Electronic Supplementary Material (ESI) for RSC Sustainability.

Supplementary information

Hydrothermal Liquefaction of Different Waste Biomass using Green Solvent 2-Methyltetrahydrofuran as Extractant and Co-Solvent

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Table S1. The list of products detected in GC-MS in TCM HTL under different reaction conditions.

Compounds	Extractant				Co-solvent				
	Under air		*Under CO_2*		*5 mL*	*10 mL*	*5 mL*		
	DCM	2-MeTHF	DCM	2-MeTHF	2-MeTHF	2-MeTHF	THF	1-BuOH	EtOH
Phenol	✓	✓	✓	✓	✓	✓	✓	✓	✓
3-Methyl-1,2-cyclopentanedione	✓	✓	✓	✓	✓	✓			✓
Guaiacol		✓			✓	✓		✓	✓
Syringol	✓	✓	✓	✓				✓	
Hexadecanoic acid	✓	✓		✓	✓		✓	✓	✓
Octadecanoic acid	✓	✓	✓	✓	✓	✓		✓	
9,12,15-Octadecatrienoic acid, (Z,Z,Z)-		✓	✓		✓	✓		✓	
Oleic acid	✓	✓	✓	✓	✓	✓	✓	✓	✓
Erucic acid	✓	✓	✓	✓	✓	✓	✓		✓
9-Octadecenamide, (Z)-	✓	✓	✓	✓	✓	✓	✓		✓
γ-Sitosterol	✓	✓			✓	✓		✓	
Stigmastan-3,5-diene		✓	✓	✓	✓	✓	✓	✓	
Hexadecanoic acid, butyl ester								✓	
Octadecanoic acid, butyl ester								✓	
Hexadecanoic acid, ethyl ester									✓
Octadecanoic acid, ethyl ester									✓
Linoleic acid ethyl ester									✓
Eicosanoic acid, ethyl ester									✓
Ethyl oleate									✓
13,17,21-Trimethyltritriacontane		✓		✓	✓		✓		✓

Table S2. The list of products detected in GC-MS in pine sawdust HTL under different reaction conditions.

Compounds	**Extractant**				**Co-solvent**				
	Under air		*Under CO_2*		*5 mL*	*10 mL*	*5 mL*		
	DCM	2-MeTHF	DCM	2-MeTHF	2-MeTHF	2-MeTHF	THF	1-BuOH	EtOH
Phenol	✓	✓	✓	✓	✓	✓	✓	✓	✓
3-Methyl-1,2-cyclopentanedione		✓		✓	✓	✓		✓	
3,4,5-Trimethyl-2-cyclopentene-1-one		✓		✓			✓		✓
Cresols	✓	✓	✓		✓	✓	✓		
Guaiacol		✓		✓	✓	✓		✓	✓
4-Methylguaiacol				✓	✓	✓			✓
Catechol		✓			✓	✓	✓		
4-Methylcatechol	✓	✓	✓		✓	✓	✓		
5-Hydroxymethylfurfural					✓	✓		✓	✓
4-Ethylguaiacol		✓			✓				
Acetovanillone	✓	✓	✓	✓	✓	✓	✓	✓	✓
Eugenol					✓			✓	
Vanillin	✓	✓	✓	✓	✓	✓	✓	✓	✓
Isoeugenol					✓	✓		✓	✓
4-Propylguaiacol		✓			✓	✓			
Butyl levulinate								✓	
Ethyl levulinate									✓

Table S3. The list of products detected in GC-MS in paper towel HTL under different reaction conditions.

Compounds	**Extractant**				**Co-solvent**				
	Under air		*Under CO_2*		*5 mL*	*10 mL*	*5 mL*		
	DCM	2-MeTHF	DCM	2-MeTHF	2-MeTHF	2-MeTHF	THF	1-BuOH	EtOH
3-Methyl-2-cyclopenten-1-one	✓	✓	✓	✓	✓	✓			
Phenol	✓	✓	✓	✓	✓	✓	✓	✓	✓
Dimethyl-2-Cyclopenten-1-ones	✓	✓	✓	✓	✓	✓	✓		✓
2-Hydroxy-3-methyl-2-cyclopenten-1-one					✓	✓	✓		
Methyl-1,2-cyclopentanedione								✓	✓
Cresols	✓	✓	✓	✓	✓	✓	✓		✓
Guaiacol			✓		✓			✓	✓
3-Ethyl-2-hydroxy-2-cyclopenten-1-one		✓	✓		✓	✓	✓	✓	✓
Catechol		✓		✓	✓	✓	✓	✓	✓
Methylcatechols	✓	✓	✓	✓	✓	✓	✓	✓	✓
Syringol	✓	✓	✓	✓	✓			✓	✓
Vanillin	✓	✓	✓	✓		✓	✓		
Syringaldehyde	✓	✓	✓	✓			✓		✓
Acetosyringone	✓	✓	✓	✓	✓	✓	✓		

Table S4. C, H, N, O wt % of bio-oils from HTL of different substrates under different conditions.

Entry	Substrate	Extraction solvent (mL)	Co-solvent (mL)	Processing atmosphere	C (%)	H (%)	N (%)	O (%)
1	TCM Residue	DCM	/	Air	78.7	10.5	1.7	9.1
2	TCM Residue	DCM	/	CO_2	74.5	8.4	2.9	14.2
3	TCM Residue	2-MeTHF	/	Air	76.5	10.7	2.2	10.6
4	TCM Residue	2-MeTHF	/	CO_2	78.3	11.0	0.8	9.9
5	TCM Residue	DCM	5 (2-MeTHF)	Air	74.9	9.1	2.9	13.1
6	TCM Residue	DCM	10 (2-MeTHF)	Air	75.4	9.4	1.7	13.5
7	TCM Residue	DCM	5 (THF)	Air	73.4	9.6	2.9	14.1
8	TCM Residue	DCM	5 (1-BuOH)	Air	73.4	7.9	3.1	15.7
9	TCM Residue	DCM	5 (EtOH)	Air	74.6	9.1	2.7	13.6
10	Pine Sawdust	DCM	/	Air	68.4	6.4	0.0	25.2
11	Pine Sawdust	DCM	/	CO_2	69.2	6.3	0.0	24.5
12	Pine Sawdust	DCM	/	N_2	68.0	6.8	0.0	25.2
13	Pine Sawdust	2-MeTHF	/	Air	70.2	6.7	0.0	23.1
14	Pine Sawdust	2-MeTHF	/	CO_2	67.4	5.6	0.0	27.0
15	Pine Sawdust	2-MeTHF	/	N_2	65.8	6.5	0.3	27.4
16	Pine Sawdust	DCM	5 (2-MeTHF)	Air	71.6	7.8	0.2	20.4
17	Pine Sawdust	DCM	10 (2-MeTHF)	Air	69.0	7.3	0.3	23.4
18	Pine Sawdust	DCM	5 (THF)	Air	69.5	6.4	0.0	24.1
19	Pine Sawdust	DCM	5 (1-BuOH)	Air	68.8	6.7	0.0	24.5

20	Pine Sawdust	DCM	5 (EtOH)	Air	69.8	5.7	0.0	24.5
^21	Pine Sawdust	DCM	/	Air	69.2	6.9	0.0	23.9
^22	Pine Sawdust	2-MeTHF	/	Air	64.2	6.7	0.1	29.0
23	Paper Towel	DCM	/	Air	70.1	7.0	0.3	22.6
24	Paper Towel	DCM	/	CO_2	71.5	7.2	0.1	21.2
25	Paper Towel	2-MeTHF	/	Air	65.2	7.0	0.1	27.7
26	Paper Towel	2-MeTHF	/	CO_2	66.6	7.3	0.4	25.7
27	Paper Towel	DCM	5 (2-MeTHF)	Air	69.8	7.4	0.4	22.4
28	Paper Towel	DCM	10 (2-MeTHF)	Air	71.2	7.3	0.2	21.3
29	Paper Towel	DCM	5 (THF)	Air	70.3	7.2	0.2	22.3
30	Paper Towel	DCM	5 (1-BuOH)	Air	68.3	6.6	0.0	25.0
31	Paper Towel	DCM	5 (EtOH)	Air	68.8	6.7	0.0	24.5

^30mL of 0.1M NaOH was used.

Table S5. Percentage change in biocrude yield and HHV when comparing the extraction performance of DCM and 2-MeTHF.

Entry	Substrate	Extraction solvent	Processing atmosphere	Biocrude (%)	% change (% [N#])	HHV (MJ kg^{-1})	% change (% [N#])
1	TCM Residue	DCM	Air	10.1		39.7	
2	TCM Residue	DCM	CO_2	10.7		34.3	
3	TCM Residue	2-MeTHF	Air	11.6	+40.2 [1]	38.9	-2.0 [1]
4	TCM Residue	2-MeTHF	CO_2	13.7	+28.0 [2]	40.2	+17.2 [2]
5	Pine Sawdust	DCM	Air	22.8		28.1	
6	Pine Sawdust	DCM	CO_2	19.2		28.4	
7	Pine Sawdust	DCM	N_2	9.7		28.6	
8	Pine Sawdust	2-MeTHF	Air	28.1	+23.2 [5]	29.4	+4.6 [5]
9	Pine Sawdust	2-MeTHF	CO_2	30.8	+60.4 [6]	26.5	-6.7 [6]
10	Pine Sawdust	2-MeTHF	N_2	18.9	+94.8 [7]	27.0	-5.6 [7]
11^	Pine Sawdust	DCM	Air	27.9		29.3	
12^	Pine Sawdust	2-MeTHF	Air	37.2	+33.3 [11]	26.6	-9.2 [11]
13	Paper Towel	DCM	Air	16.9		30.0	
14	Paper Towel	DCM	CO_2	24.2		30.9	
15	Paper Towel	2-MeTHF	Air	23.1	+36.7 [13]	27.6	-8.0 [13]
16	Paper Towel	2-MeTHF	CO_2	25.2	+4.1 [14]	28.7	-7.1 [14]

^30mL of 0.1M NaOH solution was used instead of water.
#N = number of entry comparing to

Table S6. Percentage hydrogen distribution of biocrudes from HTL of TCM residue, pine sawdust and paper towel using DCM or 2-MeTHF as the extraction solvent.

Entry	Substrate	Extraction solvent	Processing atmosphere	Saturated C–H (0–3.5 ppm)	O–R (3.5–4.5 ppm)	Unsaturated C–H & PhOH (4.5–8.5 ppm)	RCHO & RCOOH (>9 ppm)
1	TCM Residue	DCM	Air	77.5%	5.4%	16.3%	0.8%
2	TCM Residue	DCM	CO_2	82.0%	4.1%	14.0%	0.0%
3	TCM Residue	2-MeTHF	Air	82.1%	3.4%	14.5%	0.0%
4	TCM Residue	2-MeTHF	CO_2	77.6%	4.1%	18.4%	0.0%
5	Pine Sawdust	DCM	Air	57.1%	12.6%	28.0%	2.3%
6	Pine Sawdust	DCM	CO_2	50.5%	13.7%	34.8%	1.1%
7	Pine Sawdust	DCM	N_2	71.4%	5.0%	22.9%	0.7%
8	Pine Sawdust	2-MeTHF	Air	55.0%	6.0%	38.0%	1.0%
9	Pine Sawdust	2-MeTHF	CO_2	59.6%	6.1%	33.4%	1.0%
10	Pine Sawdust	2-MeTHF	N_2	59.9%	8.4%	31.1%	0.6%
11^	Pine Sawdust	DCM	Air	62.9%	13.2%	23.9%	0.0%
12^	Pine Sawdust	2-MeTHF	Air	57.4%	9.0%	33.7%	0.0%
13	Paper Towel	DCM	Air	70.1%	9.7%	20.1%	0.0%
14	Paper Towel	2-MeTHF	Air	68.0%	9.5%	22.5%	0.0%
15	Paper Towel	DCM	CO_2	71.9%	7.4%	19.8%	0.8%
16	Paper Towel	2-MeTHF	CO_2	71.3%	7.0%	21.7%	0.0%

Table S7. Percentage change in biocrude yield and HHV when 2-MeTHF, THF, 1-BuOH or EtOH was used as the co-solvent.

Entry	Substrate	Co-solvent (mL)	Biocrude (%)	% change (% [N#])	HHV (MJ kg^{-1})	% change (% [N#])
1	TCM Residue	/	10.1		39.7	
2	TCM Residue	5 (2-MeTHF)	15.0	+48.5 [1]	35.6	-10.3 [1]
3	TCM Residue	10 (2-MeTHF)	18.1	+79.2 [1]	36.3	-8.6 [1]
4	TCM Residue	5 (THF)	11.8	-27.1 [2]	35.9	+0.8 [2]
5	TCM Residue	5 (1-BuOH)	23.4	+56.0 [2]	32.6	-8.4 [2]
6	TCM Residue	5 (EtOH)	10.8	-28.0 [2]	35.4	-0.6 [2]
7	Pine Sawdust	/	22.8		28.1	
8	Pine Sawdust	5 (2-MeTHF)	35.4	+55.3 [7]	31.9	+13.5 [7]
9	Pine Sawdust	10 (2-MeTHF)	50.9	+123.2 [7]	29.9	+6.4 [7]
10	Pine Sawdust	5 (THF)	24.2	-46.3 [8]	28.7	-11.1 [8]
11	Pine Sawdust	5 (1-BuOH)	30.7	-13.3 [8]	28.8	-9.7 [8]
12	Pine Sawdust	5 (EtOH)	22.1	-37.6 [8]	27.8	-12.9 [8]
13	Paper Towel	/	16.9		30.0	
14	Paper Towel	5 (2-MeTHF)	21.0	+24.3 [13]	30.4	+1.3 [13]
15	Paper Towel	10 (2-MeTHF)	29.3	+73.4 [13]	30.9	+3.0 [13]
16	Paper Towel	5 (THF)	16.9	-24.3 [14]	30.3	-0.3 [14]
17	Paper Towel	5 (1-BuOH)	20.4	-2.9 [14]	28.5	-6.3 [14]
18	Paper Towel	5 (EtOH)	17.0	-19.0 [14]	28.8	-5.3 [14]

#N = number of entry comparing to

Table S8. Percentage hydrogen distribution of biocrudes from HTL of TCM residue, pine sawdust and paper towel using 2-MeTHF, THF, 1-BuOH or EtOH as the co-solvent.

Entry	Substrate	Co-solvent (mL)	Saturated C–H (0–3.5 ppm)	O–R (3.5–4.5 ppm)	Unsaturated C–H & PhOH (4.5–8.5 ppm)	RCHO & RCOOH (>9 ppm)
1	TCM Residue	/	77.5%	5.4%	16.3%	0.8%
2	TCM Residue	2-MeTHF (5)	72.4%	5.1%	21.4%	1.0%
3	TCM Residue	2-MeTHF (10)	71.8%	4.5%	23.6%	0.0%
4	TCM Residue	THF (5)	75.5%	4.9%	18.6%	1.0%
5	TCM Residue	1-BuOH (5)	80.8%	5.0%	14.1%	0.0%
6	TCM Residue	EtOH (5)	79.5%	4.1%	16.4%	0.0%
7	Pine Sawdust	/	57.1%	12.6%	28.0%	2.3%
8	Pine Sawdust	2-MeTHF (5)	55.8%	8.0%	36.6%	1.1%
9	Pine Sawdust	2-MeTHF (10)	52.1%	7.9%	38.9%	1.0%
10	Pine Sawdust	THF (5)	48.5%	10.7%	38.2%	2.6%
11	Pine Sawdust	1-BuOH (5)	54.1%	12.8%	32.7%	0.4%
12	Pine Sawdust	EtOH (5)	53.8%	14.5%	30.1%	1.6%
13	Paper Towel	/	70.1%	9.7%	20.1%	0.0%
14	Paper Towel	2-MeTHF (5)	72.5%	6.5%	21.0%	0.0%
15	Paper Towel	2-MeTHF (10)	71.4%	7.9%	20.7%	0.0%
16	Paper Towel	THF (5)	69.4%	8.3%	22.2%	0.0%
17	Paper Towel	1-BuOH (5)	70.9%	8.7%	20.5%	0.0%
18	Paper Towel	EtOH (5)	72.1%	8.6%	25.8%	0.0%

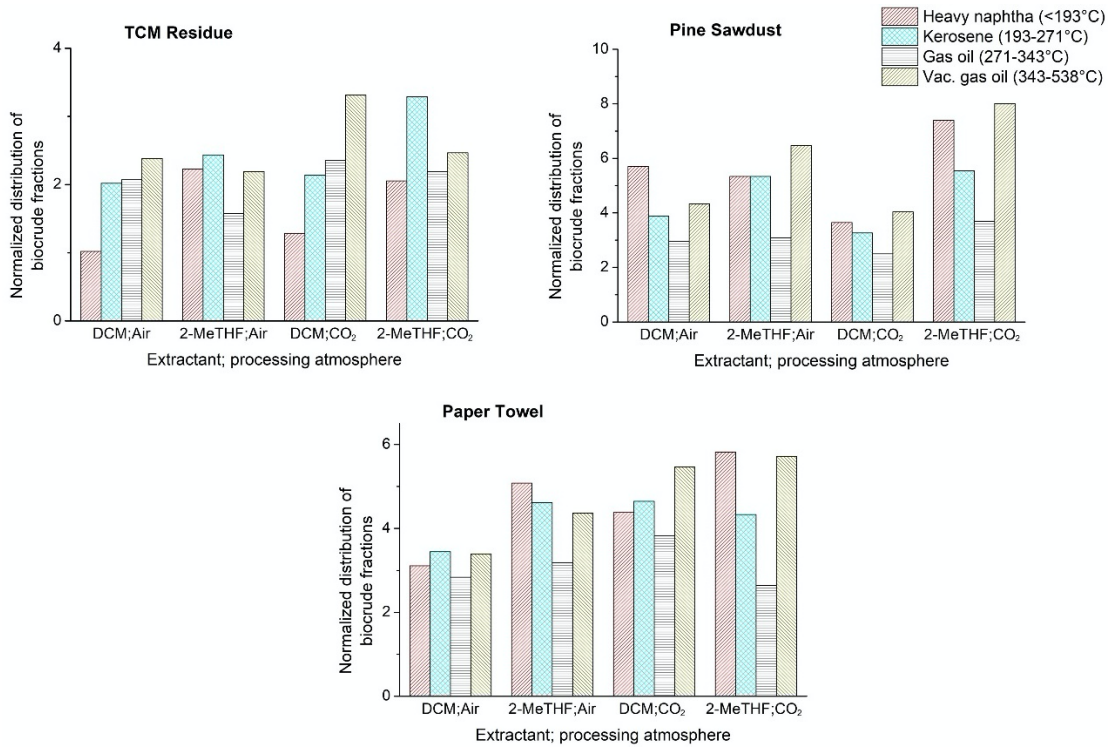

Fig. S1. Normalized distribution of biocrude fractions for TCM residue, pine sawdust and paper towel by using DCM or 2-MeTHF as extractant.

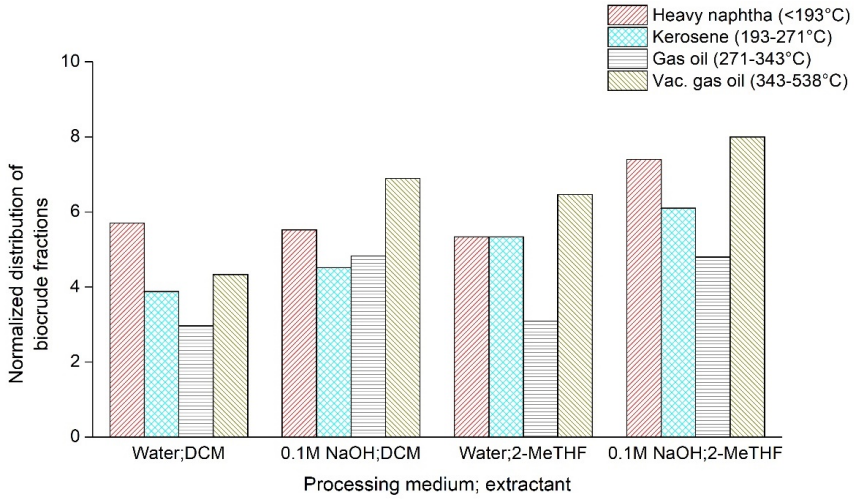

Fig. S2. Normalized distribution of biocrude fractions for HTL of TCM residue, pine sawdust and paper towel over 0.1 M NaOH catalyst.

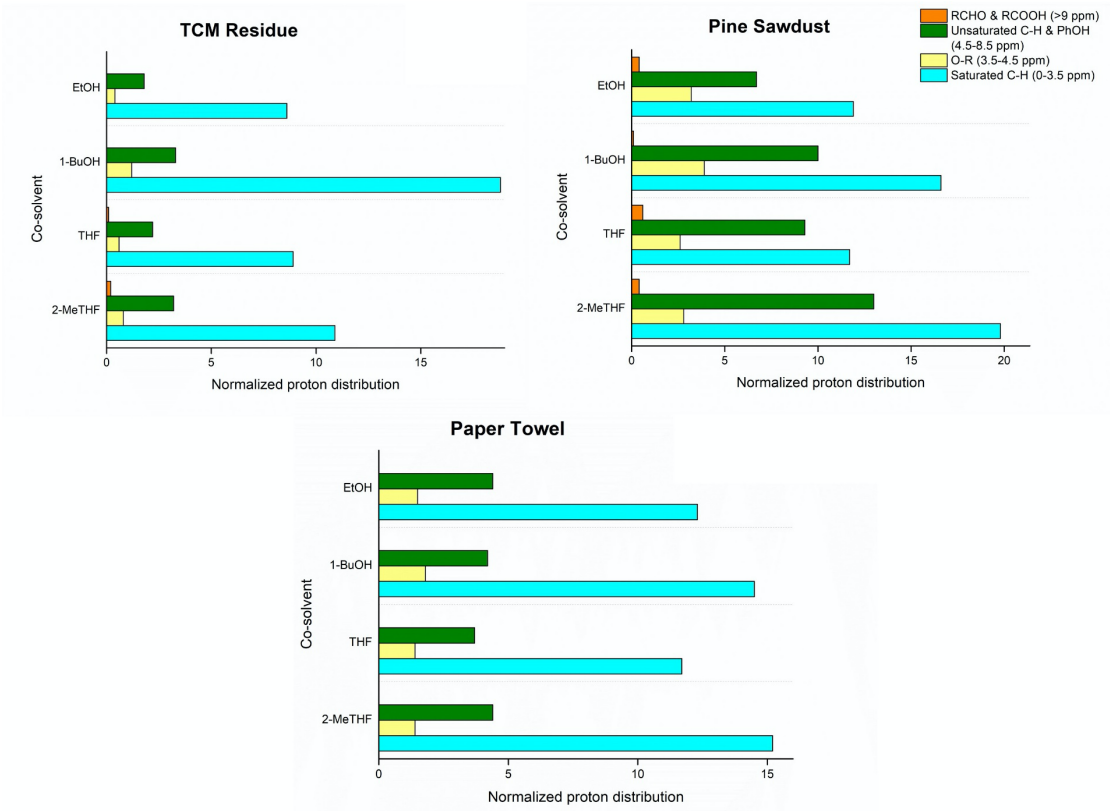

Fig. S3. Normalized distribution of biocrude fractions for HTL of TCM residue, pine sawdust and paper towel with 2-MeTHF, THF, 1-BuOH or EtOH as the co-solvents (5 mL).

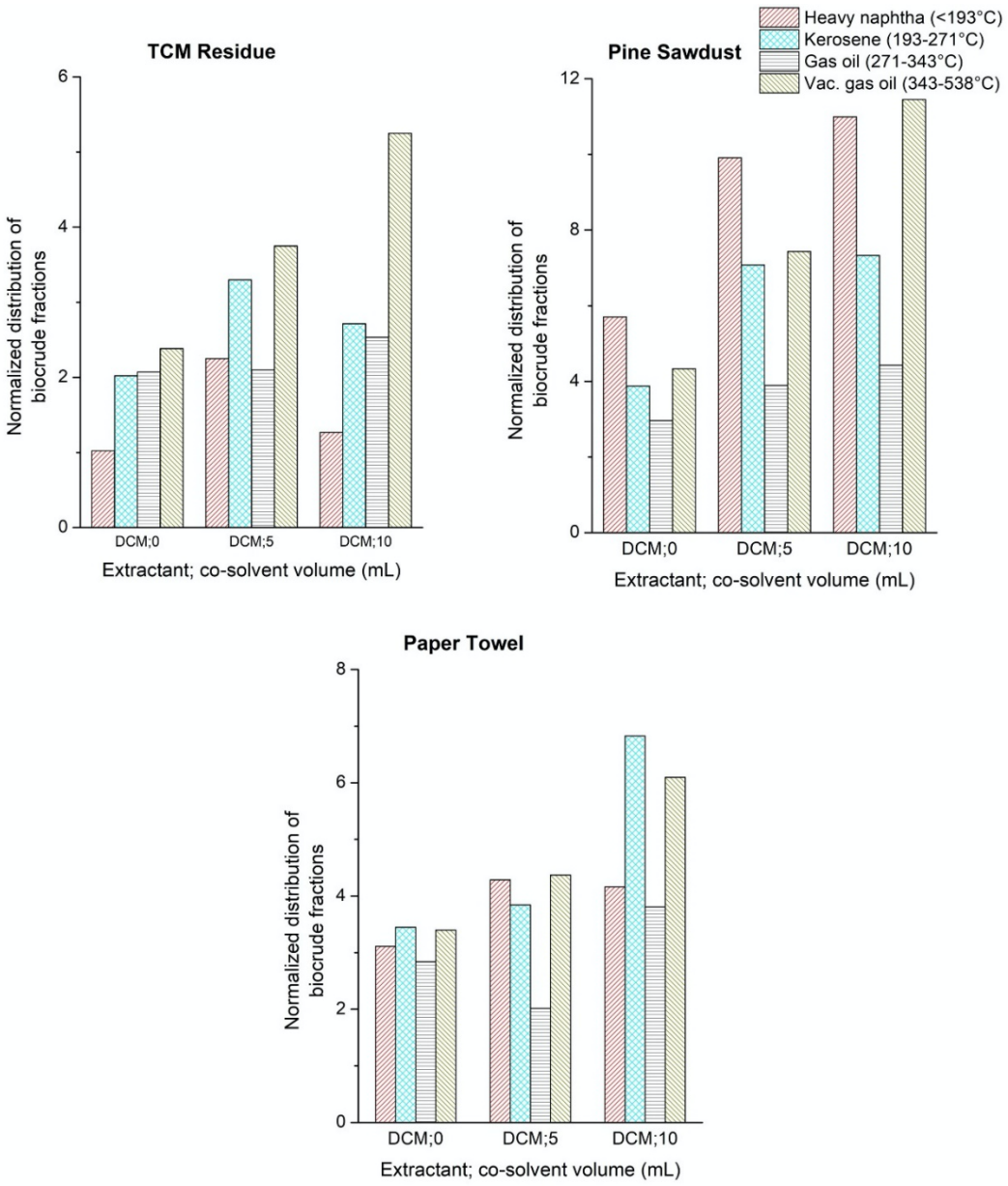

Fig. S4. Normalized distribution of biocrude fractions for HTL of TCM residue, pine sawdust and paper towel with increasing amount of 2-MeTHF co-solvent.

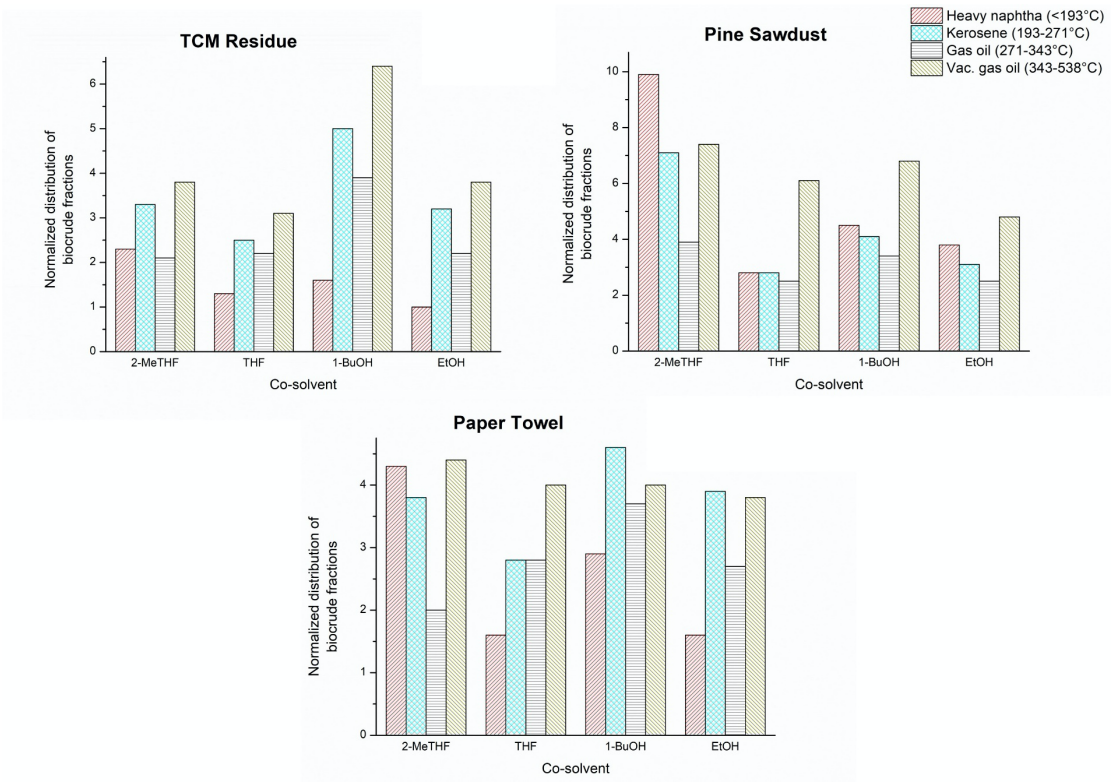

Fig. S5. Normalized distribution of biocrude fractions for HTL of TCM residue, pine sawdust and paper towel with 2-MeTHF, THF, 1-BuOH or EtOH as the co-solvents (5 mL).