Electronic Supporting Information

Conversion of birch bark to biofuel

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1. Analysis of the bark feedstock

The bark of birch (*Betula Pendula*) was provided by Däcksta Såg, Gimo, Sweden.

1.1. Extractives & moisture

A sample of bark was extracted with EtOH in Soxhlet extractor for 12 h and then dried in air at 50 °C for 12 h. Weight loss: 29% of bark weight. Mass of the EtOH-solubilized material: 26% of bark weight.

1.2. Suberin

Extractive-free bark sample (0.347 g) was treated with 3% MeONa solution in MeOH (25 mL) under reflux for 2 h. The solution was centrifugated and the residue was washed with MeOH and water. Centrifugation and washing were repeated until the pH became neutral. Solid residue was dried (0.131 g, 38% of extractive-free bark, 27% of total). Solution was acidified to pH 3 with H_2SO_4 and extracted with DCM (3 x 10 mL). The organic fraction was dried, filtered and concentrated to afford suberin oil (0.160 g, 46% of extractive-free bark, 33% of total).

1.3. Lignin

The solid residue which remained after alkaline methanolysis (extractive-free desuberized bark) was dried in air at 70 °C for 12 h. A sample (91 mg) was treated with 72% aqueous H_2SO_4 (1 mL) at 30 °C for 1 h. Then the mixture was diluted with water (30 mL) and refluxed for 3 h. After cooling to rt, the mixture was filtered through paper filter. The filter was washed with water until a neutral pH was reached, and the residue was dried in air at 70 °C for 12 h to afford acid-insoluble lignin (51 mg, 21% of extractive-free bark, 15% of total).

1.4. Lignin S/G ratio

A sample of untreated bark (50 mg) was placed into a stainless steel reactor together with 3% aqueous KOH (3 mL) and nitrobenzene (0.1 mL). The reactor was heated with stirring at 170°C for 1 h. After cooling, the mixture was acidified with HCl to pH 1 and extracted with DCM (3x5 mL). Combined organic fraction was dried with Na_2SO_4, diluted with Et_2O and subjected to GC-MS. GC measurements were performed on a Shimadzu Shimadzu GC-MS-QP2020 equipped with a HP-5 MS capillary column (30 m × 0.25 mm × 0.25 μm) and an MS detector. Syringol and guaiacol units were detected as syringaldehyde and vanillin. Though the reproducibility of the method is low, syringol to guaiacol ratio was determined to be 2.2–2.7 based on three runs.

1.5. Carbohydrates

Analysis for carbohydrates was carried out according to previously published procedure.[1] No carbohydrates were detected.

Table S1. Composition of birch bark feedstock

Moisture	3%
EtOH extractives	26%

Suberin, hydrophilic monomers	11%
Suberin, hydrophobic monomers	33%
Klason lignin	15%
Balance	*88%*

1.6. Elemental analysis

The direct elemental analysis by combustion was performed by Analytische Laboratorien Prof. Dr. H. Malissa und G. Reuter GmbH, Industriepark Kaiserau (Haus Heidbruch), Lindlar, Germany, and in Sunbury Technology Centre, Sunbury-on-Thames, Middlesex, UK.

C, 70.1% // H, 9.2% // N, 0.3% // O, 19.5%

2. Solubilization of bark (stage 1)

2.1. Experimental procedure

In a typical experiment Grinded birch bark (~1 mm particle size, 0.30 g) was placed into a stainless steel reactor (internal volume 7 mL) together with a mixture of triethylamine (0.15–0.35 mL), methanol (1.0–2.3 mL) and water (1.0–2.3 mL; total volume 7–15 mL per g of bark feedstock) and magnetic stirring bar. The reactor was heated at 220°C in oil bath for 2 hours with 800 rpm stirring. After cooling, the mixture was filtered through paper filter. The solid residue was dried at 60°C for 12 hours and weighted (0.02 g, 6% of initial bark weight). The filtrate was distilled to recover the solvent. The residual brown gum was dried in air at 60°C or 130°C for 12 hours (0.28 g, 94% of initial bark weight) and subjected to analyses.

Solvent recycling by distillation was performed as follows. A set of 10 reaction mixtures was combined to obtain a 50-70 mL total volume. The mixture was distilled in a simple distillation apparatus with a reflux condenser while cooling the receiving flask with ice. The obtained solvent was weighted, analyzed (see paper text, Table 1) and used for the next reaction.

2.2. Optimization

The procedure was optimized with regard to minimization of weight of the solid residue. Each experiment was repeated at least twice to address possible issues of samples' heterogenity. For graphical representation of the results, see the paper text, Figure 2.

Table S2. Bark solubilization in MeOH–H_2O–Et_3N

#	Solvent (MeOH–H_2O–Et_3N) v/v	Solvent volume, mL (mL per g of bark)	T°C	Time, h	Bark, g	% solubilized (of wax-free bark)	Deviation, % (+/–)
1	46 : 47 : 7	4.5 (15)	200	0.3	0.30	34	4
2	46 : 47 : 7	4.5 (15)	200	0.5	0.30	38	5
3	46 : 47 : 7	4.5 (15)	200	1.0	0.30	54	3

4	46 : 47 : 7	4.5 (15)	200	2.0	0.30	58	9
5	46 : 47 : 7	4.5 (15)	200	3.0	0.30	77	0
6	46 : 47 : 7	4.5 (15)	160	0.5	0.30	13	0
7	46 : 47 : 7	4.5 (15)	180	1.0	0.30	45	0
8	46 : 47 : 7	4.5 (15)	220	1.0	0.30	79	1
9	46 : 47 : 7	4.5 (15)	220	2.0	0.30	91	1
10	48 : 48 : 4	4.5 (15)	220	2.0	0.30	69	1
11	50 : 50 : 0	4.5 (15)	220	2.0	0.30	27	1
12	44 : 44 : 12	4.5 (15)	220	2.0	0.30	73	2
13	62 : 31 : 7	4.5 (15)	220	2.0	0.30	72	1
14	31 : 62 : 7	4.5 (15)	220	2.0	0.30	93	0
15	0 : 93 : 7	4.5 (15)	220	2.0	0.30	89	3
16	93 : 0 : 7	4.5 (15)	220	2.0	0.30	70	1
17	46 : 47 : 7	4.5 (7.5)	220	2.0	0.60	90	2
18	46 : 47 : 7	4.5 (10)	220	2.0	0.45	91	4

2.2. NMR spectroscopy

0.1 g of the gum was suspended in 0.6 mL of $CDCl_3$ at 60°C, the mixture was cooled to room temperature without filtration and subjected to NMR analysis. The spectra were recorded with a Bruker 400 (400 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CHCl_3$ (δ = 7.26 ppm) as an internal standard. ^{13}C NMR spectra were recorded as solutions in $CDCl_3$ with complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CDCl_3$ (δ = 77.0 ppm) as an internal standard. 2D-NMR spectra were acquired on an Agilent 400-MR spectrometer. The standard Agilent implementations of gHSQCAD experiments were used. For assignment, please see the paper text, Figure 3, A.

2.3. Size exclusion chromatography

SEC was performed using a YL 9110 HPLC-GPC system (YL Instrument Co., Ltd., Dongan-gu, Anyang-si, Kyounggi-do, 431-836, The Republic of Korea) with three Styragel columns (HR 0.5, HR 1, and HR 3, 7.8×300 mm each) connected in series (flow rate: 1 mL·min^{-1}; injection volume: 50 µL; THF), a UV detector (254 nm), and an auto-sampler. The system was calibrated using ReadyCal-Kit poly(styrene) (M_P 266, 682, 1250, 2280, 3470, 4920, 9130, 15700, 21500, 28000, 44200, 66000 Da). Samples were dissolved in THF to concentration 0.5 g·L^{-1}.

The detected oligomers possess the following properties:

- Molecular weight of the most abundant species M_P = 1584 Da
- Number average molecular weight M_N = 932 Da
- Weight average molecular weight M_W = 2630 Da
- Polydispersity index PD = M_W/M_N = 2.82

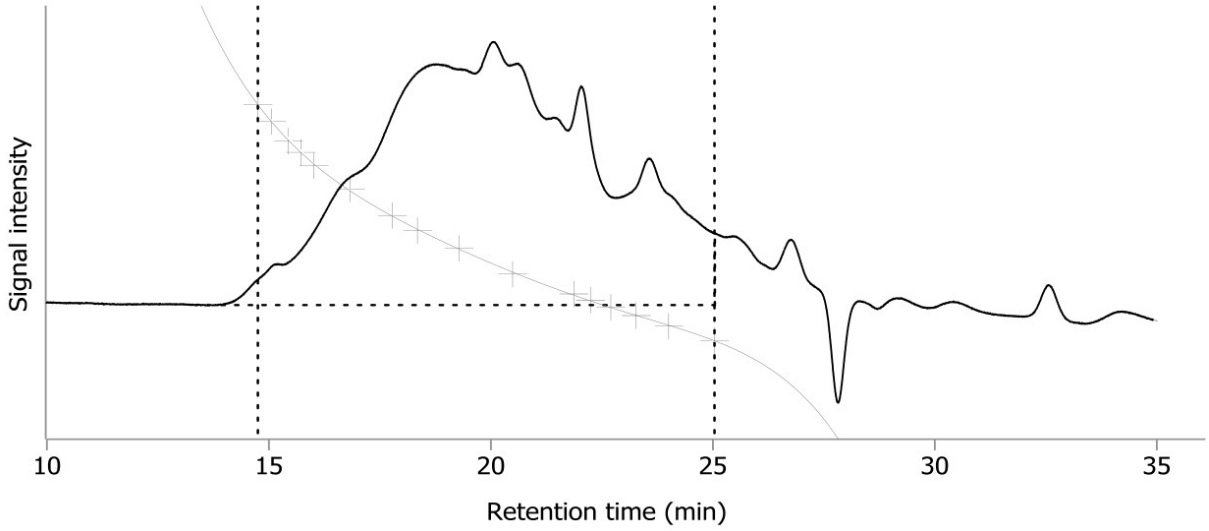

Figure S1. SEC of the bark-derived gum (in THF)

2.4. Elemental analysis

Gum dried at 60°C in air: C, 66.7% // H, 10.2% // N, 2.1% // O, 21.4%
Gum dried at 130°C in air: C, 71.4% // H, 9.9% // N, 1.1% // O, 17.2%

2.5. Tests for solubility of the gum

Solubility of the gum in various organic solvents was measured as follows. The gum (0.05 g) was treated with a solvent (1 mL) at 60–70°C for 30 min, the solution was cooled 20°C and filtered through a 0.2 μm syringe filter. Mass of the filtrate was measured. Then the filtrate was concentrated in vacuum and the residue dried in air at 60°C for 12 hours. Mass of the residue was measured.

Table S3. Solubility of the bark gum in various solvents (ca. 0.05 g in 1 mL)

Solvent	*Gum dissolved, wt%*	*Concentration of the solution, g·L^{-1}*
Hexane	0	0
Toluene	28	16
Ethyl acetate	65	33
Methanol	87	48

2.6. Suspension of the gum in tall oil

Tall oil is a naturally occuring liquid mixture of fatty acids and rosins which has been demonstated to be useful carrier liquid for hydrotreatment of biomass derivatives.[2] For this purpose, viscosity of the mixture is crucial. The gum forms a suspension in tall oil fatty acids

mixture (TOFA) at 120°C which remains practically stable at room temperature (illustration, Figure S11). Viscosity of the suspension was measured with Anton Paar Rheolab QC rotational rheometer with a CC10 sensor (stirring rates 50 to 1400 s^{-1}).

Table S4. Viscosity of the gum suspension in TOFA at different temperatures and concentrations (mPa·s)

	25°C	*50°C*	*70°C*
7 wt.%	13	<10	<10
16 wt.%	120	35	<10
33 wt.%	500	125	44

2.7. 1D GC-MS of the gum methanolysate

1D GC was used for analysis of monomeric composition of the gum. A sample of the gum (0.1 g) was refluxed with 3% KOH/MeOH (5 mL) for 1 h. The mixture was acidified with HCl, diltued with water and extracted with $CHCl_3$ (3 x 10 mL). Combined organic phases were dried with Na_2SO_4, filtered and concentrated. A sample of the residue (10–20 mg) was dissolved in THF (1 mL) and silylated with bis(trimethylsilyl)acetamide (50 µL) in the presence of pyridine (50 µL). The solution was subjected to GC. GC measurements were performed on a Shimadzu Shimadzu GC-MS-QP2020 equipped with a HP-5 MS capillary column (30 m × 0.25 mm × 0.25 µm) and an MS detector. Compounds were identified by comparing the observed fragmentation patterns to literature data.[3,4] (See paper text, Figure 3, B.) MS spectra of each identified derivative are given below.

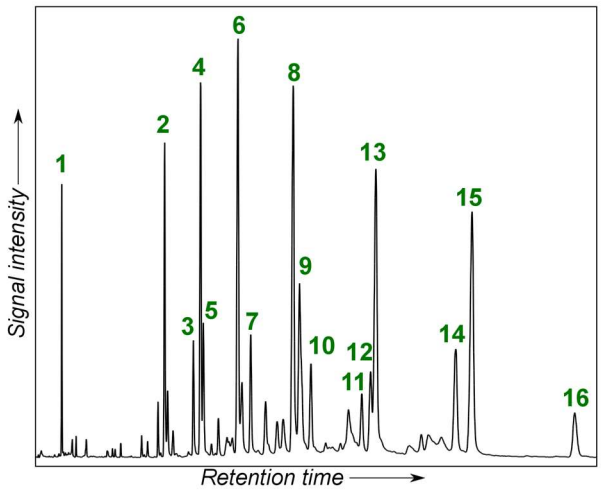

Figure S2. GC of the gum methanolysate.

Table S5. Mass spectra of silylated bark monomers

#	*Name*	*Retention time, min*	*m/z*
1	Ferullic acid, Me ester, TMS ether	11.40	280, 265, 250, 219, 192
2	18-hydroxyoctadec-9-enoic acid, Me ester, TMS ether	14.28	384, 369, 353, 337, 262, 220, 213, 159, 135, 123, 109, 101
3	1,18-octadec-9-enedioic acid, Me ester, TMS ether	15.08	383, 366, 308, 276, 248, 194, 151, 129, 109
4	18-hydroxyoctadec-9-enoic acid, TMS ester, TMS ether	15.28	444, 427, 411, 399, 352, 337, 271, 262, 243, 217, 199, 147, 129, 117, 103
5	1,18-octadecanedioic acid, Me ester, TMS ester	15.36	489, 399, 385, 369, 331, 317, 303, 275, 241, 217, 204, 185, 159, 147, 129, 117, 103
6	1,18-octadec-9-enedioic acid, di TMS ester	16.32	441, 397, 385, 353, 335, 323, 276, 243, 229, 213, 199, 171, 153, 129, 109, 103
7	20-hydroxyeicosanoic acid, Me ester, TMS ether	16.69	401, 399, 367, 146, 129, 103
8	1,18-octadecanedioic acid, di TMS ester	17.88	455, 443, 427, 335, 317, 301, 279, 261, 243, 217, 185, 153, 147, 129, 109
9	1,20-eicosanedioic acid, Me ester TMS ester	18.06	443, 413, 397, 369, 363, 335, 325, 288, 279, 261, 243, 215, 201, 168, 149, 129, 117, 107
10	20-hydroxyeicosanoic acid, TMS ester, TMS ether	18.37	457, 441, 382, 382, 367, 325, 293, 231, 218, 147, 103
11	1,22-docosanedioic acid, di Me ester	19.80	385, 367, 334, 325, 306, 293, 275, 252, 237, 224, 210, 185, 172, 154, 140, 135, 112, 101
12	9,10-dihydroxyoctadecane-1,18-dioic acid, Me ester TMS ester	20.05	390, 317, 303,217, 147, 129, 109
13	22-hydroxydocosanoic acid, Me ester, TMS ether	20.19	427, 395, 146, 103
14	1,22-docosanedioic acid, Me ester TMS ester	22.42	441, 391, 353, 159, 117
15	22-hydroxydocosanoic acid, TMS ester, TMS ether	22.88	485, 469, 395, 147, 117
16	1,22-docosanedioic acid, di TMS ester	25.77	499, 455, 423, 383, 367, 327, 293, 217, 170, 129, 109

3. Hydrodeoxygenation of the gum (stage 2)

3.1. Preparation of the catalyst

$Pt(NH_3)_4(NO_3)_2$, TiO_2 (mixture of rutile and anatase) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were purchased from Sigma Aldrich. The catalyst was prepared according to a modified reported procedure.[5] TiO_2 (2.00 g) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.30 g, 1.7 mmol or 0.16 g Mo) were mixed in water (20 mL) in a round-bottomed flask and the mixture was stirred vigorously for 1 h. Water was evaporated in vacuum at 50 °C, residue was dried (100 °C, 12 h) and calcinated (500 °C, 3 h). The solid was mixed with $Pt(NH_3)_4(NO_3)_2$ (0.21 g, 0.6 mmol or 0.12 g Pt) in water (20 mL) in a round-bottomed flask and the mixture was stirred vigorously for 1 h. Water was evaporated in vacuum at 50 °C, residue was dried (100 °C, 12 h) and calcinated (300 °C, 2 h). The catalyst $Pt/MoO_3/TiO_2$ was obtained as black powder (2.16 g) and used for hydrotreatment reaction without preliminary reduction.

3.2. Hydrotreatment

The gum obtained by bark solubilization (1.0 g) was placed in a stainless steel reactor (internal volume 7 mL) together with the catalyst $Pt/MoO_3/TiO_2$ (0.05 g; 0.3 wt.% Pt). Hydrogen pressure 50 bar was applied or, alternatively, formic acid (1.0 mL) was added as hydrogen source. The reactor was heated to 360–370°C in a heating block for 2 h. After cooling to 0°C, contents of the reactor were dissolved in diethyl ether and the solution was filtered through a plug of sodium sulfate. Solvent was removed at 200 mbar and 0–20°C. The residue was distilled in Kugelrohr (20–200°C, 1 mbar), with the receiving flask being cooled with acetone and dry ice. The obtained hydrocarbon bio-oil (0.5 g, 50% of initial bark weight) was subjected to 2D GC and simulated distillation analyses.

3.3. Simulated distillation

2D GC (method UOP 990) and simulated distillation (method IP480) were performed in Sunbury Technology Centre, Sunbury-on-Thames, Middlesex TW16 7EE, UK.

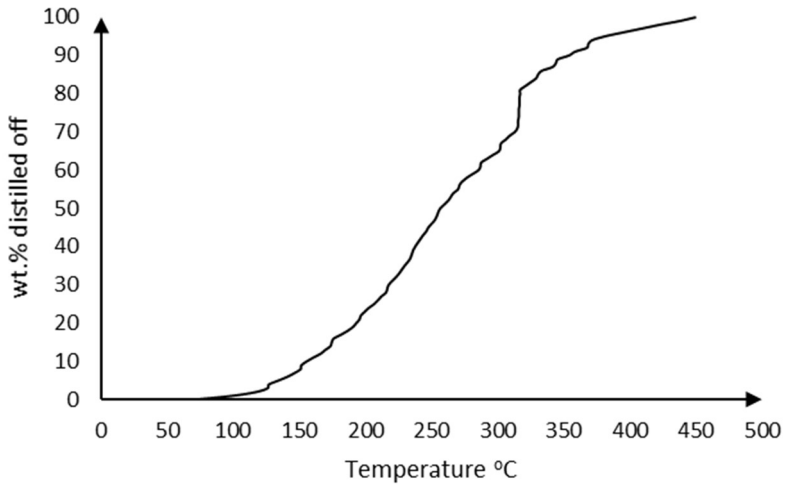

Figure S3. Simulated distillation of the bio-oil

Table S6. Simulated distillation of the bio-oil

T°C	*wt.% distilled off*	*T°C*	*wt.% distilled off*	*T°C*	*wt.% distilled off*	*T°C*	*wt.% distilled off*
69.5	0	209.5	26	262.5	52	316.5	78
98.5	1	212	27	264.5	53	316.5	79
117	2	215.5	28	266.5	54	317	80
126	3	216.5	29	270	55	317	81
127	4	217.5	30	271	56	321	82
134	5	220	31	273	57	325	83
141	6	223	32	276.5	58	329	84
146.5	7	225.5	33	281	59	330.5	85
151	8	227.5	34	285.5	60	333.5	86
151.5	9	229.5	35	287	61	341.5	87
155.5	10	232	36	287.5	62	344	88
160.5	11	234	37	292	63	345.5	89
166	12	235	38	296.5	64	354	90
169.5	13	236	39	301	65	358.5	91
173.5	14	237.5	40	302	66	367.5	92
174.5	15	239.5	41	302.5	67	368.5	93
176	16	241.5	42	306	68	371.5	94
181.5	17	243.5	43	309	69	381	95
186.5	18	246	44	313	70	394.5	96
190.5	19	247.5	45	315	71	408.5	97
193	20	250	46	315.5	72	422	98
195.5	21	252.5	47	315.5	73	437.5	99
196.5	22	254	48	316	74	450	100
199.5	23	255	49	316	75		
202.5	24	256.5	50	316	76		
206.5	25	259.5	51	316.5	77		

3.4. 2D GC

Table S7. 2D GC of the bio-oil

Name of the component	*wt.%*
n-hexane	0
n-heptane	0
n-octane	0
n-nonane	0.01
n-decane	0.04
n-undecane	0.11
n-dodecane	0.29
n-tridecane	0.51
n-tetradecane	1.18
n-pentadecane	2.19
n-hexadecane	2.71
n-heptadecane	2.75
n-octadecane	2.64
n-nonadecane	2.17
n-eicosane	1.96
n-heneicosane	1.47
n-docosane	1.19
n-tricosane	1.07
n-tetracosane	0.9
n-pentacosane	1.13
n-hexacosane	0.97
n-heptacosane	0.73
isoparaffins eluting between nC5 and nC6	0
isoparaffins eluting between nC6 and nC7	0
isoparaffins eluting between nC7 and nC8	0
isoparaffins eluting between nC8 and nC9	0
isoparaffins eluting between nC9 and nC10	0.05
isoparaffins eluting between nC10 and nC11	0.12
isoparaffins eluting between nC11 and nC12	0.13
isoparaffins eluting between nC12 and nC13	0.52
isoparaffins eluting between nC13 and nC14	0.96
isoparaffins eluting between nC14 and nC15	1.81
isoparaffins eluting between nC15 and nC16	1.87
isoparaffins eluting between nC16 and nC17	2.52
isoparaffins eluting between nC17 and nC18	3.44
isoparaffins eluting between nC18 and nC19	2.92
isoparaffins eluting between nC19 and nC20	1.74

isoparaffins eluting between nC20 and nC21	1.75
isoparaffins eluting between nC21 and nC22	1.21
isoparaffins eluting between nC22 and nC23	1.35
isoparaffins eluting between nC23 and nC24	1.38
isoparaffins eluting between nC24 and nC25	1
isoparaffins eluting between nC25 and nC26	0.74
isoparaffins eluting between nC26 and nC27	0.16
naphthenes and olefins eluting between nC6 and nC7	0
naphthenes and olefins eluting between nC7 and nC8	0
naphthenes and olefins eluting between nC8 and nC9	0
naphthenes and olefins eluting between nC9 and nC10	0.03
naphthenes and olefins eluting between nC10 and nC11	0.17
naphthenes and olefins eluting between nC11 and nC12	0.48
naphthenes and olefins eluting between nC12 and nC13	1.07
naphthenes and olefins eluting between nC13 and nC14	1.94
naphthenes and olefins eluting between nC14 and nC15	3.08
naphthenes and olefins eluting between nC15 and nC16	2.97
naphthenes and olefins eluting between nC16 and nC17	3.39
naphthenes and olefins eluting between nC17 and nC18	2.61
naphthenes and olefins eluting between nC18 and nC19	2.25
naphthenes and olefins eluting between nC19 and nC20	1.9
naphthenes and olefins eluting between nC20 and nC21	1.37
naphthenes and olefins eluting between nC21 and nC22	1.46
naphthenes and olefins eluting between nC22 and nC23	0.8
naphthenes and olefins eluting between nC23 and nC24	0.75
naphthenes and olefins eluting between nC24 and nC25	0.73
naphthenes and olefins eluting between nC25 and nC26	0
naphthenes and olefins eluting between nC26 and nC27	0
naphthenes and olefins eluting between nC27 and nC28	0
benzene	0
toluene	0
C2-alkylbenzenes	0
C3-alkylbenzenes	0.04
C4-alkylbenzenes	0.12
C5-alkylbenzenes	0.14
C6-alkylbenzenes	0.2
C7-alkylbenzenes	0.29
C8-alkylbenzenes	0.69
C9-alkylbenzenes	1
C10-alkylbenzenes	0.97
C11-alkylbenzenes	0.9
C12-alkylbenzenes	0.89

C13-alkylbenzenes	1.02
C14-alkylbenzenes	0.9
C15-alkylbenzenes	0.34
C16 and higher alkylbenzenes	0.2
indane	0.01
C1-indans	0.01
tetralin	0.01
C2-indans and C1-tetralins	0.09
C3-indans and C2-tetralins	0.24
C4-indans and C3-tetralins	0.51
C5-indans and C4-tetralins	1.19
other naphthenic substituted monoaromatics	5.1
indene	0
C1-indenes	0
C2-indenes	0
C3-indenes	0.01
naphthalene	0.04
C1-naphthalenes	0.37
C2-naphthalenes	1.12
C3-naphthalenes	1.44
C4-naphthalenes	1.21
C5-naphthalenes	0.93
C6-naphthalenes	0.67
C7 and higher naphthalenes	0.49
benzothiophene	0
C1-benzothiophenes	0
biphenyl	0.04
C1-biphenyls	0.14
acenaphthene	0
dibenzofuran	0.02
C1-dibenzofurans	0.1
fluorene	0.06
C1-fluorenes	0.2
dibenzothiophene	0.06
C1-dibenzothiophenes	0.08
C2-dibenzothiophenes	0.09
other diaromatics ?	3.6
anthracene and phenanthrene	0.14
C1-triaromatics	0.33
C2-triaromatics	0.41
C3-triaromatics	0.53
C4-triaromatics	0.32

C5 and higher triaromatics	0
fluoranthene	0
pyrene	0.02
C1-4ring aromatics	0
C2-4ring aromatics	0
C3 and higher 4ring aromatics	0

3.5. Estimation of average molecular formula and the heating value

The average molecular formula of the obtained oil was calculated from 2D GC data (section 3.4). The following formulas were used for the calculation:

$$x_i = \frac{\sum_A n_i(A)\nu(A)}{\sum_A \nu(A)} \quad \text{(Eq. S1)}$$

$$\omega_i = \frac{\sum_A n_i(A)\nu(A)M_i}{\sum_A \nu(A)M(A)} \quad \text{(Eq. S2)}$$

where x_i and ω_i are molar and mass fractions of element i in the bio-oil, $n_i(A)$ is the number of atoms of element i in the component A of the bio-oil, $\nu(A)$ is molar content of A in the bio-oil, M_i is molar weight of element i, $M(A)$ is molar weight of A.

The fraciton of the oil detected as unknown diaromatics by GC is 3.6 wt.%. Composition of this fraction was approximated as $C_{10}H_8$ (naphtalene) to $C_{12}H_8O$ (dibenzofuran).

The resulting molecular formula of the oil is $C_{16.24\ldots16.45}H_{29.26\ldots29.52}O_{0.00\ldots0.07}$.

Elemental composition by weight, C, 86.57…86.93%; H, 12.95…13.05%; O, 0.01…0.48%.

Heat of combustion (the higher heating value, HHV) of the bio-oil was estimated with according to the formula[6]: $\mathrm{HHV} = a_C\omega_C + a_H\omega_H + a_O\omega_O$ (Eq. S3) with various increments. The values of a_i increments and the HHV values are given in the table S8.

Table S8. Estimated HHV

Name of the formula	a_C	a_H	a_O	**HHV**
	(MJ·kg^{-1})			
Dulong	33.83	144.28	–14.05	**47.9…48.2**
Boie	35.17	116.25	–11.10	**45.4…45.7**
Mott, Spooner	33.62	141.93	–14.53	**47.4…47.8**

4. Estimation of energy demand

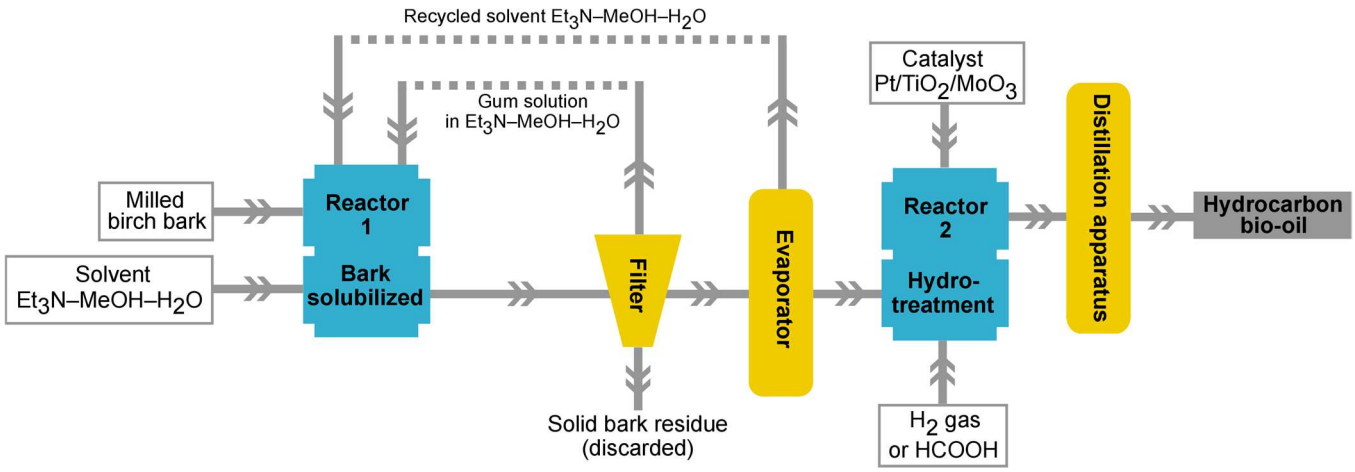

Figure S4. Technological scheme of the process

First, a general equation for the energy demand of the process is derived. Then it is applied to certain numerical values. List of the variables is given below in the Table S9.

Table S9. Variables and parameters used for the estimation of energy demand

Symbol	*Meaning*	*Value*	*Units*	*Estimation method*
V	volume of the solvent per kg of bark feedstock (stage 1)	8–10	L·kg^{-1}	experiment
Y	yield of the bio-fuel per kg of bark feedstock (stage 2), $0 < Y < 1$	0.4	dimensionless	experiment
Q_1	vaporization heat of the solvent (stage 1)	1.48	MJ · L^{-1}	calculated additively
Q_2	vaporization heat of the bio-fuel (stage 2)	0.31	MJ · kg^{-1}	vaporization enthalpy of hexadexane
C_1	heat capacity of the solvent (stage 1)	2.86 · 10^{-3}	MJ · K^{-1} · L^{-1}	calculated additively
C_2	heat capacity of the bio-fuel (stage 2)	2.21 · 10^{-3}	MJ · K^{-1} · kg^{-1}	heat capacity of hexadecane
T_{b1}	boiling point of the solvent (stage 1)	< 358	K	calculated through Raoult law as the temperature at which the vapor reaches saturation
T_{b2}	boiling pouint of the bio-fuel (stage 2)	< 553	K	calculated from Simdis and 2D GC data
C_r	heat capacity of the reactor material	5 · 10^{-4}	MJ · K^{-1} · kg^{-1}	heat capacity of stainless steel
m	mass of the reactor divided by the bark mass	see *Estimation method*	dimensionless	$m \approx \frac{4.17\rho_R}{x} \cdot \left((0.24x/\rho)^{1/3} + \Delta r\right)^3 - \frac{\rho_R}{\rho}$ x [kg] is loading of the bark feedstock $\rho_R = 8 \cdot 10^3$ [kg · m^{-3}] is density of stainless steel $\Delta r = 0.01 \ldots 0.05$ [m] is thickness of the reactor wall $\rho = 150$ [kg · m^{-3}] is density of bark packing in the reactor
S	surface area of the reactor divided by the bark mass	see *Estimation method*	m^2 · kg^{-1}	$S \approx \frac{12.56}{x} \cdot \left((0.24x/\rho)^{1/3} + \Delta r\right)^2$ x [kg] is loading of the bark feedstock $\Delta r = 0.01 \ldots 0.05$ [m] is thickness of the reactor wall $\rho = 150$ [kg · m^{-3}] is the density of bark packing in the reactor

w	coefficient of heat transfer between the reactor and air	10^{-3}	MJ · m^{-2} · K^{-1} · min^{-1}	coefficient of heat transfer between the stainless steel and air
t_1	reaction time (stage 1)	120	min	experiment
t_2	reaction time (stage 2)	120	min	experiment
T_{r1}	reaction temperature (stage 1)	493	K	experiment
T_{r2}	reaction temperature (stage 2)	643	K	experiment
n_C	number of reaction cycles proceeding without cooling down the system	1–20	dimensionless	different values are considered, see Table S10
n_S	number of reaction cycles proceeding without evaporation or replacing the solvent	1–3	dimensionless	different values are considered, see Table S10
D_1	energy required for distillation of the solvent (stage 1)	(to be calculated)	MJ per kg of the bio-fuel	
D_2	energy required for distillation of the bio-fuel (stage 2)	(to be calculated)	MJ per kg of the bio-fuel	
H_1	energy required for heating of the reactor (stage 1)	(to be calculated)	MJ per kg of the bio-fuel	
H_2	energy required for heating of the reactor (stage 2)	(to be calculated)	MJ per kg of the bio-fuel	

$$\text{Energy [MJ per kg of the biofuel]} = H_1 + D_1 + H_2 + D_2 \qquad \text{(eqn. S3)}$$

$$D_1 = (Q_1 + C_1 \cdot (T_{d1} - 293)) \cdot V/(Y \cdot n_S) \qquad \text{(eqn. S4)}$$

$$D_2 = Q_2 + C_2 \cdot (T_{d2} - 293) \qquad \text{(eqn. S5)}$$

$$H_1 = (C_1 \cdot V + C_r \cdot m/n_C + S \cdot w \cdot t_1) \cdot (T_{r1} - 293)/Y \qquad \text{(eqn. S6)}$$

$$H_2 = (C_2 \cdot Y + C_r \cdot m/n_C + S \cdot w \cdot t_2) \cdot (T_{r2} - 293)/Y \qquad \text{(eqn. S7)}$$

Table S10. Theoretically estimated energy demand of the described process with variable parameters.

n_C	n_S	x [kg]	V [L·kg^{-1}]	Energy demand for each step [MJ · kg^{-1}] (with % of total)								Total energy demand [MJ · kg^{-1}]
				H_1	%	D_1	%	H_2	%	D_2	%	
1	1	1	10	36	31	42	35	40	33	1	1	119
1	1	10^3	10	16	26	42	67	4	6	1	1	62
1	1	10^4	10	15	25	42	70	2	4	1	2	60
10	1	10^3	10	15	25	42	71	2	3	1	2	59
10	3	10^4	10	15	47	14	44	2	5	1	3	31
10	3	10^4	7	11	46	10	43	2	7	1	4	23

5. Life Cycle Assessment

Environmental impacts related to the two-stage process for birch bark conversion into biofuel were evaluated by Life Cycle Assessment (LCA) following the four-phases framework standardized by ISO 14040.[6] Details of the applied methodology are given in the following sections.

5.1. Goal and scope definition

This LCA case aims to identify benefits, caveats and process improvements for the conversion of birch bark into biodiesel on an industrial scale. Additionally, the environmental performance of biodiesel production (from biomass - birch bark) and fossil-based diesel production (from crude oil) were compared. For a direct comparison both systems must have the same functional performance. The capacity to produce 46.5 MJ of energy was then the functional unit chosen for this study. Since the average heating value is higher for biodiesel than for fossil-based diesel (see Table S11), the reference flow is the production of 1kg of biodiesel and 1.04 kg of fossil-based diesel, which are the quantities required to reach the functional unit.

Table S11. Heating value for biodiesel and fossil-based diesel

	Heating value	Average
The biodiesel	45.4 … 48.2 [a]	46.5 MJ/kg
Fossil-based diesel	43.2 … 46.0 MJ/kg[7]	44.6 MJ/kg

[a] Theoretically estimated. See section S4, table S8

A cradle to gate approach was chosen. The environmental impacts of use of two diesels are assumed to be the same, and hence would not influence the comparative results. Thus, use-phase is not included in the scope of the study.

For biodiesel production from birch bark, the system boundary is shown in Figure S5 and it presents the processes divided in two main stages: raw material supply (including extraction of raw material, production and transport) and biodiesel production.

- Feedstock supply: These are the main resources for the production of biodiesel. It includes the inputs and outputs for the production and supply of bark chips, methanol, trimethylamine, water, catalyst, heat energy and fuels for their transportation.
- Birch bark conversion into biodiesel: These are the main processes for the biodiesel production. It includes the inputs and outputs for bark solubilization, filtration and distillation, bark residue incineration, wastewater treatment and hydro-deoxygenation treatment.

For fossil-based diesel production from crude oil the system boundary includes the following processes: extraction of crude oil, distillation/fractionation of crude oil, and treating processing for production of diesel.

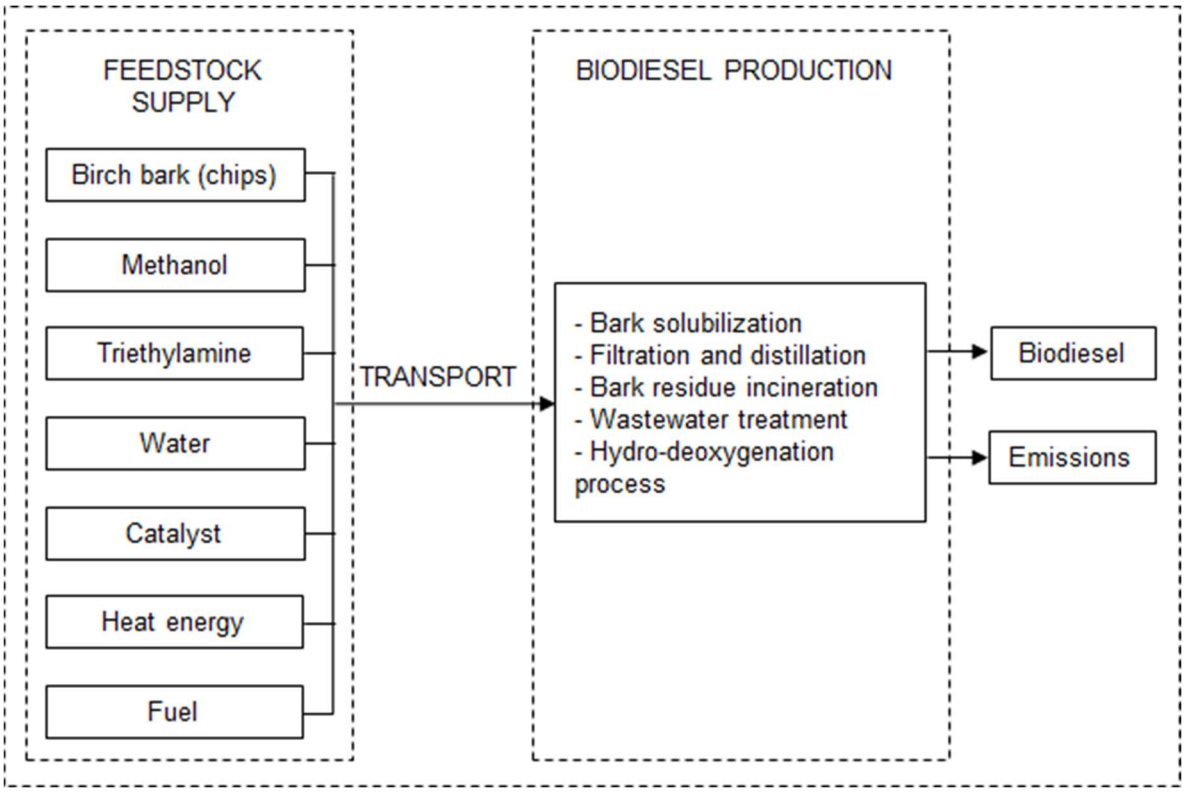

Figure S5. Cradle to gate system boundary of the biodiesel production

Four scenarios were defined to support the environmental performance assessment and enable the identification of improvements to the developed process for converting birch bark into biodiesel. These scenarios, shown in Table S12, vary mainly with respect to the energy sources used in the processes.

Table S12. Scenarios for the environmental performance assessment of birch bark conversion into biofuel

Scenario	Description
Scenario 1	**Baseline, continuous process** Reaction in a continuous process. Milled bark is treated in the solvent and the mixture is filtered. The filtrate, which includes solubilized bark, is returned to the system to play the role of solvent for the next portion of feedstock. After two runs recirculating the solvent, the filtrate becomes viscous and it is then distilled to recover the solvent for subsequent reactions. New solvent is continuously added to substitute the solvent loss of 2% by volume per distillation. Natural gas is the source of heat energy.
Scenario 2	**Electricity mix as input for heat energy, Europe** Reaction in a continuous process (baseline). The average electricity mix of Europe, mostly based on fossil fuel electricity generation, is the source of heat energy.
Scenario 3	**Electricity mix as input for heat energy, Sweden** Reaction in a continuous process (baseline). The average electricity mix of Sweden is the source of heat energy. Sweden was chosen for this scenario as an example of a country with electricity production based on low-carbon technologies (mainly hydropower and nuclear power).[8]

Scenario 4	**Heat energy and methanol as waste streams of paper and pulp industry** Best-case scenario specifically for countries like Sweden, where excess heat and methanol from the paper and pulp industries can be used in the bark valorization process. The environmental impacts of these two feedstocks are thus considered zero.

Based on these scenarios primary and secondary data were collected to build the inventory for the next phases (see section 5.2). Data processing and system modelling was carried out using the LCA software GaBi (8.7.0.18). ReCiPe 2016 was the methodology chosen for the impact assessment and the following impact categories were addressed in the study: climate change, fine particulate matter formation, fossil depletion, freshwater consumption, freshwater ecotoxicity, freshwater eutrophication, human toxicity (cancer and non-cancer), ionizing radiation, land use, marine ecotoxicity, marine eutrophication, metal depletion, photochemical ozone formation, stratospheric ozone depletion, terrestrial acidification, terrestrial ecotoxicity. A sensitivity analysis was performed to test the sensitivity of the results to the following key parameters: milled bark, methanol, triethylamine, water and heat energy.

This study is representative on a European scale. The background data is collected for EU-28. Wherever the dataset for EU-28 was not available, a dataset with the geographical average across the world was used.

5.2. Inventory analysis

This phase involves the compilation and quantification of inputs and outputs for the product system throughout its life cycle. Table S13 shows the inventory for the developed process on the birch bark conversion into biodiesel.

For the fossil-based diesel, the complete cradle to gate inventory, that is including extraction of crude oil, distillation/fractionation of crude oil, and treating processing for production of diesel, was available in the Ecoinvent v3.3 database and has been used for analysis.

Due to the unavailability of data in the Ecoinvent database for $Pt/MoO_3/TiO_2$ (0.05 g; 0.3 wt.% Pt) and Ni/Mo catalysts, used in the laboratory and industry respectively, manufacturing of MoS_2/NiS on Al_2O_3 catalyst was chosen as a proxy for the catalyst modelling in this study. It has thus been modelled based on the data available in the literature.[9] The amount of catalyst required for production of 1kg biofuel was calculated based on its weight and lifetime. Based on industry data it was found out that 100 tons of catalyst remains active for 3-4 years. During that time period an average size hydrotreatment plant processes around 840-1120 kton of bark (average of 980 kton was considered for the calculations). Thus, 0.000255 kg of catalyst is required to produce 1 kg of biodiesel (see Table S13).

Table S13. Inventory to the birch bark conversion into biodiesel (for the production of 1 kg of biodiesel)

Bark solubilization process			
Input	**Value**	**Unit**	**Data source**
Milled birch bark	2.5	kg	Ecoinvent v3.3
Methanol (solvent)	8.125	L	Ecoinvent v3.3

Triethylamine (solvent)	1.25	L	Ecoinvent v3.3
Water (solvent)	8.125	L	Ecoinvent v3.3
Heat energy	10	MJ	Ecoinvent v3.3
Output	**Value**	**Unit**	**Data source**
Solubilized bark	2.5	kg	Intermediate product
Methanol (solvent)	8.125	L	Intermediate product
Triethylamine (solvent)	1.25	L	Intermediate product
Water (solvent)	8.125	L	Intermediate product

Filtration and distillation			
Input	**Value**	**Unit**	**Data source**
Solubilized bark	2.5	kg	Intermediate product
Methanol (solvent)	8.125	L	Intermediate product
Triethylamine (solvent)	1.25	L	Intermediate product
Water (solvent)	8.125	L	Intermediate product
Heat energy	10	MJ	Ecoinvent v3.3
Output	**Value**	**Unit**	**Data source**
Product mixture	2.3325	kg	Intermediate product
Bark residue	0.1675	kg	Intermediate product
Methanol (solvent)	7.9625	L	Intermediate product
Triethylamine (solvent)	1.225	L	Intermediate product
Water (solvent)	7.9625	L	Intermediate product
Waste water	0.35	L	Waste (treated before emitting to the environment)

Hydro-deoxygenation process			
Input	**Value**	**Unit**	**Data source**
Product mixture	2.3325	kg	Intermediate product
Water	1.925	kg	Ecoinvent v3.3
MoS_2/NiS on Al_2O_3 (catalyst)	$2.55 \cdot 10^{-4}$	kg	Literature [9]
Heat energy	3	MJ	Ecoinvent v3.3
Hydrogen gas	0.275	kg	Ecoinvent v3.3
Output	**Value**	**Unit**	**Data source**
Biodiesel	1	kg	Final product
CO_2	3.025	kg	Emissions
Hydrogen gas	0.55	kg	Emission that is captured and recycled

The excess hydrogen emitted by the HDO reaction can be separated from the rest of the gases, collected and reused. This has been modelled as an avoided impact of producing hydrogen from alternate method, most typically by steam reforming of natural gas. Additionally, the heat energy produced by burning bark residue, that can be used to supply energy required for other reaction, has been modelled as an avoided impact of producing required energy from alternate sources.

5.3. Impact assessment

The main LCA comparison results are presented in Table S14. An overview of the main potential impacts of the two-stage process for converting birch bark to biofuel is thus provided in this section as a supplement to the information exposed in the manuscript.

Table S14. Potential environmental impacts for different scenario

	Fossil-based diesel production	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Climate change, incl biogenic carbon [kg CO2 eq.]	6.03E-01	1.70E+00	2.98E+00	4.95E-01	-5.82E-02
Fine particulate matter formation [kg PM2.5 eq.]	1.70E-03	-4.19E-04	2.71E-03	-6.73E-04	-1.19E-03
Fossil depletion [kg oil eq.]	1.28E+00	9.52E-02	8.29E-01	1.77E-01	-6.03E-01
Freshwater consumption [m3]	6.45E-03	-2.11E-02	1.47E-02	1.14E-02	-2.36E-02
Freshwater ecotoxicity [kg 1,4 DB eq.]	2.78E-03	5.10E-03	2.24E-02	6.20E-03	2.65E-03
Freshwater eutrophication [kg P eq.]	7.17E-05	2.16E-04	2.36E-03	1.99E-04	1.19E-04
Human toxicity, cancer [kg 1,4-DB eq.]	1.22E-02	1.83E-02	1.39E-01	2.07E-02	6.85E-03
Human toxicity, non-cancer [kg 1,4-DB eq.]	2.17E-01	1.07E+00	3.64E+00	1.36E+00	8.87E-01
Ionizing radiation [Bq C-60 eq. to air]	4.81E-02	3.21E-02	1.15E+00	1.50E+00	1.58E-03
Land use [Annual crop eq.·y]	9.00E-03	4.53E-01	5.63E-01	7.02E-01	4.51E-01
Marine ecotoxicity [kg 1,4-DB eq.]	5.84E-03	8.95E-03	3.03E-02	8.94E-03	3.30E-03
Marine eutrophication [kg N eq.]	2.03E-05	1.86E-05	1.82E-04	4.32E-05	1.14E-05
Metal depletion [kg Cu eq.]	9.75E-04	2.24E-03	2.88E-03	2.58E-03	1.63E-03
Photochemical ozone formation, Ecosystems [kg NOx eq.]	2.23E-03	-5.95E-03	-2.63E-03	-6.01E-03	-7.06E-03
Photochemical ozone formation, Human health [kg NOx eq.]	2.09E-03	-6.01E-03	-2.69E-03	-6.05E-03	-7.07E-03
Stratospheric ozone depletion [kg CFC-11 eq.]	9.44E-07	4.93E-07	1.22E-06	7.02E-07	-2.64E-08
Terrestrial acidification [kg SO2 eq.]	4.92E-03	-2.38E-03	6.41E-03	-2.93E-03	-4.26E-03
Terrestrial ecotoxicity [kg 1,4-DB eq.]	8.23E-01	1.00E+00	2.69E+00	2.16E+00	7.74E-01

Table S15. Potential environmental impacts of each process of the bark treatment (Scenario 1)

	Bark valorisation process	Bark solubalisation	Filtration	HDO	Bark residue incineration
Climate change, incl biogenic carbon [kg CO2 eq.]	1,7	0,235	0,755	0,691	0,024
Fine Particulate Matter Formation [kg PM2.5 eq.]	-0,000419	0,000592	0,000305	-0,0012	-0,000111
Fossil depletion [kg oil eq.]	0,0952	0,36	0,29	-0,449	-0,106
Freshwater Consumption [m3]	-0,0211	0,00195	0,000885	-0,0236	-0,000361
Freshwater ecotoxicity [kg 1,4 DB eq.]	0,0051	0,00183	0,000989	0,00264	-0,00036
Freshwater Eutrophication [kg P eq.]	0,000216	7,77E-05	4,01E-05	1,13E-04	-1,46E-05
Human toxicity, cancer [kg 1,4-DB eq.]	0,0183	0,00902	0,00473	0,00623	-0,00172
Human toxicity, non-cancer [kg 1,4-DB eq.]	1,07	0,168	0,0675	0,859	-0,0245
Ionizing Radiation [Bq C-60 eq. to air]	0,0321	0,0196	0,013	0,00425	-0,00474
Land use [Annual crop eq.·y]	0,453	0,452	0,00105	0,000623	-0,000383
Marine ecotoxicity [kg 1,4-DB eq.]	0,00895	0,00383	0,00234	0,00363	-0,000854
Marine Eutrophication [kg N eq.]	1,86E-05	1,17E-05	3,72E-06	4,33E-06	-1,10E-06

Metal depletion [kg Cu eq.]	0,00224	0,000501	0,000236	0,00159	-8,57E-05
Photochemical Ozone Formation, Ecosystems [kg NOx eq.]	-0,00595	0,000953	0,000459	-0,00719	-0,000168
Photochemical Ozone Formation, Human Health [kg NOx eq.]	-0,00601	0,000909	0,000435	-0,0072	-0,000159
Stratospheric Ozone Depletion [kg CFC-11 eq.]	4,93E-07	2,79E-07	2,20E-07	7,53E-08	-8,01E-08
Terrestrial Acidification [kg SO2 eq.]	-0,00238	0,00134	0,000722	-0,00418	-0,000263
Terrestrial ecotoxicity [kg 1,4-DB eq.]	1	0,692	0,0807	0,26	-0,0294

5.4. Sensitivity analysis

The goal of the sensitivity analysis is to gain an overview of the parameters that have strong impacts on the results. It gives useful information about the sensitivity of the model to parameter uncertainties. In this study, a local sensitivity analysis was carried out with one-at-a-time (OAT) approach. In OAT approach one input parameter is varied at a time by 10%, keeping other parameters fixed to see how much that parameter influences the results. The parameters that were varied were – material inputs (bark chips, solvent - methanol, water and trimethylamine – catalyst and hydrogen) and energy inputs for each of the three processes.

The results of the sensitivity analysis shows that the parameter that affect the results most is hydrogen input (Table S15). The sensitivity analysis specifically for impact category climate change, increase in hydrogen use decreases the GWP by 14.70%. The negative correlation in the result is because the hydrogen is being produced in the HDO, and is included in the analysis as an avoided impact of producing hydrogen from other sources. Hydrogen has an impact also on other categories, most importantly fine particulate matter, fossil depletion, freshwater consumption, photochemical ozone formation and stratospheric ozone depletion. The most significant impact is on the impact category fossil depletion. The increase of hydrogen produced in the HDO process by 10% decreases the fossil depletion impact category results by 56%. This is because the hydrogen is alternatively being produced by steam reforming process of natural gas. Similarly, if the hydrogen produced in the HDO process decreased by 10%, the GWP increases by 14.7%.

The other parameters that the results are sensitive to are energy and bark chips. Energy affects the categories – fossil depletion, whereas bark chips affects the category – land use change. These results of sensitivity analysis suggest that the value for the amount of hydrogen (produced and consumed), energy and bark chips needed in the process should be accurately known before concluding the results.

The results also show that the amount of solvent consumed in the process does not significantly affect the results. The current analysis assumes that 2% of solvent is lost every time the solvent is distilled. The increase of solvent loss by 10% (i.e. to 2.2%) increases the GWP by 1.1% (0.588% increase due to methanol and 0.588% due to trimethylamine). The impact on other categories is also not significant.

Table S16. Sensitivity analysis

Impact category	Baseline	Bark solubilization					Filtration and distillation	HDO			
		Bark chips	Methanol	Water	Et_3N	Energy	Energy	Catalyst	Energy	Hydrogen	Water
Climate change, incl biogenic carbon [kg CO2 eq.]	1.7	-2.941%	0.588%	0.000%	0.588%	4.706%	4.706%	0.588%	1.765%	**-14.706%**	0.000%
Fine Particulate Matter Formation [kg PM2.5 eq.]	-0.000419	4.535%	1.909%	0.000%	0.477%	7.399%	7.399%	1.432%	2.148%	**-32.458%**	0.000%
Fossil depletion [kg oil eq.]	0.0952	2.941%	3.256%	0.000%	1.155%	30.252%	30.252%	0.105%	9.244%	**-56.513%**	0.000%
Freshwater Consumption [m3]	-0.0211	0.000%	0.000%	0.000%	0.000%	0.474%	0.474%	0.000%	0.000%	**-12.322%**	0.948%
Freshwater ecotoxicity [kg 1,4 DB eq.]	0.0051	1.176%	0.392%	0.000%	0.196%	1.961%	1.961%	**4.902%**	0.588%	-0.392%	0.000%
Freshwater Eutrophication [kg P eq.]	0.000216	1.389%	0.463%	0.000%	0.463%	1.852%	1.852%	**5.093%**	0.926%	0.000%	0.463%
Human toxicity, cancer [kg 1,4-DB eq.]	0.0183	1.639%	0.000%	0.000%	0.000%	2.186%	2.186%	**2.186%**	0.546%	0.000%	0.000%
Human toxicity, non-cancer [kg 1,4-DB eq.]	1.07	0.935%	0.000%	0.000%	0.000%	0.935%	0.935%	**7.477%**	0.000%	0.000%	0.000%
Ionizing Radiation [Bq C-60 eq. to air]	0.0321	1.558%	0.312%	0.000%	0.000%	**4.050%**	4.050%	0.000%	1.246%	0.000%	0.000%
Land use [Annual crop eq.·y]	0.453	**9.934%**	0.000%	0.000%	0.000%	0.000%	0.000%	0.000%	0.000%	0.000%	0.000%
Marine ecotoxicity [kg 1,4-DB eq.]	0.00895	1.229%	0.335%	0.000%	0.112%	2.682%	2.682%	**3.575%**	0.782%	-0.223%	0.000%
Marine Eutrophication [kg N eq.]	0.0000186	1.613%	0.538%	0.538%	**3.226%**	1.613%	1.613%	2.151%	0.538%	0.000%	0.000%
Metal depletion [kg Cu eq.]	0.00224	0.893%	0.446%	0.000%	0.000%	0.893%	0.893%	**7.143%**	0.446%	-0.446%	0.000%
Photochemical Ozone Formation, Ecosystems [kg NOx eq.]	-0.00595	0.672%	0.168%	0.000%	0.168%	0.840%	0.840%	0.168%	0.336%	**-12.269%**	-0.00668
Photochemical Ozone Formation, Human Health [kg NOx eq.]	-0.00601	0.499%	0.000%	0.000%	0.000%	0.666%	0.666%	0.000%	0.166%	**-12.313%**	0.000%
Stratospheric Ozone Depletion [kg CFC-11 eq.]	4.93E-07	0.811%	0.406%	0.000%	0.203%	**4.462%**	**4.462%**	0.203%	1.420%	0.000%	0.000%
Terrestrial Acidification [kg SO2 eq.]	-0.00238	1.261%	0.840%	0.000%	0.000%	2.941%	2.941%	0.420%	0.840%	**-19.328%**	0.000%
Terrestrial ecotoxicity [kg 1,4-DB eq.]	1	**6.000%**	1.000%	0.000%	1.000%	1.000%	1.000%	3.000%	1.000%	0.000%	0.000%

6. Illusrations

Figure S6. Grinded birch bark as used for the reaction.

Figure S7. Bark solubilized in H_2O–MeOH–Et_3N.

Figure S8. Residue after solubilization and filtration.

Figure S9. Bark gum after evaporation of solvent. This material was directly used for hydrodeoxygenation.

Figure S10. Bark gum suspended/solubilized in tall oil. This mixture was not used for hydrodeoxygenation in the present work.

Figure S11. The final product, hydrocarbon bio-oil.

7. HDO of lignin

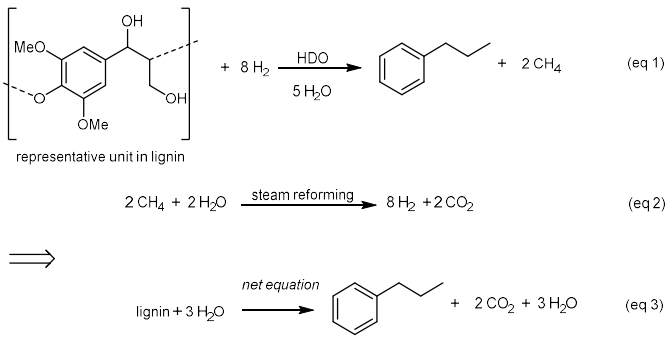

Figure S12. HDO of lignin is hydrogen balanced

8. References

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