative to the amount of high pressure, medium pressure and low-pressure steam that has entered the process.

CHP-Parameters	
boiler efficiency (%)	85
steam turbine efficiency (%)	85
condensate return (%)	90

Table S5 Economic parameters used in the techno-economic assessment of the RCF biorefinery process. Cost escalation indices and the location factor were obtained from Sinnott & Towler.[8]

Economic Parameters	
currency exchange rate (€.$^{-1}$)	0.9
cost escalation index 2007	2059.1
cost escalation index 2020	2686.6
location factor	1.11
project lifetime (no. y)	20
depreciation period (no. y)	10
weighted average cost of capital (%)	15
taxation rate (%)	25
plant down time (%)	2

Table S6 List of the process in- and output prices. Similar pricing was used as by Liao *et al*.[9] (detailed info can be found in their supplementary info). Prices for the high, medium and low pressure steam levels were obtained from Sinnott & Towler.[8] Prices for bisphenol A, phenol and benzene were reported by ICIS, over a period between 2019-2020.[10–12]

Prices of refinery in- and outputs			
product	**value**	**unit**	**reference**
wood feedstock	0.158	€/kg	Pricing as estimated by Tschulkow *et al*.[13]
hydrogen	1.05	€/kg	Pricing obtained from Liao *et al*.[9]
methanol	0.393	€/kg	Pricing obtained from Liao *et al*.[9]
water	0.0005	€/kg	Chemical Engineering Design, Sinnott & Towler[8]
ethyl acetate	2.5	€/kg	Ethyl acetate market analysis by echemi.com[14]
Pd/C catalyst (5 wt% Pd on C)	3000	€/kg	Conservative estimate based on Pd price of 50 000 €/kg (coininvest.com)[15]
pulp	0.4	€/kg	Estimate from Liao *et al*.[9]
aqueous sugars	0.4	€/kg	Estimate from Liao *et al*.[9]
electricity	0.1	€/kWh	Eurostat, electricity price statistics (non-households consumers)[16]
high pressure steam	0.01306	€/kg	Chemical Engineering Design, Sinnott & Towler[8]
medium pressure steam	0.0104	€/kg	Chemical Engineering Design, Sinnott & Towler[8]
low pressure steam	0.00664	€/kg	Chemical Engineering Design, Sinnott & Towler[8]
bisphenol A	1.5	€/kg	ICIS report[17]
phenol	1.1	€/kg	ICIS report[12]
benzene	0.4	€/kg	ICIS report[11]

Table S7 GWP values of the refinery in- and outputs. The background processes and technologies of the life cycle inventory (LCI) of each of these inputs are shown. The LCIs were obtained from Ecoinvent v3.8 and Thinkstep Gabi professional database.

In/out	GWP	Process/Technology (LCI)	Unit
wood feedstock	0.15	harvesting, debarking, chipping	kg CO_2 eq. / kg input
methanol	0.64	natural gas steam reforming + syngas conversion	kg CO_2 eq. / kg input
grey hydrogen	9.32	natural gas steam reforming	kg CO_2 eq. / kg input
green hydrogen	0.97	water electrolysis by wind power[18]	kg CO_2 eq. / kg input
Pd/C catalyst (5 wt% Pd on C)	200	5% Pd GWP as reported by[19]	kg CO_2 eq. / kg input
ethyl acetate	2.73	ethyl acetate production (fossil-based)	kg CO_2 eq. / kg input
steam	0.19	steam in chemical industry	kg CO_2 eq. / kg input
electricity mix	0.464	electricity, high voltage	kg CO_2 eq. / kWh
renewable electricity	0.013	high-voltage electricity, wind mix (onshore/offshore)	kg CO_2 eq. / kWh
bisphenol A	3.49	bisphenol A production, powder	kg CO_2 eq. / kg input
phenol	2.79	phenol production, from cumene	kg CO_2 eq. / kg input
benzene	1.86	benzene production	kg CO_2 eq. / kg input

Table S8 Tabulated data of Fig. 3 in the main text. The composition and flowrate on a mass basis are also given.

Liquor Recycling (LR) (%)	Vol. Flow ($m^3 \cdot h^{-1}$)	Volumetric fraction (%)					Mass Flow ($kg \cdot h^{-1}$)	Mass fraction (%)				
		MeOH	MeOAc	H_2O	HOAc	CLO		MeOH	MeOAc	H_2O	HOAc	CLO
0	256	72	26	1	0	0	124170	69	30	2	0	0
5	253	72	26	1	0	0	124224	68	30	2	0	0
10	250	72	26	2	0	0	124270	68	29	2	0	0
15	246	72	26	2	0	0	124322	68	29	2	0	1
20	241	71	26	2	0	1	124384	68	29	2	0	1
25	237	71	26	2	0	1	124454	68	29	2	0	1
30	232	71	26	2	0	1	124519	67	29	3	0	1
35	227	71	25	2	0	1	124591	67	28	3	0	1
40	220	70	25	3	0	2	124680	67	28	3	0	2
45	214	70	25	3	0	2	124791	66	28	4	0	2
50	209	69	24	3	0	2	124932	66	27	4	0	3
55	208	69	24	4	0	3	125115	65	27	5	1	3
60	207	68	23	4	1	4	125355	64	26	5	1	4
65	206	67	23	5	1	4	125680	63	26	6	1	5
70	205	65	23	6	1	5	126134	61	25	7	1	6
75	203	62	22	7	1	7	126795	58	24	9	1	8
80	200	58	22	9	1	9	127815	54	24	11	2	10
85	196	52	21	12	2	13	129551	47	23	14	2	14
90	191	38	20	18	3	21	132919	34	21	20	4	21

Table S9 Tabulated data of Fig. 4a in the main text.

	Operational Expenditure (M€.y^{-1})										
LR (%)	Wood	MeOH	H_2	Pd/C	EtOAc	H_2O	Fuel (H_2)	Steam	Electricity	FC	TOTAL
0	24.2	2.2	0.1	2.5	1.4	0.5	21.2	0.0	1.8	13.2	67.2
5	24.2	2.1	0.1	2.5	1.8	0.5	20.1	0.0	1.8	13.3	66.4
10	24.2	0.9	0.1	2.5	1.6	0.5	18.7	0.0	1.6	13.2	63.4
15	24.2	1.4	0.1	2.5	1.5	0.5	17.5	0.0	1.5	13.1	62.4
20	24.2	1.4	0.1	2.5	1.6	0.4	16.5	0.0	1.4	13.0	61.2
25	24.2	0.9	0.1	2.5	1.6	0.4	15.4	0.0	1.3	12.6	59.1
30	24.2	1.1	0.1	2.5	1.5	0.4	14.8	0.0	1.3	12.7	58.6
35	24.2	1.1	0.1	2.5	1.8	0.4	13.7	0.0	1.2	12.3	57.3
40	24.2	1.1	0.1	2.5	1.6	0.4	12.6	0.0	1.1	12.2	55.7
45	24.2	1.1	0.1	2.5	1.6	0.3	11.6	0.0	1.0	12.0	54.4
50	24.2	1.2	0.1	2.5	1.8	0.3	10.4	0.0	0.9	11.8	53.2
55	24.2	1.2	0.1	2.5	1.8	0.3	9.2	0.0	0.8	11.6	51.8
60	24.2	1.3	0.1	2.5	1.9	0.2	8.0	0.0	0.6	11.5	50.4
65	24.2	1.4	0.1	2.5	1.8	0.2	6.8	0.0	0.5	11.7	49.3
70	24.2	1.5	0.1	2.5	1.7	0.2	5.6	0.0	0.4	11.3	47.6
75	24.2	1.7	0.1	2.5	1.8	0.2	4.3	0.0	0.3	10.9	46.1
80	24.2	1.1	0.1	2.5	1.9	0.1	3.0	0.0	0.2	10.6	43.8
85	24.2	1.4	0.1	2.5	2.0	0.1	1.6	0.0	0.0	10.3	42.1
90	24.2	1.4	0.1	2.5	1.9	0.1	0.1	0.0	-0.2	9.8	39.9

Table S10 Tabulated data of Fig. 4b in the main text.

	Capital Expenditure (M€)							
LR (%)	**Reactor**	**Distillation**	**HEN-Network**	**CHP**	**WC**	**Other**	**TOTAL**	**Reactor Volume (m3)**
5	98.0	9.2	24.7	20.3	8.5	4.0	165	391
10	98.0	8.6	24.3	19.1	8.2	4.0	162	391
15	97.9	8.0	24.8	18.0	8.1	4.0	161	390
20	97.6	7.6	24.2	17.1	7.9	4.0	158	389
25	97.3	7.1	19.8	16.2	7.7	4.0	152	387
30	96.5	6.8	21.9	15.7	7.6	4.0	153	383
35	96.1	6.3	18.1	14.7	7.4	4.0	147	381
40	95.6	5.9	17.4	13.7	7.2	4.0	144	379
45	95.1	5.4	16.3	12.8	7.1	4.0	141	376
50	94.5	4.9	16.1	11.7	6.9	4.0	138	373
55	93.8	4.4	14.8	10.8	6.7	4.0	134	369
60	92.9	4.2	15.4	9.7	6.6	4.0	133	365
65	91.9	3.7	19.9	8.7	6.5	4.0	135	360
70	90.6	3.1	16.3	7.6	6.2	4.0	128	354
75	89.0	2.6	13.4	6.5	6.0	4.0	121	346
80	86.7	2.0	12.2	5.5	5.7	4.0	116	335
85	83.3	1.4	11.9	4.4	5.5	4.0	110	318
90	77.4	0.8	12.2	3.4	5.2	4.0	103	289
0	0.0	0.0	0.0	0.0	0.0	0.0	0	0

Table S11 Tabulated data of Fig. 5a in the main text.

LR (%)	MSP-RLO (€.t^{-1})
0	2261
5	2238
10	2109
15	2054
20	1985
25	1866
30	1840
35	1750
40	1666
45	1590
50	1523
55	1441
60	1374
65	1342
70	1224
75	1115
80	984
85	870
90	733

Table S12 Tabulated data of Fig. 5b in the main text.

GWP-RLO ($kgCO_2.kgRLO^{-1}$)										
LR (%)	Wood	MeOH	H_2 (RCF)	Pd/C	EtOAc	CO_2	Fuel (H_2)	Steam	Electricity	TOTAL
0	0.45	0.08	0.0171	0.0032	0.03	0.09	3.60	0.00	0.1637	4.42
5	0.45	0.07	0.0171	0.0032	0.04	0.10	3.40	0.00	0.1552	4.22
10	0.45	0.03	0.0171	0.0032	0.03	0.10	3.18	0.00	0.1446	3.95
15	0.45	0.05	0.0171	0.0032	0.03	0.10	2.97	0.00	0.1335	3.74
20	0.45	0.05	0.0171	0.0032	0.03	0.10	2.79	0.00	0.1250	3.56
25	0.45	0.03	0.0171	0.0032	0.03	0.10	2.61	0.00	0.1166	3.36
30	0.45	0.04	0.0171	0.0032	0.03	0.10	2.51	0.00	0.1121	3.25
35	0.45	0.04	0.0171	0.0032	0.04	0.10	2.33	0.00	0.1036	3.07
40	0.45	0.04	0.0171	0.0032	0.03	0.10	2.14	0.00	0.0948	2.87
45	0.45	0.04	0.0171	0.0032	0.03	0.10	1.96	0.00	0.0859	2.68
50	0.45	0.04	0.0171	0.0032	0.04	0.10	1.76	0.00	0.0761	2.48
55	0.45	0.04	0.0171	0.0032	0.04	0.10	1.57	0.00	0.0668	2.28
60	0.45	0.05	0.0171	0.0032	0.04	0.10	1.36	0.00	0.0565	2.06
65	0.45	0.05	0.0171	0.0032	0.04	0.10	1.16	0.00	0.0468	1.86
70	0.45	0.05	0.0171	0.0032	0.04	0.11	0.95	0.00	0.0361	1.64
75	0.45	0.06	0.0171	0.0032	0.04	0.11	0.74	0.00	0.0250	1.43
80	0.45	0.04	0.0171	0.0032	0.04	0.12	0.51	0.00	0.0134	1.18
85	0.45	0.05	0.0170	0.0032	0.04	0.13	0.26	0.00	-0.0007	0.95
90	0.45	0.05	0.0171	0.0032	0.04	0.16	0.02	0.00	-0.0195	0.71

Table S13 Tabulated data of Fig. 6 in the main text.

Wood/Pulp Composition (wt%)				
	Hemicellulose	Cellulose	Acetyl	Lignin
Birch	25.59%	40.08%	4.31%	25.10%
MeOH	22.5%	40.8%	0.8%	9.3%
0% recycle	21.5%	38.2%	1.3%	5.6%
25% recycle	20.8%	39.6%	0.8%	3.4%
50% recycle	20.4%	39.2%	0.9%	2.9%
70% recycle	17.2%	38.0%	1.0%	2.9%
80% recycle	13.9%	38.2%	1.0%	1.7%
90% recycle	3.2%	33.0%	0.7%	3.9%

Table S14 Tabulated data of Fig. 7a in the main text.

Monomer yield of syringyl-type monomers vs. protolignin and delignification					
	Delignification	POHS	POAcS	PS	Sum
MeOH	62.87%	18.13%	0.00%	0.82%	18.94%
0% recycle	77.7%	14.0%	0.5%	0.6%	15.2%
25% recycle	86.3%	14.8%	0.6%	0.6%	16.0%
50% recycle	88.4%	15.2%	0.7%	0.5%	16.5%
70% recycle	88.4%	17.4%	1.2%	0.6%	19.3%
80% recycle	93.3%	18.6%	1.5%	0.7%	20.8%
90% recycle	84.4%	19.4%	3.2%	1.8%	24.3%

Table S15 Tabulated data of Fig. 7b in the main text.

RLO composition										
	Delignification	**POMeG**	**PS**	**PG**	**POHS**	**POHG**	**POAcS**	**POAcG**	**Oligomers**	**Monomers**
Spruce RLO	\	1.3%	0.0%	1.7%	0.0%	27.5%	0.0%	0.0%	69.5%	30.5%
MeOH	62.9%	0.0%	1.4%	0.4%	30.7%	10.6%	0.0%	0.0%	56.8%	43.2%
0% recycle	77.7%	0.6%	1.2%	0.4%	25.6%	9.2%	1.0%	0.4%	61.6%	38.4%
25% recycle	86.3%	0.6%	0.7%	0.7%	17.7%	13.4%	0.8%	0.7%	65.4%	34.6%
50% recycle	88.4%	0.6%	0.4%	0.7%	13.2%	16.2%	0.6%	1.1%	67.2%	32.8%
70% recycle	88.4%	0.6%	0.3%	1.0%	8.5%	20.2%	0.6%	2.0%	66.8%	33.2%
80% recycle	93.3%	0.6%	0.2%	1.0%	5.5%	20.5%	0.4%	2.3%	69.5%	30.5%
90% recycle	84.4%	0.7%	0.2%	1.0%	2.6%	19.9%	0.4%	3.7%	71.4%	28.6%

Table S16 Tabulated data of Fig. 8a in the main text.

MSP-RLO w/ experimental feedback			
base case		**w/ feedback**	
LR (%)	**MSP-RLO (€.t^{-1})**	**LR (%)**	**MSP-RLO (€.t^{-1})**
0	2261	0	2045
25	1866	22.5	1492
50	1523	40	1438
70	1224	58	1234
80	984	67	1089
90	733	76.5	1053

Table S17 Tabulated data of Fig. 8b in the main text.

GWP-RLO w/ experimental feedback			
base case		**w/ feedback**	
LR (%)	**GWP-RLO (kgCO$_2$.kgRLO^{-1})**	**LR (%)**	**GWP-RLO (kgCO$_2$.kgRLO^{-1})**
0	1.030	0	0.979
25	0.893	22.5	0.801
50	0.816	40	0.796
70	0.749	58	0.752
80	0.704	67	0.710
90	0.704	76.5	0.757

Table S18 Tabulated data of Fig. 9a in the main text.

Pulp Composition (wt%)				
	Hemicellulose	**Cellulose**	**Acetyl**	**Lignin**
Birch	25.59%	40.08%	4.31%	25.10%
220°C - 2h	13.9%	38.2%	1.0%	1.7%
220°C - 1h	17.6%	41.2%	1.6%	4.9%
200°C - 2h	20.1%	40.9%	1.8%	7.5%

Table S19 Tabulated data of Fig. 9b in the main text.

Monomer yield of syringyl-type monomers vs. protolignin and delignification					
	Delignification	**POHS**	**POAcS**	**PS**	**Sum**
220°C - 2h	93.3%	18.6%	1.5%	0.7%	20.8%
220°C - 1h	80.6%	13.4%	0.7%	0.6%	14.7%
200°C - 2h	70.1%	10.7%	0.5%	0.5%	11.7%

Table S20 Tabulated data of Fig. 9c in the main text.

CAPEX (M€)							
Case	**Reactor**	**Distillation**	**HEN-Network**	**CHP**	**WC**	**Other**	**TOTAL**
220°C - 2h	86.5	3.3	15.4	8.1	6.4	4.0	123.7
220°C - 1h	50.3	2.8	15.9	7.1	5.5	4.0	85.6
200°C - 2h	60.3	2.6	13.2	6.9	5.6	4.0	92.7

Table S21 Tabulated data of Fig. 9d in the main text.

OPEX (M€.y^{-1})											
Case	**Wood**	**MeOH**	**H_2**	**Pd/C**	**EtOAc**	**H_2O**	**Fuel (H_2)**	**Steam**	**Electricity**	**Fixed Costs**	**TOTAL**
220°C - 2h	24.2	1.2	0.1	2.5	3.9	0.2	6.0	0.0	0.4	11.0	49.7
220°C - 1h	24.2	1.1	0.2	2.5	3.1	0.2	4.9	0.0	0.3	8.8	45.4
200°C - 2h	24.2	1.5	0.2	2.5	3.0	0.2	4.4	0.0	0.2	9.2	45.4

Table S22 Tabulated data of Fig. 9e in the main text.

GWP-RLO (kgCO_2.kgRLO^{-1})										
Case	**Wood**	**MeOH**	**H_2 (RCF)**	**Pd/C**	**EtOAc**	**CO_2**	**Fuel (H_2)**	**Steam**	**Electricity**	**TOTAL**
220°C - 2h	0.41	0.04	0.0158	0.0032	0.07	0.10	0.93	0.00	0.0358	1.60
220°C - 1h	0.43	0.04	0.0326	0.0032	0.06	0.11	0.79	0.00	0.0289	1.48
200°C - 2h	0.44	0.05	0.0340	0.0032	0.06	0.13	0.73	0.00	0.0205	1.47

Table S23 Tabulated data of Fig. 9e in the main text.

MSP-RLO (€.t^{-1})	
Case	**MSP**
220°C - 2h	1089
220°C - 1h	783
200°C - 2h	875

Table S24 Tabulated data of Fig. 10a in the main text.

Pulp Composition (wt%)				
	Hemicellulose	**Cellulose**	**Acetyl**	**Lignin**
Spruce	22.5%	43.9%	1.4%	27.1%
MeOH	18.4%	44.3%	1.2%	16.5%
80% recycle	15.5%	45.7%	1.3%	11.6%

Table S25 Tabulated data of Fig. 10b in the main text.

RLO composition										
	Delignification	**POMeG**	**PS**	**PG**	**POHS**	**POHG**	**POAcS**	**POAcG**	**Oligomers**	**Monomers**
Spruce RLO	\	1.3%	0.0%	1.7%	0.0%	27.5%	0.0%	0.0%	69.5%	30.5%
MeOH	39.0%	1.1%	0.0%	1.0%	0.0%	31.0%	0.0%	0.0%	66.4%	33.6%
80% recycle	57.1%	1.0%	0.0%	1.6%	0.0%	25.6%	0.0%	0.6%	71.2%	28.8%

Table S26 Tabulated data of Fig. 11a in the main text.

Solvent Composition						
Case	**MeOH (v%)**	**MeOAc (v%)**	**H2O (v%)**	**HOAc (v%)**	**CLO (v%)**	**Vol. Flow (m^3.h^{-1})**
Birch	60.3	20.6	8.7	1.0	9.4	200.9
Spruce	74.7	11.7	7.7	0.4	5.4	202.8

Table S27 Tabulated data of Fig. 11b in the main text.

MSP-RLO (€.t^{-1})	
Case	**MSP**
Birch	1089
Spruce	1228

Table S28 Tabulated data of Fig. 11b in the main text.

GWP-RLO (kgCO_2.kgRLO^{-1})										
Case	**Wood**	**MeOH**	**H_2 (RCF)**	**Pd/C**	**EtOAc**	**CO_2**	**Fuel (H_2)**	**Steam**	**Electricity**	**TOTAL**
Birch	0.41	0.04	0.0158	0.0032	0.07	0.10	0.93	0.00	0.0358	1.60
Spruce	0.45	0.02	0.0174	0.0032	0.05	0.09	1.20	0.00	0.0578	1.88

Table S29 Tabulated data of Fig. 12a in the main text.

Pulp Composition (wt%)				
Case	**Hemicellulose**	**Cellulose**	**Acetyl**	**Lignin**
Birch	25.6%	40.1%	4.3%	25.1%
MeOH	22.5%	40.8%	0.8%	9.3%
15% MC	13.9%	38.2%	1.0%	1.7%
30% MC	8.4%	40.4%	1.2%	1.2%

Table S30 Tabulated data of Fig. 12b in the main text.

Monomer yield of syringyl-type monomers vs. protolignin and delignification					
Case	**Delignification**	**POHS**	**POAcS**	**PS**	**Sum**
MeOH	62.9%	18.1%	0.0%	0.8%	18.9%
15% MC	93.3%	18.6%	1.5%	0.7%	20.8%
30% MC	95.1%	14.7%	0.7%	0.9%	16.3%

Table S31 Tabulated data of Fig. 13a in the main text.

Solvent Composition						
Case	**MeOH (v%)**	**MeOAc (v%)**	**H2O (v%)**	**HOAc (v%)**	**CLO (v%)**	**Vol. Flow (m^3.h^{-1})**
15% MC	60.3	20.6	8.7	1.0	9.4	200.9
30% MC	62.3	7.8	19.7	0.8	9.3	195.3

Table S32 Tabulated data of Fig. 13b in the main text.

Case	**Wood**	**MeOH**	**H_2 (RCF)**	**Pd/C**	**EtOAc**	**CO_2**	**Fuel (H_2)**	**Steam**	**Electricity**	**TOTAL**
15% MC	0.41	0.04	0.0158	0.0032	0.07	0.10	0.93	0.00	0.0358	1.60
30% MC	0.40	0.05	0.0459	0.0032	0.10	0.09	1.13	0.00	0.0572	1.88

Table S33 Tabulated data of Fig. 13b in the main text.

MSP-RLO (€.t^{-1})	
Case	**MSP**
15% MC	1089
30% MC	1113

References

1 C. Gourson, R. Benhaddou, R. Granet, P. Krausz, B. Verneuil, P. Branland, G. Chauvelon, J. F. Thibault and L. Saulnier, *J. Appl. Polym. Sci.*, 1999, **74**, 3040–3045.

2 J. Snelders, E. Dornez, B. Benjelloun-Mlayah, W. J. J. Huijgen, P. J. de Wild, R. J. A. Gosselink, J. Gerritsma and C. M. Courtin, *Bioresour. Technol.*, 2014, **156**, 275–282.

3 H. N. Englyst and J. H. Cummings, *Analyst*, 1984, **109**, 937–942.

4 C. W. Dence and S. Y. Lin, in *Methods in Lignin Chemistry*, Springer, 1992, pp. 33–58.

5 A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton and D. Crocker, *Determination of structural carbohydrates and lignin in Biomass*, 2012.

6 A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter and D. Templeton, *Determiniation of Ash*, 2008.

7 S. Steven, European pulp prices: BEK moved up again while NBSK spread widened in July, https://www.fastmarkets.com/insights/european-pulp-prices-continue-to-rise-in-july-2022.

8 R. Sinnott and G. Towler, in *Chemical Engineering Design*, Elsevier, 5th edn., 2009, pp. 291–388.

9 Y. Liao, S.-F. Koelewijn, G. Van den Bossche, J. Van Aelst, S. Van den Bosch, T. Renders, K. Navare, T. Nicolaï, K. Van Aelst, M. Maesen, H. Matsushima, J. M. Thevelein, K. van Acker, B. Lagrain, D. Verboekend and B. F. Sels, *Science*, 2020, **367**, 1385–1390.

10 M. Condon, *ICIS Chem. Bus.*, 2019, **1-7 Feb.**, 19.

11 Anonymous, *ICIS Chem. Bus.*, 2020, **9-15 Oct.**, 15.

12 F. J. London, *ICIS Chem. Bus.*, 2020, **14-20 Aug.**, 32.

13 M. Tschulkow, T. Compernolle, S. Van den Bosch, J. Van Aelst, I. Storms, M. Van Dael, G. Van den Bossche, B. Sels and S. Van Passel, *J. Clean. Prod.*, 2020, **266**, 1–11.

14 echemi.com, Ethyl acetate Market Price & Analysis, https://www.echemi.com/productsInformation/pid_Seven5613-ethyl-acetate.html.

15 Coininvest.com, Palladium Price Charts Kilogram, https://www.coininvest.com/en/charts/palladium-price/kilogram/.

16 Eurostat, Electricity price statistics, https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Electricity_price_statistics#Electricity_prices_for_non-household_consumers.

17 L. Milner, Chemical Profile: Europe Bisphenol A, https://www.icis.com/explore/resources/news/2017/02/02/10075664/chemical-profile-europe-bisphenol-a/, (accessed 15 April 2021).

18 E. Cetinkaya, I. Dincer and G. F. Naterer, *Int. J. Hydrogen Energy*, 2012, **37**, 2071–2080.

19 P. Nuss and M. J. Eckelman, *PLoS One*, , DOI:10.1371/journal.pone.0101298.