Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Hydrotreating of Hydrofaction™ biocrude in the presence of presulfided commercial catalysts

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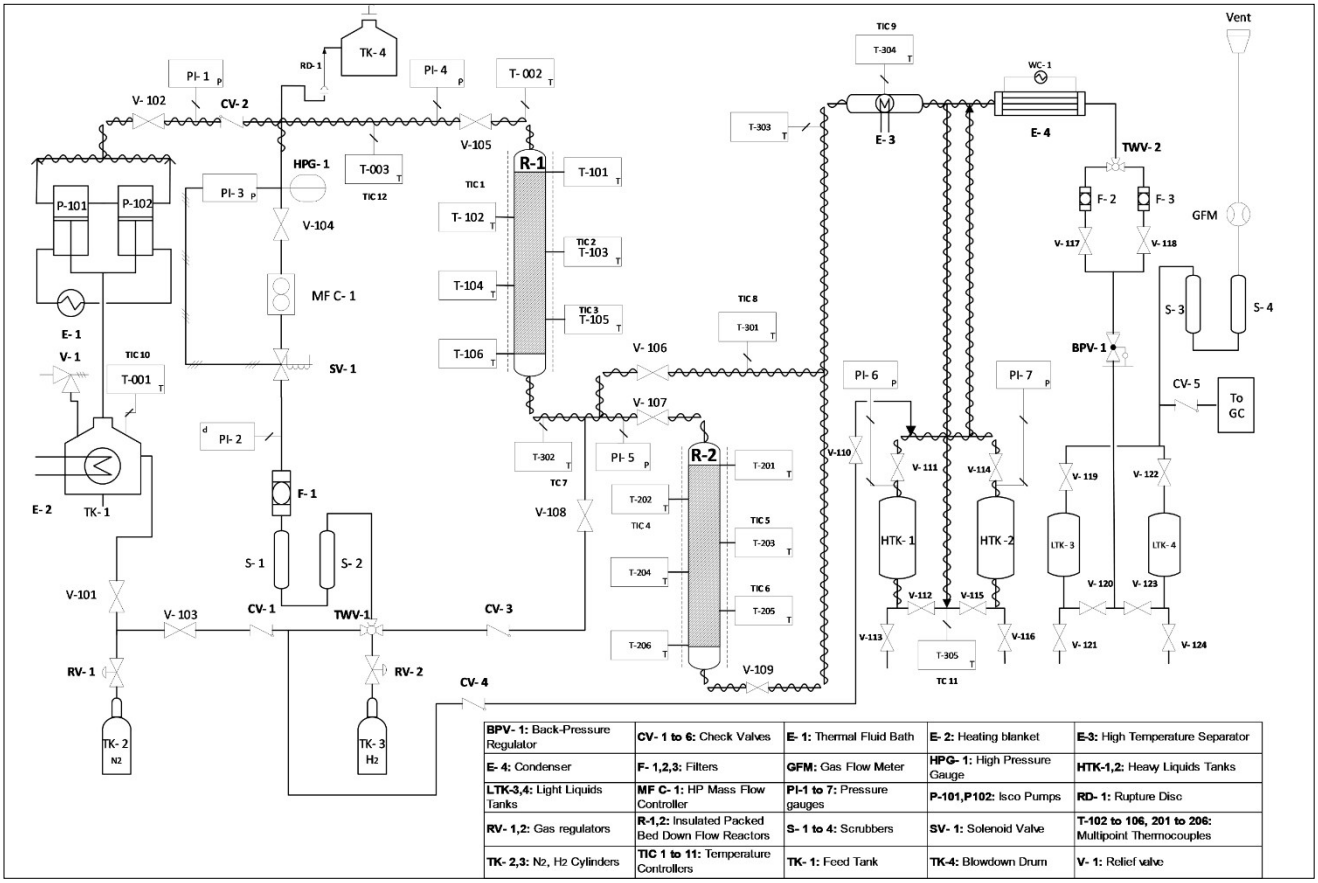

BPV- 1: Back-Pressure Regulator	**CV- 1 to 6:** Check Valves	**E- 1:** Thermal Fluid Bath	**E- 2:** Heating blanket	**E-3:** High Temperature Separator
E- 4: Condenser	**F- 1,2,3:** Filters	**GFM:** Gas Flow Meter	**HPG- 1:** High Pressure Gauge	**HTK-1,2:** Heavy Liquids Tanks
LTK-3,4: Light Liquids Tanks	**MF C- 1:** HP Mass Flow Controller	**PI-1 to 7:** Pressure gauges	**P-101,P102:** Isco Pumps	**RD- 1:** Rupture Disc
RV- 1,2: Gas regulators	**R-1,2:** Insulated Packed Bed Down Flow Reactors	**S- 1 to 4:** Scrubbers	**SV- 1:** Solenoid Valve	**T-102 to 106, 201 to 206:** Multipoint Thermocouples
TK- 2,3: N2, H2 Cylinders	**TIC 1 to 11:** Temperature Controllers	**TK- 1:** Feed Tank	**TK-4:** Blowdown Drum	**V- 1:** Relief valve

Figure S1. P&ID diagram of the hydrotreater unit.

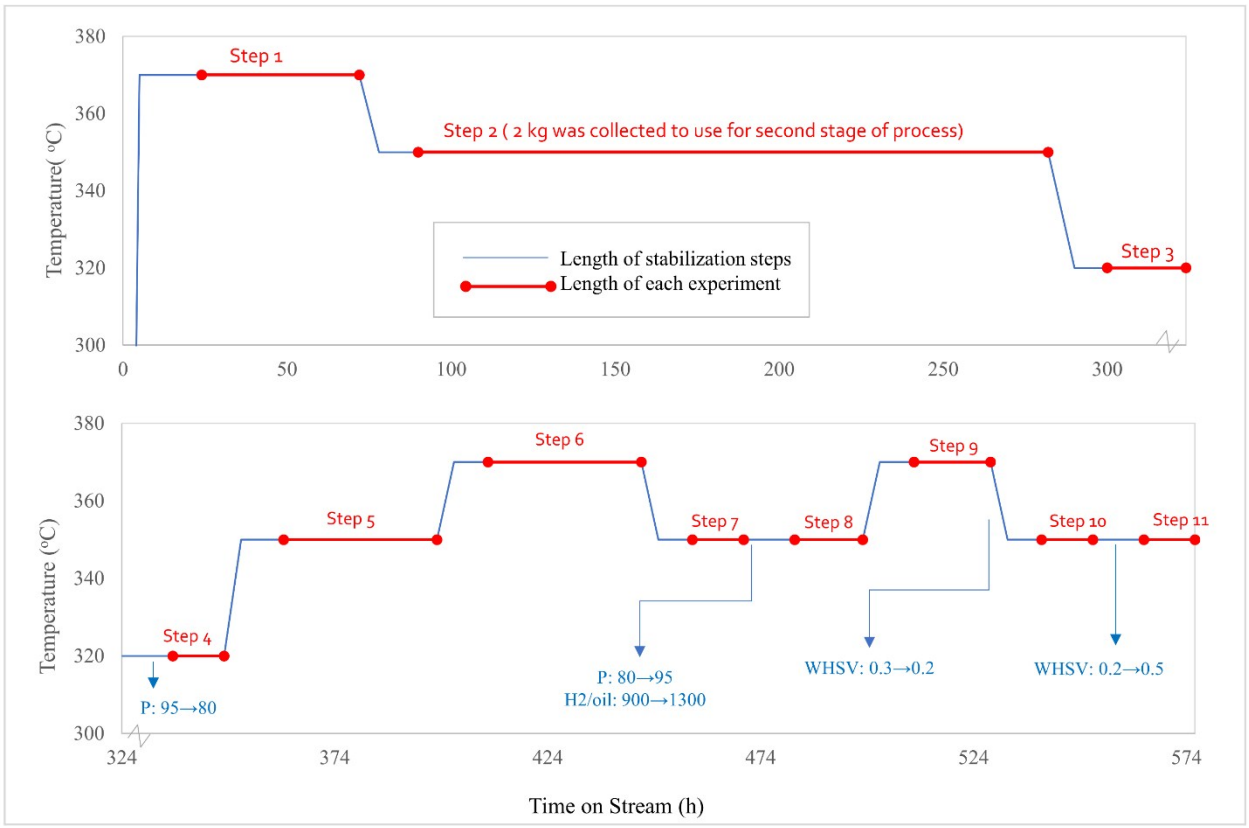

Figure S2. Time on stream plot, presenting the sequence of upgrading experiments at different operating conditions.

Table S1-The comparison of different collected samples at different day at the same conditions of upgrading at step 2 in experimental plan. Experiments were carried out at 350 °C, 95 bar, WHSV of 0.3 h^{-1} and H_2:oil of 900 Nm^3 H_2/m^3 oil.

	Mass balance obtained after 100 hours of operation	***Mass balance obtained after 170 hours of operation***	***Mass balance obtained after 260 hours of operation***	***unit***
***Density** at 20 °C*	**991.2**	**990.8**	**991.0**	*kg/m³*
***Viscosity** at 40 °C*	**339**	**332**	**336**	*cP*
TAN	**8.2**	**8.1**	**8.2**	*mgKOH/g*
HHV[a]	**40.6**	**40.6**	**40.6**	*MJ/Kg*
O[b]	**3.2**	**3.1**	**3.2**	*wt%*
Water Yield	**7.3**	**7.3**	**7.3**	*wt%*

[a] On dry basis
[b] Oxygen by difference

Table S2-The results of reproducibility evaluation obtained from step 5 and step 7 of upgrading. Experiments were carried out at 350 °C, 80 bar, WHSV of 0.3 h^{-1} and H_2:oil of 900 Nm^3 H_2/m^3 oil.*

	Step 5	***Step 7****	***unit***
***Density** at 20 °C*	**1004.8**	**1004.2**	*kg/m³*
***Viscosity** at 40 °C*	**375**	**371**	*cP*
TAN	**9.2**	**9.0**	*mgKOH/g*
HHV[a]	**40.54**	**40.58**	*MJ/Kg*
O[b]	**3.8**	**3.7**	*wt%*
Water Yield	**7.2**	**7.2**	*wt%*

[a] On dry basis
[b] Oxygen by difference
* The slight difference between the properties of oil collected at two steps could be due to the evaporation of some light fractions during the sampling period of step 5.

Table S3-Properties of Hydrofaction™ renewable crude oil, used as a feedstock for catalytic hydrotreating process.

	Renewable crude oil	***unit***
Density *at 20 °C*	**1055.1**	*kg/m³*
at 40 °C	**1043.3**	*kg/m³*
at 60 °C	**1030.1**	*kg/m³*
Viscosity *at 40 °C*	**3975**	*cP*
TAN	**63.2**	*mgKOH/g*
HHV[a]	**37.6**	*MJ/Kg*
Elemental Analysis:		
C[a]	**79.4**	*wt%*
H[a]	**9.1**	*wt%*
N[a]	**0.6**	*wt%*
O[b]	**10.9**	*wt%*
H/C	**1.37**	*molar ratio*

[a] On dry basis
[b] Oxygen by difference

Table S4 -Effect of WHSV on the boiling point distribution of products.

Effect of WHSV		*0.5 h^{-1}*	*0.3 h^{-1}*	*0.2 h^{-1}*
Fraction	**Boiling Point Range**			
1	0-180	8	9	8
2	180-260	13	14	15
3	260-350	29	31	30
4	350-454	16	16	17
5	454+	34	30	30

Table S5 -Effect of pressure on the boiling point distribution of products.

Effect of Pressure		*T=350 °C*		*T=370 °C*	
Fraction	**Boiling Point Range**	**P=80 bar**	**P=95 bar**	**P=80 bar**	**P=95 bar**
1	0-180	8	8	11	12
2	180-260	13	14	16	16
3	260-350	31	30	34	32
4	350-454	16	16	18	18
5	454+	32	32	21	22

Table S6-Effect of H_2:oil on the boiling point distribution of products.

Effect of H_2:oil		*T=350 °C*		*T=370 °C*	
Fraction	**Boiling Point Range**	**H_2:oil=900**	**H_2:oil=1300**	**H_2:oil=900**	**H_2:oil=1300**
1	0-180	8	9	12	12
2	180-260	14	14	16	17
3	260-350	30	31	32	31
4	350-454	16	16	18	18
5	454+	32	30	22	22

"Description of VMGSim simulation of H_2 solubility in liquid oil"

The following experimental data used to define a pseudo-biocrude: ρ @ 20 °C: 1055.1 kg/m^3

Table S7 -Boiling point distribution used to define pseudo-biocrude.

Distilled fraction (%)	Boiling point (°C)	Distilled fraction (%)	Boiling point (°C)	Distilled fraction (%)	Boiling point (°C)
0	101	24	303	48	397
1	103	25	308	49	403
2	132	26	312	50	408
3	153	27	318	51	414
4	168	28	324	52	420
5	181	29	329	53	426
6	191	30	334	54	433
7	201	31	338	55	439
8	208	32	342	56	446
9	218	33	347	57	454
10	225	34	349	58	461
11	233	35	354	59	469
12	240	36	358	60	478
13	247	37	360	61	485
14	252	38	363	62	496
15	258	39	365	63	509
16	263	40	367	64	524
17	267	41	371	65	543
18	273	42	374	66	565
19	277	43	377	67	588
20	283	44	380	68	633
21	288	45	384	69	686
22	292	46	388	70	726
23	298	47	392		

20 pseudo-components were generated to simulate the biocrude: 10 components within the boiling point range of 100 to 427°C; 5 components within boiling point range of 427-649 °C and 5 components within the boing point range of 649 – 871 °C. The correlation used to predict the properties of the components is provided in Table S8.

Name	Range-1	Range-2	Range-3
Number of Cuts	10	5	5
Cut Delta T [C]	38.92	44.40	44.42
Min. Temp [C]	37.8	427.0	649.0
Max. Temp [C]	427.0	649.0	871.1
MW Est	Hariu-Sage	Hariu-Sage	Hariu-Sage
LD Est	Constant UOP K	Constant UOP K	Constant UOP K
Tc Est	Twu	Twu	Twu
Pc Est	Twu	Twu	Twu
Vc Est	Twu	Twu	Twu
Acentric Est	Lee-Kesler-Lee	Lee-Kesler-Lee	Lee-Kesler-Lee
Liq Viscosity Est	API-VMG	API-VMG	API-VMG
Liq. Th. Cond. Est	API	API	API
Liq. Surf. Tension Est	API	API	API
Ideal Gas Cp Est	Lee-Kesler	Lee-Kesler	Lee-Kesler

Table S8 –Name of correlations applied to predict the properties of pseudo-components.

After defining the pseudo-components, stream of oxygenated molecules was mixed with pseudo- components to generate the pseudo-biocrude. The Peng Robinson equation of state (PR-EoS) was used to simulate the H_2 solubility in the biocrude, the equation of Peng Robinson equation is provided is Equation S1. (For the case of oxygenates/H_2, the binary coefficients(kij) were adjusted).

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{{V_m}^2 + 2bV_m - b^2} \qquad \text{Equation S.1}$$

$$a \approx 0.45724\frac{R^2{T_c}^2}{p_c},\ b \approx 0.07780\frac{RT_c}{p_c},\ \alpha = \left(1 + k\left(1 - {T_r}^{\frac{1}{2}}\right)\right)^2,\ k = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

The H_2/briocrude model created in VMGSim is presented in Figure S3. The results of hydrogen solubility in liquid biocrude are in Figure S4.

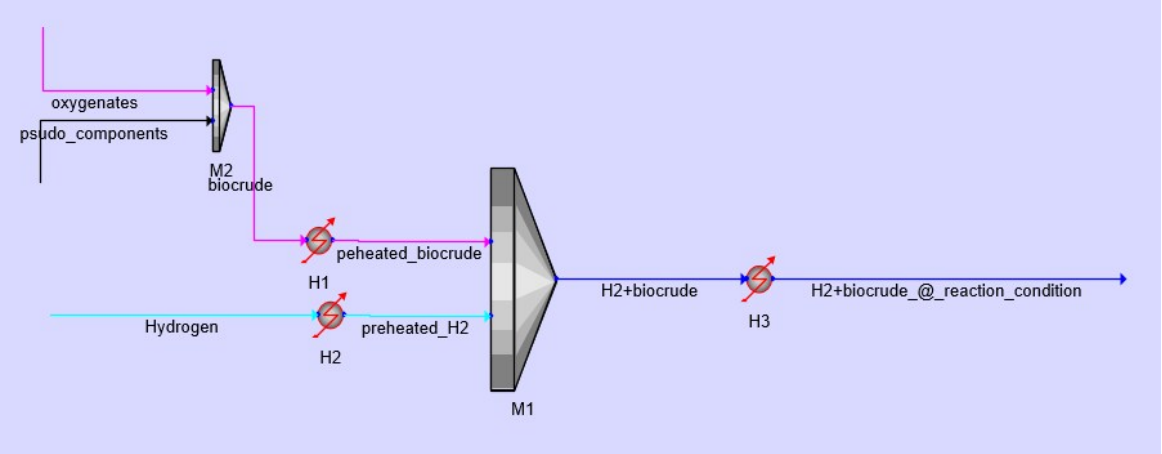

Figure S3.PFD of H_2/biocrude system in VMGSim environment.

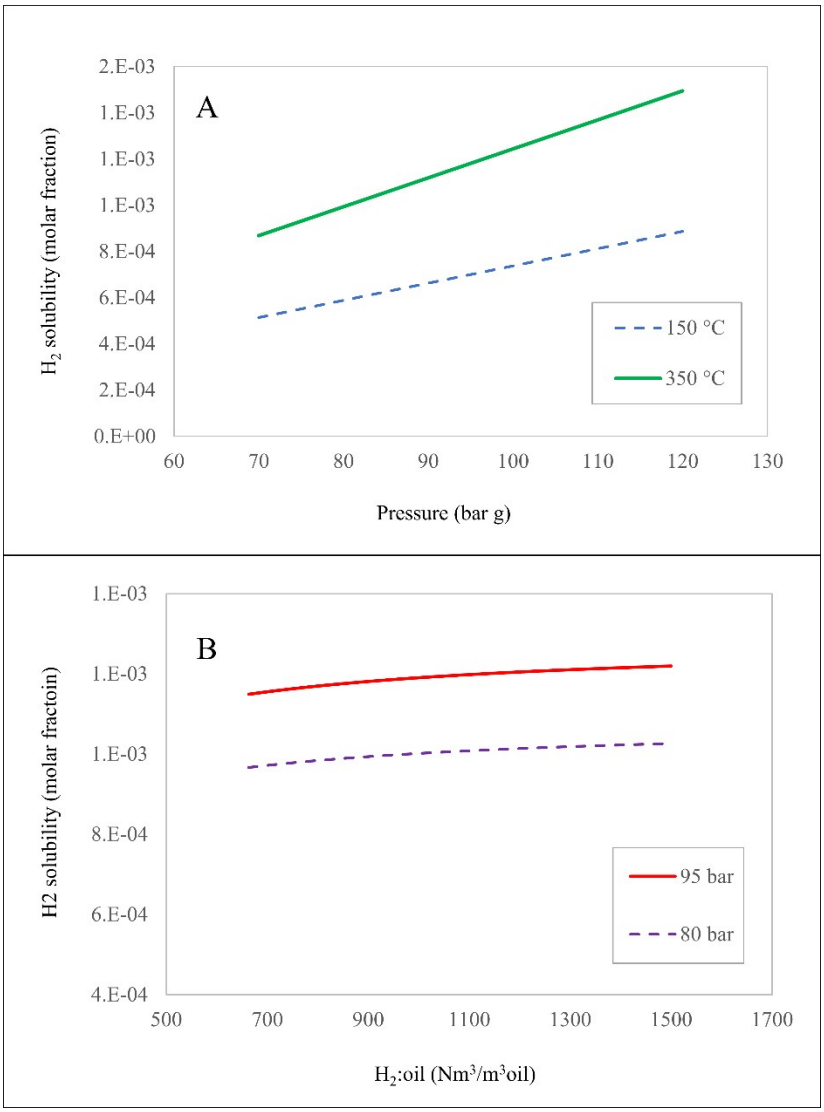

Figure S4. A) Effect of pressure on H_2 solubility in oil at H_2:oil=900 Nm^3/m^3 oil. B) Effect of H_2:oil ratio on H_2 solubility in oil at T=350 ^oC.

. *"Description of macro-elemental correlation generation"*

Step 1) First, the model compounds in the bio-oil which are frequently reported in the literature are collected. These model molecules are categorized into three families of oxygen functional groups:

- Paraffinic oxygenate compounds and their derivatives such as carboxylic acids.
- Aromatic oxygenate compounds and their derivatives such as phenolic compounds.
- Furan compounds group.

Note: The abundance of each oxygenate family in the bio-oil depends on the type of the bio-oil and the origin of the feedstock. In this work, the same weight factor for three categories are considered, aiming to cover all types of biocrudes.

Step 2) To correlate various types of FP and HTL products, around 30 compounds, reported by European Chemical Agency (ECHA) as chemical constituents of registered pyrolysis bio-oil, were added to the list.

Step 3) In the next step, the possible reaction pathways through upgrading of the previously collected model molecules are considered; Reactions such as hydrodeoxygenation, decarboxylation, and hydrogenation are included as possible pathways for bio-oil upgrading. Then, the model compound obtained from conversion of the model molecules through these possible pathways were added to the list. The produced molecules at this step represent the compounds that can be found in the products of bio-oil upgrading.

The following example clarifies this step where toluene/benzene are produced from different pathways conversions of Phthalic acid:

$C_8H_6O_4$ (Phthalic acid) $\rightarrow$ $C_7H_6O_2$ (Benzoic acid) + CO_2 Decarboxylation reaction

$C_7H_6O_2$(Benzoic acid) $\rightarrow$ C_6H_8 (Benzene) + CO_2 Decarboxylation reaction

$C_7H_6O_2$(Benzoic acid) $+$ $2H_2 \rightarrow$ C_7H_8O (Benzyl alcohol) + H_2O HDO reaction

C_7H_8O (Benzyl alcohol) + $H_2 \rightarrow$ C_7H_8 (Toluene) + H_2O HDO reaction

Phthalic acid is an oxygenated aromatic model compound which is found in the bio-oils. As it was shown in last page, benzene is produced from decarboxylation of benzoic acid. Benzoic acid is also produced from Phthalic acid decarboxylation. Toluene is produced via HDO of benzyl alcohol, which produced from HDO of benzoic acid. Therefore, benzoic acid, benzyl alcohol, toluene and benzene were added to the list. The possibility of such reaction through upgrading of biomass derived feedstocks is reported by Robinson *et al*.[41]

Step 4) After preparing the complete list of the model molecule from step 1 to 3, the properties of the model molecules were collected, and the correlations were generated following the multiple linear regression method. In tables S9-11, the model molecules from each categories and their possible reaction pathways are reported.

Table S9-The model compounds from paraffinic oxygenated groups and their reaction pathways.

#	model compounds	Formula	Reaction Pathway
1	Succinic acid	$C_4H_6O_4$	original model
2	Butyric acid	$C_4H_8O_2$	HDO of # 1
3	Propionic acid	$C_3H_6O_2$	DCO_2 of # 1
4	Propanol	C_3H_8O	HDO of # 3
5	Glutaric acid	$C_5H_8O_4$	original model
6	Pentane	C_5H_{12}	HDO of # 5
7	Butyric acid	$C_4H_8O_2$	DCO_2 of # 5
8	Butonal	C_4H_9O	HDO of # 7
9	Butyraldehyde	C_4H_8O	HDO of # 7
10	Butane	C_4H_{10}	HDO of # 9
11	Isocrotonic acid	$C_4H_6O_2$	original model
12	Oleic acid	$C_{18}H_{34}O_2$	original model
13	Octadecane	$C_{18}H_{38}$	HDO of #12
14	Palmitic acid	$C_{16}H_{32}O_2$	original model
15	Hexadeecane	$C_{16}H_{34}$	HDO of #14
16	Glycerol	$C_3H_8O_3$	original model
17	Propylene glycol	$C_3H_8O_2$	HDO of #16
18	Isopropyl alcohol	C_3H_8O	HDO of #17

HDO=Hydrodeoxygenation; DCO_2 =Decarboxylation

Table S10-The model compounds from aromatic oxygenated groups and their reaction pathways.

#	model compounds	Formula	Reaction Pathway
1	Phthalic acid	$C_8H_6O_4$	original model
2	Methylbenzoic acid	$C_8H_8O_2$	HDO of # 1
3	Benzoic acid	$C_7H_6O_2$	DCO_2 of # 1
4	Benzyl alcohol	C_7H_8O	HDO of # 3
5	Toluene	C_7H_8	HDO of #4
6	Guaiacol	$C_7H_8O_2$	original model
7	Anisole	C_7H_8O	HDO of #6
8	Catechol	$C_6H_6O_2$	original model
9	Cresol	C_7H_8O	original model
10	Phenol	C_6H_6O	Dealkylation of #9
11	Cyclohexanol	$C_6H_{12}O$	HY of #10
12	Benzene	C_6H_6	DCO_2 of # 3
13	Cyclohexane	C_6H_{12}	HY of #12
14	4-Propylguaiacol	$C_{10}H_{14}O_2$	original model
15	Benzophenone	$C_{13}H_{10}O$	original model
16	2-Naphthol	$C_{10}H_8O$	original model
17	Naphthalene	$C_{10}H_8$	HDO of #16

HDO=Hydrodeoxygenation; DCO_2 =Decarboxylation; HY= Hydrogenation

Table S11-The model compounds from aromatic oxygenated groups and their reaction pathways.

#	model compounds	Formula	Reaction Pathway
1	2-Acetylfuran	$C_6H_6O_2$	original model
2	Furfural	$C_5H_4O_2$	Dealkylation of #1
3	Methyl furan	C_5H_6O	HDO of #2
4	Furan	C_4H_4O	Dealkylation of #3
5	Tetrahydrofuran	C_4H_8O	HY of #4
6	Dibenzofuran	$C_{12}H_8O$	original model
7	Tetrahydrodibenzofuran	$C_{12}H_{12}O$	HY of #6
8	Hexahydrodibenzofuran	$C_{12}H_{14}O$	HY of #7
9	Octahydrodibenzofuran	$C_{12}H_{16}O$	HY of #8
10	Benzofuran	C_8H_6O	original model*
11	Tetrahydrobenzofuran	$C_8H_{10}O$	HY of #10
12	Ethyl phenol	$C_8H_{10}O$	Ring opening of #10*
13	2-cyclohexylphenol	$C_{12}H_{16}O$	Ring opening of #8*
14	cyclohexylcyclohexanol	$C_{12}H_{22}O$	HY of #13*
15	Bicyclohezane	$C_{12}H_{22}$	HDO of #14*

HDO=Hydrodeoxygenation; DCO_2 =Decarboxylation; HY= Hydrogenation.
*The reaction pathway was obtained from the work of Want *et al*.[41]

The complete list of model molecules obtained from step 1 and step 3 and their properties used to generate the correlation is reported in Table S12.

Table S12-The name and properties of compounds in the bio-oil and upgraded product, obtained at step 1 and 3.

#	Formula	C atomic number	H atomic number	O atomic number	Density kg/m^3	BP ^{o}C	H wt%	O wt wt%
1	Succinic acid	4	6	4	1539	317	7.0	37.2
2	Butyric acid	4	8	2	953	164	11.1	22.2
3	Propionic acid	3	6	2	988	141	10.3	27.6
4	Propanol	3	8	1	802	97	15.4	15.4
5	Glutaric acid	5	8	4	1268	322	8.0	32.0
6	Pentane	5	12	0	630	36	16.7	0.0
7	Butyric acid	4	8	2	953	163	11.1	22.2
8	Butonal	4	9	1	806	117	13.8	12.3
9	Butyraldehyde	4	8	1	797	74	12.5	12.5
10	Butane	4	10	0	583	0	17.2	0.0
11	Isocrotonic acid	4	6	2	1023	171	8.6	22.9
12	Oleic acid	18	34	2	888	359	12.8	6.0
13	Octadecane	18	38	0	775	316	15.0	0.0
14	Palmitic acid	16	32	2	852	322	13.3	6.7
15	Hexadeecane	16	34	0	770	286	15.0	0.0
16	Glycerol	3	8	3	1261	290	11.8	35.3
17	Propylene glycol	3	8	2	1036	188	13.3	26.7
18	Isopropyl alcohol	3	8	1	786	82	15.4	15.4
19	Phthalic acid	8	6	4	1308	324	4.5	23.9
20	Methylbenzoic acid	8	8	2	1223	263	6.7	13.3
21	Benzoic acid	7	6	2	1177	249	5.7	15.1
22	Benzyl alcohol	7	8	1	1044	205	8.0	8.0
23	Toluene	7	8	0	870	111	8.7	0.0
24	Guaiacol	7	8	2	1112	205	7.4	14.8
25	Anisole	7	8	1	995	153	8.0	8.0
26	Catechol	6	6	2	1340	245	6.4	17.0
27	Cresol	7	8	1	1041	191	8.0	8.0
28	Phenol	6	6	1	1069	181	7.0	9.3
29	Cyclohexanol	6	12	1	965	160	13.0	8.7
30	Benzene	6	6	0	883	80	7.7	0.0
31	Cyclohexane	6	12	0	773	80	14.3	0.0
32	4-Propylguaiacol	10	14	2	1046	271.4	9.3	10.7
33	Benzophenone	13	10	1	1102	306	5.7	4.6
34	2-Naphthol	10	8	1	1144	288	5.9	5.9

35	Naphthalene	10	8	0	1022	218	6.3	0.0
36	2-Acetylfuran	6	6	2	1097.5	169	6.4	17.0
37	Furfural	5	4	2	1160	161	5.0	20.0
38	Methyl furan	5	6	1	927	63	8.1	10.8
39	Furan	4	4	1	936	31	6.7	13.3
40	Tetrahydrofuran	4	8	1	889	66	12.5	12.5
41	Dibenzofuran	12	8	1	1151	284	5.0	5.0
42	Tetrahydrodibenzofuran	12	12	1	1124	279.5	7.3	4.9
43	Hexahydrodibenzofuran	12	14	1	-	-	8.4	4.8
44	Octahydrodibenzofuran	12	16	1	1104	261	9.5	4.8
45	Benzofuran	8	6	1	1072	174	5.5	7.3
46	Tetrahydrobenzofuran	8	10	1	-	-	8.8	7.0
47	Ethyl phenol	8	10	1	1014	204	8.8	7.0
48	2-cyclohexylphenol	12	16	1	1042	238.5	9.5	4.8
49	cyclohexylcyclohexanol	12	22	1	980	264	12.6	4.6
50	Bicyclohezane	12	22	0	864	227	13.3	0.0

The list of compounds reported by European Chemical Agency (ECHA) as chemical constituents of registered pyrolysis bio-oil is provided in Table S13.[42]

Table S13-The name and properties of the compounds in fast pyrolysis bio-oil, reported by ECHA (collected at Step 2)

#	Formula	*CAS* #	C atomic number	H atomic number	O atomic number	Density kg/m^3
1	Propanoic acid	201-176-3	3	6	2	988
2	2-hydroxyacetic acid	201-180-5	2	4	3	1490
3	4-Hydroxy-5,6-dihydro-2H-pyran-2-one	33177-29-6	6	8	3	1200
4	5-(hydroxymethyl)-2-furaldehyde	200-654-9	6	6	3	1243
5	2-(4-hydroxy-3-methoxyphenyl)acetaldehyde	5703-24-2	9	10	3	1200
6	1-(4-hydroxy-3-methoxyphenyl)ethanone	207-854-5	9	10	3	1130
7	3-methylcyclopentane-1,2-dione	212-154-8	18	34	2	1000
8	3-(4-hydroxy-3-methoxyphenyl)acrylaldehyde	207-278-4	10	10	3	1200
9	acetoxyacetic acid	237-541-9	4	6	4	1300
10	2,2,4-trimethyl-1,3-dioxolane	214-766-0	6	12	2	897
11	2-methoxy-4-prop-1-en-1-ylphenol	202-590-7	10	12	2	1100
12	abieta-8,11,13-trien-18-oic acid	217-102-8	20	28	2	1000
13	ethyl 5-oxooxolane-2-carboxylate	1126-51-8	7	10	4	1200
14	(Furan-2-yl)methanol	202-626-1	5	6	2	1128
15	2-methoxy-4-methylphenol	202-252-9	8	10	2	1092
16	2,4-dimethylphenol	105-67-9	8	10	1	1015
17	4-ethyl-2-methoxyphenol	220-500-4	9	12	2	1100
18	4-hydroxy-3-methoxybenzaldehyde	121-33-5	8	8	3	1056
19	3-methylcyclopentane-1,2-dione	212-154-8	6	8	2	1100
20	(5-formyl-2-furyl)methyl acetate	234-137-4	8	8	4	1300
21	4-(ethoxymethyl)-2-methoxyphenol	236-136-4	10	14	3	1100
22	2-methoxy-4-propylphenol	220-499-0	10	14	2	1000
23	4-ethoxybutan-2-one	60044-74-8	6	12	2	920
24	Propanoic acid	201-176-3	3	6	2	988
25	2-hydroxyacetic acid	201-180-5	2	4	3	1490