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ELECTRONIC SUPPORTING INFORMATION (ESI)

Experimental-Based Mechanistic Study and Optimization of Hydrothermal Liquefaction of Anaerobic Digestates

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Table S1. Compositions of Pre-selected Model Compounds (in g/200 mL water) in Synthetic Anaerobic Digestate Mixtures for Each Experiment

Experiment Number	Cellulose	Lignin	NH_4-Ac	GA	Inorganics				Estimated Ash Content[a]	AcOH	NaOH
					DCPD	KCl	$CaCO_3$	$MgCO_3$			
1	9.3	6.7	4	2.5	1.0	1.30	0.58	1.13	15.09%	18	0
2	6.0	10.0	4	2.5	1.0	1.30	0.58	1.13	15.09%	18	0
3	6.0	10.0	4	2.5	1.0	1.30	0.58	1.13	15.09%	18	0
4	9.3	6.7	4	2.5	1.0	1.30	0.58	1.13	15.09%	18	0
5	6.0	10.0	4	2.5	1.0	1.30	0.58	1.13	15.09%	0	0
6	9.3	6.7	4	2.5	1.0	1.30	0.58	1.13	15.09%	0	0
7	9.3	6.7	4	2.5	1.0	1.30	0.58	1.13	15.09%	0	0
8	6.0	10.0	4	2.5	1.0	1.30	0.58	1.13	15.09%	0	0
9	6.0	10.0	4	2.5	2.0	2.59	1.16	2.25	26.23%	18	0
10	9.3	6.7	4	2.5	2.0	2.59	1.16	2.25	26.23%	18	0
11	9.3	6.7	4	2.5	2.0	2.59	1.16	2.25	26.23%	18	0
12	6.0	10.0	4	2.5	2.0	2.59	1.16	2.25	26.23%	18	0
13	9.3	6.7	4	2.5	2.0	2.59	1.16	2.25	26.23%	0	0
14	6.0	10.0	4	2.5	2.0	2.59	1.16	2.25	26.23%	0	0
15	6.0	10.0	4	2.5	2.0	2.59	1.16	2.25	26.23%	0	0
16	9.3	6.7	4	2.5	2.0	2.59	1.16	2.25	26.23%	0	0
17	8.0	8.0	4	2.5	1.5	1.94	0.87	1.69	21.05%	8	0
18	8.0	8.0	4	2.5	1.5	1.94	0.87	1.69	21.05%	8	0
19	8.0	8.0	4	2.5	1.5	1.94	0.87	1.69	21.05%	8	0
20	8.0	8.0	4	2.5	1.5	1.94	0.87	1.69	21.05%	8	0
21	8.0	8.0	4	2.5	1.5	1.94	0.87	1.69	21.05%	40	0
22	8.0	8.0	4	2.5	1.5	1.94	0.87	1.69	21.05%	0	0.5
23	8.0	8.0	4	2.5	0.5	0.65	0.29	0.56	8.16%	8	0
24	8.0	8.0	4	2.5	2.5	3.24	1.45	2.82	30.77%	8	0
25	2.7	13.3	4	2.5	1.5	1.94	0.87	1.69	21.05%	8	0
26	10.3	5.7	4	2.5	1.5	1.94	0.87	1.69	21.05%	8	0
27	8.0	8.0	4	2.5	1.5	1.94	0.87	1.69	21.05%	8	0
28	8.0	8.0	4	2.5	1.5	1.94	0.87	1.69	21.05%	8	0
29	8.0	8.0	4	2.5	1.5	1.94	0.87	1.69	21.05%	8	0
30	8.0	8.0	4	2.5	1.5	1.94	0.87	1.69	21.05%	8	0
31	8.0	8.0	4	2.5	1.5	1.94	0.87	1.69	21.05%	8	0
32	8.0	8.0	4	2.5	1.5	1.94	0.87	1.69	21.05%	8	0

[a]Estimated ash content = (total weight of inorganics) / (total weight of dry solid feedstock)

Table S2. Half-Fractional Central Composite Design Matrix for HTL Experiments

Experiment Number	Run Order	Temperature (°C)	Reaction Time (min)	Feedstock pH	Salt content, wt%	Cel/Lig, g/g
1	26	300	20	4	2	1.4
2	20	340	20	4	2	0.6
3	4	300	40	4	2	0.6
4	7	340	40	4	2	1.4
5	14	300	20	7	2	0.6
6	23	340	20	7	2	1.4
7	9	300	40	7	2	1.4
8	11	340	40	7	2	0.6
9	18	300	20	4	4	0.6
10	1	340	20	4	4	1.4
11	28	300	40	4	4	1.4
12	32	340	40	4	4	0.6
13	16	300	20	7	4	1.4
14	12	340	20	7	4	0.6
15	3	300	40	7	4	0.6
16	21	340	40	7	4	1.4
17	25	280	30	5.5	3	1
18	6	360	30	5.5	3	1
19	5	320	10	5.5	3	1
20	13	320	50	5.5	3	1
21	29	320	30	2.5	3	1
22	19	320	30	8.5	3	1
23	24	320	30	5.5	1	1
24	15	320	30	5.5	5	1
25	27	320	30	5.5	3	0.2
26	30	320	30	5.5	3	1.8
27	17	320	30	5.5	3	1
28	31	320	30	5.5	3	1
29	8	320	30	5.5	3	1
30	22	320	30	5.5	3	1
31	2	320	30	5.5	3	1
32	10	320	30	5.5	3	1

Table S3. Statistics for regression models of biocrude yield and energy recovery

Term	$Y_{oil,daf}$ (%)		$C_{yield\text{-}oil}$ (%)		ER_{oil} (%)		ΔpH_{liq}	
	Coded Coef.	*p*	Coded Coef.	*p*	Coded Coef.	*p*	Coded Coef.	*p*
Constant	40.06303	0.000	69.46077	0.000	66.46327	0.000	-0.56600	0.000
T	2.38999	0.000	5.78888	0.000	6.57667	0.000	-0.03300	0.000
t	-	-	-	-	1.65828	0.033	-0.02100	0.033
pH	-6.66426	0.000	-8.94008	0.000	-9.52902	0.000	-0.49083	0.000
Salt	-4.88278	0.000	-4.27239	0.000	-4.03354	0.000	0.19333	0.000
Cel/Lig	1.50805	0.000	3.95997	0.000	3.37738	0.000	-0.20366	0.000
T^2	-1.18775	0.001	-2.30456	0.007	-2.09009	0.004	-0.09900	0.004
pH^2	-6.25438	0.000	-11.63554	0.000	-10.85220	0.000	0.14350	0.002
pH x Cel/Lig	1.46132	0.003	2.35814	0.036	-	-	-0.21300	0.001
R^2	97.59%		94.68%		96.07%		89.41%	
R^2 *(pred)*	93.57%		88.31%		91.00%		73.92%	
Lack-of-fit's p	0.173		0.190		0.300		0.206	
Center point	39.99% ± 0.99%		70.67% ± 1.70%		67.51% ± 1.63%		67.51% ± 1.63%	

Table S4. Statistics for regression models of nutrient yield in HTL aqueous coproduct

Term	P_{AP} (%)		NH_3-N_{AP} (%)		Mg_{AP} (%)		Ca_{AP} (%)	
	Coded Coef.	*p*	Coded Coef.	*p*	Coded Coef.	*p*	Coded Coef.	*p*
Constant	17.02733	0.000	34.92830	0.000	64.54000	0.000	32.41632	0.000
T	0.76565	0.254	-0.87824	0.127	1.54020	0.385	-1.91744	0.003
t	-0.32975	0.619	-0.58389	0.303	-0.75001	0.587	-0.67002	0.250
pH	-12.67306	0.000	-4.33216	0.000	-11.80399	0.000	-8.55227	0.000
Salt	-5.80657	0.000	-	-	-6.620	0.000	-2.52303	0.000
Cel/Lig	5.70779	0.000	-2.92406	0.000	-	-	2.33127	0.000
T^2	-	-	2.68717	0.000	-5.36412	0.000	-	-
t^2	-	-	2.10981	0.000	-2.53979	0.020	-	-
pH^2	7.62380	0.000	1.04091	0.049	-	-	-1.77271	0.002
Cel/Lig^2	-	-	-2.21937	0.000	-	-	-	-
T x t	2.67664	0.003	-1.45329	0.044	-	-	2.21839	0.004
T x pH	-	-	1.90960	0.010	-	-	-	-
pH x Salt	4.98428	0.000	-	-	7.79401	0.000	-1.98846	0.009
pH x Cel/Lig	-4.80525	0.000	-	-	-	-	-	-
Salt x Cel/Lig	-4.06916	0.000	-	-	-	-	-2.22216	0.004
R^2	97.49%		89.51%		89.77%		93.53%	
R^2 *(pred)*	93.21%		67.58%		79.29%		80.21%	
Lack-of-fit's p	0.254		0.505		0.385		0.085	
Center point	19.69% ± 0.85%		34.12% ± 2.62%		64.54% ± 2.82%		32.06% ± 1.62%	

Table S5. Statistics for regression models of heteroatom content in DWO and DSO biocrudes

Term	$\%O_{oil\text{-}DWO}$		$\%O_{oil\text{-}DSO}$		$\%N_{oil\text{-}DWO}$		$\%N_{oil\text{-}DSO}$	
	Coded Coef.	*p*	Coded Coef.	*p*	Coded Coef.	*p*	Coded Coef.	*p*
Constant	60.34103	0.000	22.89199	0.000	4.20000	0.000	2.11544	0.000
T	-2.70542	0.000	-1.32374	0.001	0.04958	0.019	0.05749	0.000
t	-1.29875	0.033	-1.12543	0.003	0.05792	0.014	0.02918	0.033
pH	-0.52250	0.000	-1.60043	0.000	0.03583	0.038	0.37251	0.000
Salt	-0.94750	0.064	-0.84374	0.022	0.12500	0.002	0.02499	0.064
Cel/Lig	-0.18750	0.000	-1.58959	0.000	0.14333	0.000	0.23668	0.000
T^2	-	-	-	-	-0.59026	0.000	-0.25688	0.000
t^2	-	-	-	-	-0.56776	0.000	-0.24438	0.000
pH^2	1.21535	0.000	0.87478	0.010	-	-	-	-
$Salt^2$	-	-	-	-	0.24214	0.001	0.20687	0.000
T x t	-0.11188	0.000	-0.81302	0.064	-	-	-	-
T x Salt	-0.22438	0.000	-0.83811	0.027	-	-	-	-
t x pH	0.01562	0.000	0.79804	0.039	-	-	-	-
t x Cel/Lig	0.44750	0.000	0.95903	0.046	-	-	-	-
pH x Salt	-	-	-	-	0.01563	0.048	0.03623	0.031
pH x Cel/Lig	0.28375	0.000	1.08300	0.017	-	-	-	-
Salt x Cel/Lig	0.25000	0.000	0.77899	0.041	-	-	-	-
R^2	83.44%		85.63%		90.01%		99.14%	
R^2 *(pred)*	75.29%		76.55%		65.98%		97.48%	
Lack-of-fit's p	0.335		0.363		0.340		0.452	
Center point	33.32% ± 1.13%		22.85% ± 0.48%		4.53% ± 0.32%		2.12% ± 0.06%	

Table S6. Operating Conditions for GC-MS Analysis

Operating conditions	Details
Column:	DB-5 MS+DG capillary column (30 m × 0.25 mm, 0.25 μm film thickness and a 10 m DuraGuard guard column section)
Carrier:	Helium (1.5 ml/min)
Sample injected:	1 μl of dichloromethane-dissolved biocrude
Split mode:	1:50
Oven temperature:	40ºC hold 5 min, 5ºC/min to 170ºC, hold 5 min, 5ºC/min to 300ºC, hold 5 min (67 min run time)
MS operation:	*m/z* from 33 to 500 with 3 scan/s
Spectra analysis:	TSSPro 3.0 (Shrader) and the NIST 20 Mass Spectral Library for chemical compound identification

Table S7. GC-MS Results for Selected Biocrude Oil Samples

Components	RT (min)	Area% - DSO Biocrudes						Area% - DWO Biocrudes					
		pH 5.5 (Exp 27)	pH 8.5 (Exp 22)	Salt 5% (Exp 24)	360 °C (Exp 18)	50 min (Exp 20)	Cel/Lig 0.2 (Exp 25)	pH 5.5 (Exp 27)	pH 8.5 (Exp 22)	Salt 5% (Exp 24)	360 °C (Exp 18)	50 min (Exp 20)	Cel/Lig 0.2 (Exp 25)
2-Cyclopenten-1-one, 2-methyl-	7.23			3.88%		7.58%	2.42%	5.32%	8.23%		9.39%	5.93%	
2-Cyclopenten-1-one, 3-methyl-	8.55	6.33%	3.77%			3.82%	3.15%			4.56%	4.67%		
2-Cyclopenten-1-one, 2,3-dimethyl-	10.17	4.50%			11.02%					3.12%			4.65%
2-Cyclopenten-1-one, 3-ethyl-	10.91		4.13%	4.37%		3.57%	2.38%	4.58%					
Butyrolactone	23.59	1.67%	2.34%	1.62%									
Cyclohexanone, 5-methyl-2-(1-methylethyl)-	33.89	6.35%			9.45%	4.30%	5.45%						
Carvone	36.78		3.76%	3.03%		3.03%		7.40%					
2-Cyclohexen-1-one, 3-methyl-6-(1-methylethyl)-	37.26										6.54%	13.07%	10.35%
2H-Pyran-2-one, tetrahydro-	25.90								4.97%	3.92%			
2H-1-Benzopyran-2-one, 3,5,7-trihydroxy-	33.81	2.65%			3.03%								
Subtotal Ketones		***21.50%***	***14.00%***	***12.90%***	***23.50%***	***22.30%***	***13.40%***	***17.30%***	***13.20%***	***11.60%***	***20.60%***	***19.00%***	***15.00%***
2-Furanmethanol	20.86	4.99%					3.33%						
Furan, 2,5-diethyltetrahydro-	23.16	4.75%			7.36%	3.56%							
2(5H)-Furanone	23.40							12.67%			13.40%	16.00%	
2-Furancarboxaldehyde, 5-methyl-	26.18								8.40%	10.80%			
Dihydrofuranno(3,2-f) coumaran	26.62		6.00%	7.20%			4.14%						
3,7-Benzofurandiol, 2,3-dihydro-2,2-dimethyl-	27.14						2.23%						
Furan, 2-pentyl-	27.39	7.26%			3.64%	6.04%							
Benzofuran, 2,3-dihydro-	35.63							7.93%					9.50%
Subtotal Furans		***17.00%***	***6.00%***	***7.20%***	***11.00%***	***9.60%***	***9.70%***	***20.60%***	***8.40%***	***10.80%***	***13.40%***	***16.00%***	***9.50%***
1H-Pyrrole, 1-methyl-	13.77		3.98%					2.06%	5.24%		0.66%		

Components	RT (min)	Area% - DSO Biocrudes						Area% - DWO Biocrudes					
		pH 5.5 (Exp 27)	pH 8.5 (Exp 22)	Salt 5% (Exp 24)	360 °C (Exp 18)	50 min (Exp 20)	Cel/Lig 0.2 (Exp 25)	pH 5.5 (Exp 27)	pH 8.5 (Exp 22)	Salt 5% (Exp 24)	360 °C (Exp 18)	50 min (Exp 20)	Cel/Lig 0.2 (Exp 25)
1H-Pyrrole, 3-methyl-	19.94	1.07%	2.92%	5.37%		0.41%	1.13%						
1H-Pyrazole	20.69								2.16%	10.00%			
Ethanone, 1-(1H-pyrrol-2-yl)-	29.96	2.30%				0.45%	1.07%						
Pyrrolidine, 1-methyl-	31.63	1.63%			1.43%	1.63%							
Pyrrolidone, 1-methyl	32.61				0.75%	0.91%		2.24%			0.84%	2.40%	3.40%
Carbazole	33.86			3.63%	0.22%								
Subtotal Pyrroles		***5.00%***	***6.90%***	***9.00%***	***2.40%***	***3.40%***	***2.20%***	***4.30%***	***7.40%***	***10.00%***	***1.50%***	***2.40%***	***3.40%***
2,5-Piperazinedione, 3,6-bis(2-methylpropyl)-	10.31	1.27%			1.80%	1.07%							
Pyrimidine	17.16		4.72%	3.22%			2.58%						
Piperidine	21.63										2.20%	1.30%	
Pyridine, 3-Amino-2,6-dimethoxy-	22.64		3.96%			0.53%	1.38%						
Pyrazine, ethyl	24.55								3.69%	4.19%			
2,8-Dimethyl-indolizine	26.24	1.73%											
Pyrazinamide	28.59							2.70%	4.47%				
Pyrazine, 2-ethenyl-5-methyl-	28.68								2.56%	2.60%			
Ethanone, 1-(2-pyridinyl)-	29.15		2.51%	5.15%			1.24%						
Pyrazine, 2-ethyl-3,5-dimethyl-	30.57		1.36%	2.01%									
Pyrazine, 3-ethyl-2,5-dimethyl-	30.72								4.78%	9.11%			
Pyrazine, 2,3-Dimethyl-5-ethyl-	30.89		1.55%	1.82%									
Caprolactam	18.53	2.82%				3.81%							
Subtotal Pyridines & Pyrazines		***5.82%***	***14.10%***	***12.20%***	***1.80%***	***5.41%***	***5.20%***	***2.70%***	***15.50%***	***15.90%***	***2.20%***	***1.30%***	***0.00%***
Oxirane, 2-methyl-2-phenyl-	12.60								10.09%	4.59%			
3-Methylguaiacol	20.56	0.94%		5.55%	1.66%	3.56%						2.39%	3.49%
Benzenemethanol, 4-hydroxy-	21.23	3.89%			3.06%	2.00%	3.53%						
4-Methylguaiacol	21.44							1.44%	5.51%	4.75%			8.52%

Components	RT (min)	Area% - DSO Biocrudes						Area% - DWO Biocrudes					
		pH 5.5 (Exp 27)	pH 8.5 (Exp 22)	Salt 5% (Exp 24)	360 °C (Exp 18)	50 min (Exp 20)	Cel/Lig 0.2 (Exp 25)	pH 5.5 (Exp 27)	pH 8.5 (Exp 22)	Salt 5% (Exp 24)	360 °C (Exp 18)	50 min (Exp 20)	Cel/Lig 0.2 (Exp 25)
Phenol, 4-ethyl-2-methoxy-	23.69	1.12%									1.67%		
Phenol, 3-ethyl-5-methyl-	24.91				2.11%	2.59%	3.94%						
2-Phenylacetaldehyde	25.62	1.01%			1.40%		1.00%						
Phenol, 2-methoxy-methyl-ethyl-	25.87							3.65%			4.06%		7.29%
Phenol, 2,6-dimethoxy-	26.52				1.71%	2.20%							
4-Chlorodiphenyl ether	30.98		5.95%	4.79%									
Benzaldehyde, 4-hydroxy-	31.42				1.00%		3.67%						4.00%
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	32.05	1.05%		2.49%									
3-Methoxy-4-hydroxybenzyl methyl ether	32.24							2.55%				5.85%	
Oxirane, (phenoxymethyl)-	32.95		5.55%	2.47%						5.76%			
4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol	33.05							3.85%			6.77%		
2-Methoxy-4-vinylphenol	38.39		6.00%				1.22%						
1,3,5-Benzenetriol	38.45	2.10%					3.64%		4.70%	2.40%			
1,3-Benzodioxane-5-ol	39.19							4.51%			2.00%	7.36%	
1,3-Benzodioxole, 5-(1-propenyl)-	41.56	3.89%			3.56%	4.35%	4.60%						
Subtotal Phenols		***14.00%***	***17.50%***	***15.30%***	***14.50%***	***14.70%***	***21.60%***	***16.00%***	***20.30%***	***17.50%***	***14.50%***	***15.60%***	**23.30%**
Butanoic acid, 2-methyl-, methyl ester	16.40	4.60%	5.00%		4.46%								
Butanoic acid, ethyl ester	17.53								2.72%	5.20%		4.62%	
1-Butanol, 3-methyl-, acetate	22.16								1.28%				4.60%
Chloroacetic acid, 2-naphthyl ester	27.41	2.10%			5.54%								
3-Methyl-4-propyl-2,4-hexadienedioic acid dimethyl ester	28.76							11.20%			10.30%	4.58%	

Components	RT (min)	Area% - DSO Biocrudes						Area% - DWO Biocrudes					
		pH 5.5 (Exp 27)	pH 8.5 (Exp 22)	Salt 5% (Exp 24)	360 °C (Exp 18)	50 min (Exp 20)	Cel/Lig 0.2 (Exp 25)	pH 5.5 (Exp 27)	pH 8.5 (Exp 22)	Salt 5% (Exp 24)	360 °C (Exp 18)	50 min (Exp 20)	Cel/Lig 0.2 (Exp 25)
3,4-dimethoxy-mandelic acid methyl ester	28.96	1.17%		8.00%			5.00%						
Pentanedioic acid, 2-methyl-, dimethyl ester	32.89	1.13%				7.00%							
Subtotal Esters		***9.00%***	***5.00%***	***8.00%***	***10.00%***	***7.00%***	***5.00%***	***11.20%***	***4.00%***	***5.20%***	***10.30%***	***9.20%***	***4.60%***
1-Butanamine	10.13										2.23%	3.04%	
1-Pentanamine	15.65										2.07%	3.76%	
Acrylamide	22.10							7.32%	10.20%		2.00%		
Benzylamine, N,N-Dimethyl-	31.78				1.66%		13.40%						
Octylamine	31.93				2.07%	1.76%		1.28%		9.60%			
Phenylethylamine	32.05											1.00%	7.20%
n-Nonylamine	36.69	3.18%			1.27%	1.23%							
9-octadecenamide	52.85		3.37%	7.30%									
13-docosenamide	55.66		5.63%	3.00%									
Diphenylaniline	56.45												7.00%
Subtotal Amides & Amines		***3.18%***	***9.00%***	***10.30%***	***5.00%***	***2.99%***	***13.40%***	***8.60%***	***10.20%***	***9.60%***	***6.30%***	***7.80%***	***14.20%***
Pentane	4.00				6.56%	6.68%							
1,3-Butadiene	9.26		4.57%								9.26%	9.78%	
n-Decane	14.37				3.05%	3.00%							
2,3-Pentadiene, 2,4-dimethyl-	14.89	4.56%			5.53%	5.09%							
1-Butene, 1-phenyl-	16.60										4.65%	6.66%	8.26%
n-Dodecane	19.61	3.75%	3.75%			3.65%							
Naphthalene, 2-methyl-	22.34							4.72%			3.25%		5.43%
n-Tetradecane	24.61	6.11%	5.20%			2.46%							
α-Phellandrene	24.87							5.73%	4.35%	4.53%			
Pentane, 2,2,4-trimethyl-	25.26				4.00%	3.11%							
β-Myrcene	26.55	2.98%			3.20%	1.11%							
1,3,8-p-Menthatriene	28.02				1.91%	1.08%	6.61%						
n-Hexadecane	28.74							1.43%	6.13%			5.65%	
n-Octadecane	32.58	2.35%			1.19%								
Phenanthrene	33.65							2.58%	6.27%	5.41%	6.02%		3.20%

Components	RT (min)	Area% - DSO Biocrudes						Area% - DWO Biocrudes					
		pH 5.5 (Exp 27)	pH 8.5 (Exp 22)	Salt 5% (Exp 24)	360 °C (Exp 18)	50 min (Exp 20)	Cel/Lig 0.2 (Exp 25)	pH 5.5 (Exp 27)	pH 8.5 (Exp 22)	Salt 5% (Exp 24)	360 °C (Exp 18)	50 min (Exp 20)	Cel/Lig 0.2 (Exp 25)
Anthracene	33.86							2.03%	1.12%	4.15%	3.01%		2.35%
Pyrene	39.38		4.98%			1.00%	5.99%						
Terphenyl	39.90							1.11%	0.63%	2.81%	3.11%	4.31%	1.26%
Chrysene	45.54	0.55%		9.20%	2.36%	0.56%	2.90%						
Perylene	53.55	1.20%		9.00%		1.36%	3.50%						
Subtotal Alkanes		***21.50%***	***18.50%***	***18.20%***	***27.80%***	***29.10%***	***19.00%***	***17.60%***	***18.50%***	***16.90%***	***29.30%***	***26.40%***	***20.50%***
Heptanal	23.44							1.70%	2.50%	2.50%	1.90%	2.30%	9.50%
Octanal	26.94	3.00%	9.00%	4.13%	4.00%								
Nonanal	31.93			2.77%		5.50%	10.50%						
Subtotal Aldehydes		***3.00%***	***9.00%***	***6.90%***	***4.00%***	***5.50%***	***10.50%***	***1.70%***	***2.50%***	***2.50%***	***1.90%***	***2.30%***	***9.50%***
	Total	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**

Table S8. GC-MS Results for HTL Aqueous Coproduct Samples from Selected Operating Conditions and Optimized Process Conditions (Validation Experiments)

Components	RT (min)	Area%							
		pH 2.5 (Exp 21)	pH 5.5 (Exp 27)	pH 8.5 (Exp 22)	Cel/Lig 0.2 (Exp 25)	HTL-AP 1	HTL-AP 2	HTL-AP 3	HTL-AP 4
Acetic acid	5.32	6.46%	6.78%	6.67%	9.32%	9.49%	6.46%	10.75%	5.30%
Lactic acid	6.63			12.03%					
Glycolic acid	7.12			2.50%					
Formic acid	15.15	2.26%	1.99%						
Succinic acid	15.80	3.34%					2.01%		1.20%
Levulinic acid	17.88	11.62%	6.44%			2.53%	4.26%	6.56%	3.91%
2-methyl-4-chlorophenoxyacetic acid	18.08	6.45%	5.12%				7.30%		
Glutaric acid	19.40			0.72%				2.10%	
Acetyl benzoic acid	21.66		2.45%		5.44%	6.91%	2.89%		4.42%
Cinnamic acid	24.53				2.79%	7.46%		5.76%	3.43%
Butyric acid, 2-Hydroxy-3-methyl-	37.68			3.25%					2.65%
Succinic acid , 2,3-dihydroxy-2-methyl-	41.47	2.80%							
2-Oxovaleric acid	43.18				2.37%		0.30%		
Subtotal Acids		***32.93%***	***22.78%***	***25.17%***	***19.92%***	***26.39%***	***23.22%***	***25.17%***	***20.91%***
Acetaldehyde	3.58	1.70%	2.20%	4.53%			4.16%		4.25%
Butanal, 2-methyl	8.43		4.32%				1.00%		1.00%
Propionaldehyde	15.09			3.11%			2.16%		
Benzaldehyde	26.31				5.67%	5.75%		6.73%	
Propanal, 2-hydroxy-2-methyl-	41.19								
Glyoxal	50.21		0.67%	5.10%					
Methylglyoxal	51.22	1.50%		4.79%					
2,3-dioxobutane-1,4-dial	55.81	6.00%						1.31%	
2-oxopropane-1,3-dial	61.69					1.60%			1.21%
Subtotal Aldehydes		***9.20%***	***7.19%***	***17.53%***	***5.67%***	***7.35%***	***7.32%***	***8.04%***	***6.46%***
Methyl vinyl ketone	5.28				9.95%	5.44%		8.00%	
Acetoin	11.34	1.10%	2.03%	8.76%	2.36%		1.70%		4.27%
Pentanone	24.87	2.98%	1.43%				8.10%		8.62%
Acetophenone	30.52	6.67%	9.10%			8.92%		5.98%	11.45%
Butanedione	51.79	6.25%	7.97%			9.37%	9.74%	4.00%	
Subtotal Ketones		***17.00%***	***20.53%***	***8.76%***	***12.31%***	***23.73%***	***19.54%***	***17.98%***	***24.34%***
Acetyl anisole	21.69	4.78%	5.39%				5.17%		5.38%

Components	RT (min)	Area%							
		pH 2.5 (Exp 21)	pH 5.5 (Exp 27)	pH 8.5 (Exp 22)	Cel/Lig 0.2 (Exp 25)	HTL-AP 1	HTL-AP 2	HTL-AP 3	HTL-AP 4
Anisole	33.99				6.21%	4.60%		7.87%	
Subtotal Ethers		**4.78%**	**5.39%**	**0.00%**	**6.21%**	**4.60%**	**5.17%**	**7.87%**	**5.38%**
Phenol	18.08						5.67%	3.45%	
o-Cresol	19.45	3.00%	5.91%		7.10%	5.85%			
p-Cresol	20.43	1.94%	3.20%		2.20%		2.80%		2.87%
Dimethylphenol	21.71			6.00%				3.19%	5.00%
4-Aminophenol	22.84		5.09%		1.00%	7.19%			
Catechol	26.29	3.34%			4.61%	5.12%		6.82%	
4-Propylcatechol	32.17	3.96%					1.66%		2.93%
5-Amino-6,8-dimethoxyquinoline	34.99			9.28%	3.02%				1.76%
5-tert-Butylpyrogallol	36.08				2.25%	5.26%	4.29%		0.78%
Phenol, 2-allyl-4-methyl-	39.76		3.59%					4.33%	
3,5-Dihydroxycinnamic acid	42.19	2.96%	3.15%		3.64%	3.01%	2.22%	4.11%	2.66%
3,5-Dihydroxybenzoic acid	45.40		2.21%	4.60%	2.94%	3.25%		1.32%	
Subtotal Phenols		***15.20%***	***23.15%***	***19.88%***	***26.76%***	***29.68%***	***16.64%***	***23.22%***	***16.00%***
Pyridine	9.71			7.03%					
Pyrazine, 2-methyl-	19.23			6.33%					
3-Aminopyrazole	20.99	5.25%	9.41%				14.60%		15.91%
3-Amino-2,6-dimethoxypyridine	22.64				15.67%				
Pyrazine, 2,5-dimethyl-	24.01			2.03%					
Methyl nicotinate	33.02		1.00%	2.06%					
Subtotal N-heterocyclic		***5.25%***	***10.41%***	***17.45%***	***15.67%***	***0.00%***	***14.60%***	***0.00%***	***15.91%***
Acetamide	6.95		6.23%				4.34%		2.30%
Methacrylamide	8.06		2.60%				2.64%	3.20%	3.41%
Aniline	17.51			11.21%	2.00%		5.12%		1.98%
Benzylamine	31.02		1.72%		2.03%	3.28%		1.34%	
2,6-Dimethylaniline	38.18	8.18%				1.56%	1.41%		
Benzidine	40.03				4.87%			0.85%	3.31%
Dimethylbenzamide	49.77	7.46%						12.33%	
Diphenylaniline	56.45				4.56%	3.41%			
Subtotal Amines & Amides		***15.64%***	***10.55%***	***11.21%***	***13.46%***	***8.25%***	***13.51%***	***17.72%***	***11.00%***
Total		**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**

Table S9. GC-MS Results for Biocrude Oils from Optimized Conditions (Validation Experiments)

Components	RT (min)	Area% - DSO Biocrudes				Area% - DWO Biocrudes			
		Digestate 1	Digestate 2	Digestate 3	Digestate 4	Digestate 1	Digestate 2	Digestate 3	Digestate 4
2-Cyclopenten-1-one, 2-methyl-	7.23		10.70%		9.41%				
2-Cyclopenten-1-one, 3-methyl-	8.55	3.43%		5.42%					
2-Cyclopenten-1-one, 2,3-dimethyl-	10.17					4.36%		5.38%	
2-Cyclopenten-1-one, 3-ethyl-	10.91					5.28%	9.48%	3.27%	8.97%
Butyrolactone	23.59	2.68%		1.71%					
Cyclohexanone, 5-methyl-2-(1-methylethyl)-	33.89	4.25%		4.44%					
Carvone	36.78						3.96%	3.11%	
2-Cyclohexen-1-one, 3-methyl-6-(1-methylethyl)-	37.26					7.79%	7.79%	5.12%	10.50%
2H-Pyran-2-one, tetrahydro-	25.90		8.53%		9.03%				
2H-1-Benzopyran-2-one, 3,5,7-trihydroxy-	33.81	3.07%		2.76%					
Subtotal Ketones		***13.43%***	***19.23%***	***14.33%***	***18.44%***	***17.43%***	***21.23%***	***16.88%***	***19.47%***
2-Furanmethanol	20.86	3.68%		3.24%					
Furan, 2,5-diethyltetrahydro-	23.16		5.34%		3.11%				
2(5H)-Furanone	23.40						15.32%		15.21%
2-Furancarboxaldehyde, 5-methyl-	26.18					6.56%		4.57%	
Dihydrofuranno(3,2-f) coumaran	26.62	7.23%	3.14%	4.31%					
3,7-Benzofurandiol, 2,3-dihydro-2,2-dimethyl-	27.14	1.77%		3.00%	7.81%				
Furan, 2-pentyl-	27.39		6.52%		4.19%				
Benzofuran, 2,3-dihydro-	35.63					6.04%		6.10%	
Subtotal Furans		***12.68%***	***15.00%***	***10.55%***	***15.11%***	***12.60%***	***15.32%***	***10.67%***	***15.21%***
1H-Pyrrole, 1-methyl-	13.77					2.96%		1.36%	3.28%
Caprolactam	18.53		2.80%		5.79%				
1H-Pyrrole, 3-methyl-	19.94	1.93%	0.29%	2.79%					
1H-Pyrazole	20.69							1.48%	4.01%
Ethanone, 1-(1H-pyrrol-2-yl)-	29.96		1.86%		3.52%				
Pyrrolidine, 1-methyl-	31.63	1.09%	2.26%		3.12%				
Pyrrolidone, 1-methyl	32.61					1.09%	4.71%	2.77%	
Carbazole	33.86	0.69%		2.54%					
Subtotal Pyrroles		***3.71%***	***7.21%***	***5.33%***	***12.43%***	***4.05%***	***4.71%***	***5.61%***	***7.29%***

Components	RT (min)	Area% - DSO Biocrudes				Area% - DWO Biocrudes			
		Digestate 1	Digestate 2	Digestate 3	Digestate 4	Digestate 1	Digestate 2	Digestate 3	Digestate 4
Oxirane, 2-methyl-2-phenyl-	12.60						1.68%		0.87%
3-Methylguaiacol	20.56	4.48%		2.74%					
Benzenemethanol, 4-hydroxy-	21.23	7.32%	3.45%	4.68%	4.03%				
4-Methylguaiacol	21.44					5.60%		6.89%	
Phenol, 4-ethyl-2-methoxy-	23.69						7.67%		1.84%
Phenol, 3-ethyl-5-methyl-	24.91		1.75%		2.36%				
2-Phenylacetaldehyde	25.62	2.00%		1.30%					
Phenol, 2-methoxy-methyl-ethyl-	25.87					2.39%			3.49%
Phenol, 2,6-dimethoxy-	26.52		2.54%						
4-Chlorodiphenyl ether	30.98				1.08%				
Benzaldehyde, 4-hydroxy-	31.42							4.03%	
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	32.05		3.04%		2.06%				
3-Methoxy-4-hydroxybenzyl methyl ether	32.24	2.46%		5.45%					
Oxirane, (phenoxymethyl)-	32.95		0.95%		1.74%				
4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol	33.05					6.61%		4.70%	
2-Methoxy-4-vinylphenol	38.39			1.89%					
1,3,5-Benzenetriol	38.45	1.94%		2.09%					
1,3-Benzodioxane-5-ol	39.19					8.00%	7.11%	6.80%	9.00%
1,3-Benzodioxole, 5-(1-propenyl)-	41.56	4.40%	4.73%	4.27%	4.01%				
Subtotal Phenols		***22.60%***	***16.46%***	***22.42%***	***15.28%***	**22.60%**	**16.46%**	**22.42%**	**15.20%**
Butanoic acid, 2-methyl-, methyl ester	16.40		1.43%		2.06%				
Butanoic acid, ethyl ester	17.53					2.19%		1.91%	
1-Butanol, 3-methyl-, acetate	22.16						2.35%		1.23%
Chloroacetic acid, 2-naphthyl ester	27.41		3.03%						
3-Methyl-4-propyl-2,4-hexadienedioic acid dimethyl ester	28.76			0.98%			2.11%		2.33%
3,4-dimethoxy-mandelic acid methyl ester	28.96	0.90%		0.93%					
Pentanedioic acid, 2-methyl-, dimethyl ester	32.89	1.29%			1.50%				
Subtotal Esters		***2.19%***	***4.46%***	***1.91%***	***3.56%***	***2.19%***	***4.46%***	***1.91%***	***3.56%***
1-Butanamine	10.13						4.19%	1.51%	
1-Pentanamine	15.65						1.00%	3.49%	
Acrylamide	22.10						1.35%		4.99%

Components	RT (min)	Area% - DSO Biocrudes				Area% - DWO Biocrudes			
		Digestate 1	Digestate 2	Digestate 3	Digestate 4	Digestate 1	Digestate 2	Digestate 3	Digestate 4
Benzylamine, N,N-Dimethyl-	31.78	5.74%		4.56%					
Octylamine	31.93						2.12%		5.64%
Phenylethylamine	32.05					6.79%		2.81%	
n-Nonylamine	36.69		3.32%		4.77%				
9-octadecenamide	52.85			7.46%					
13-docosenamide	55.66	7.90%	3.18%						
Diphenylaniline	56.45					6.74%		4.01%	
Subtotal Amides & Amines		***13.64%***	***6.50%***	***12.02%***	***4.77%***	***13.53%***	***8.66%***	***11.82%***	***10.63%***
Pentane	4.00	9.67%	8.79%		9.33%				
1,3-Butadiene	9.26						9.13%		8.97%
n-Decane	14.37		9.43%	8.89%	5.72%				
2,3-Pentadiene, 2,4-dimethyl-	14.89					7.44%		8.47%	
1-Butene, 1-phenyl-	16.60					4.37%		8.12%	
n-Dodecane	19.61	3.35%							
Naphthalene, 2-methyl-	22.34						4.94%		10.21%
n-Tetradecane	24.61			8.05%					
α-Phellandrene	24.87					4.33%		3.45%	
Pentane, 2,2,4-trimethyl-	25.26	5.67%			6.15%				
β-Myrcene	26.55		3.98%		3.00%				
1,3,8-p-Menthatriene	28.02			2.97%					
n-Hexadecane	28.74						6.33%		2.06%
n-Octadecane	32.58		3.22%						
Phenanthrene	33.65							2.07%	2.17%
Anthracene	33.86					2.13%	4.63%		
Pyrene	39.38			3.56%					
Terphenyl	39.90					2.77%		2.11%	
Chrysene	45.54	4.14%	1.71%		2.21%				
Perylene	53.55	2.71%		2.99%					
Subtotal Alkanes		***25.54%***	***27.13%***	***26.46%***	***26.41%***	***21.04%***	***25.03%***	***24.22%***	***23.41%***
Heptanal	23.44					6.56%	4.13%	6.47%	5.23%
Octanal	26.94		4.01%		4.00%				
Nonanal	31.93	6.21%		6.98%					
Subtotal Aldehydes		***6.21%***	***4.01%***	***6.98%***	***4.00%***	***6.56%***	***4.13%***	***6.47%***	***5.23%***
Total		**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**

Table S10. Carbon yield in biocrude, hydro-char, and aqueous-phase products from HFCCD experiments

No.	T (ºC)	t (min)	pH	Salt (wt%)	Cel/Lig	Carbon yield			
						Biocrude	Hydro-char	Aqueous-phase	Total
1	300	20	4	2	1.4	62.29%	7.14%	28.35%	97.78%
2	340	20	4	2	0.6	65.35%	5.84%	26.31%	97.50%
3	300	40	4	2	0.6	62.03%	6.65%	30.53%	99.22%
4	340	40	4	2	1.4	77.41%	3.86%	18.60%	99.87%
5	300	20	7	2	0.6	42.64%	29.42%	23.19%	95.24%
6	340	20	7	2	1.4	67.68%	24.23%	5.38%	97.29%
7	300	40	7	2	1.4	55.00%	28.78%	11.12%	94.90%
8	340	40	7	2	0.6	51.37%	33.49%	9.90%	94.76%
9	300	20	4	4	0.6	53.75%	10.61%	32.92%	97.29%
10	340	20	4	4	1.4	68.80%	3.96%	26.04%	98.79%
11	300	40	4	4	1.4	59.62%	6.89%	32.03%	98.54%
12	340	40	4	4	0.6	69.84%	7.08%	21.22%	98.14%
13	300	20	7	4	1.4	46.90%	31.80%	15.16%	93.86%
14	340	20	7	4	0.6	41.42%	32.44%	19.81%	93.66%
15	300	40	7	4	0.6	35.25%	33.84%	24.91%	94.00%
16	340	40	7	4	1.4	55.51%	32.66%	6.71%	94.88%
17	280	30	5.5	3	1	54.72%	23.14%	17.40%	95.25%
18	360	30	5.5	3	1	79.26%	10.32%	8.61%	98.19%
19	320	10	5.5	3	1	72.31%	10.77%	14.51%	97.59%
20	320	50	5.5	3	1	80.24%	9.16%	8.40%	97.80%
21	320	30	2.5	3	1	44.87%	6.80%	45.52%	97.20%
22	320	30	8.5	3	1	15.76%	33.16%	46.03%	94.95%
23	320	30	5.5	1	1	80.92%	11.31%	6.45%	98.68%
24	320	30	5.5	5	1	63.14%	16.46%	15.63%	95.23%
25	320	30	5.5	3	0.2	66.61%	20.48%	10.70%	97.79%
26	320	30	5.5	3	1.8	75.53%	9.65%	12.39%	97.57%
27	320	30	5.5	3	1	73.59%	11.51%	11.62%	96.72%
28	320	30	5.5	3	1	74.70%	10.59%	11.63%	96.92%
29	320	30	5.5	3	1	75.08%	11.55%	10.90%	97.53%
30	320	30	5.5	3	1	71.53%	10.99%	14.39%	96.91%
31	320	30	5.5	3	1	75.22%	11.77%	10.01%	97.00%
32	320	30	5.5	3	1	71.74%	11.11%	14.26%	97.11%

Table S11. Nitrogen yield in biocrude, hydro-char, and aqueous-phase products from HFCCD experiments

No.	T (ºC)	t (min)	pH	Salt (wt%)	Cel/Lig	Nitrogen yield			
						Biocrude	Hydro-char	Aqueous-phase	Total
1	300	20	4	2	1.4	46.5%	9.84%	40.5%	96.9%
2	340	20	4	2	0.6	37.8%	12.86%	44.1%	94.8%
3	300	40	4	2	0.6	35.8%	8.92%	52.8%	97.5%
4	340	40	4	2	1.4	50.5%	8.84%	37.7%	97.1%
5	300	20	7	2	0.6	13.3%	35.98%	41.1%	90.3%
6	340	20	7	2	1.4	25.9%	26.55%	40.1%	92.6%
7	300	40	7	2	1.4	20.8%	32.99%	36.2%	90.0%
8	340	40	7	2	0.6	16.8%	34.07%	39.6%	90.5%
9	300	20	4	4	0.6	26.7%	14.25%	54.4%	95.3%
10	340	20	4	4	1.4	45.3%	8.72%	42.7%	96.7%
11	300	40	4	4	1.4	37.3%	10.76%	48.7%	96.7%
12	340	40	4	4	0.6	37.7%	14.30%	42.8%	94.8%
13	300	20	7	4	1.4	16.6%	34.40%	38.0%	89.0%
14	340	20	7	4	0.6	13.3%	29.88%	49.4%	92.6%
15	300	40	7	4	0.6	11.5%	34.34%	45.5%	91.3%
16	340	40	7	4	1.4	22.2%	31.69%	36.9%	90.8%
17	280	30	5.5	3	1	22.2%	20.21%	52.2%	94.6%
18	360	30	5.5	3	1	31.8%	14.03%	49.7%	95.5%
19	320	10	5.5	3	1	29.4%	16.01%	49.1%	94.5%
20	320	50	5.5	3	1	32.0%	16.29%	45.7%	94.0%
21	320	30	2.5	3	1	40.5%	7.23%	51.6%	99.3%
22	320	30	8.5	3	1	20.8%	38.84%	36.3%	96.0%
23	320	30	5.5	1	1	55.2%	7.82%	36.0%	99.1%
24	320	30	5.5	5	1	46.4%	17.38%	34.9%	98.6%
25	320	30	5.5	3	0.2	42.3%	24.07%	32.7%	99.2%
26	320	30	5.5	3	1.8	63.9%	17.57%	17.9%	99.4%
27	320	30	5.5	3	1	42.7%	14.13%	42.3%	99.0%
28	320	30	5.5	3	1	43.7%	13.85%	39.6%	97.1%
29	320	30	5.5	3	1	49.6%	13.22%	35.6%	98.4%
30	320	30	5.5	3	1	46.4%	14.35%	37.1%	97.8%
31	320	30	5.5	3	1	49.8%	13.21%	35.0%	98.1%
32	320	30	5.5	3	1	45.7%	11.45%	42.0%	99.1%

Table S12. The yield of P in biocrude, hydro-char, and aqueous-phase products from HFCCD experiments.

No.	T (ºC)	t (min)	pH	Salt (wt%)	Cel/Lig	P yield		
						Biocrude (by diff)	Hydro-char	Aqueous-phase
1	300	20	4	2	1.4	1.85%	35.53%	62.62%
2	340	20	4	2	0.6	0.94%	70.23%	28.83%
3	300	40	4	2	0.6	2.09%	68.65%	29.26%
4	340	40	4	2	1.4	0.66%	31.45%	67.89%
5	300	20	7	2	0.6	1.83%	72.79%	25.38%
6	340	20	7	2	1.4	4.48%	56.48%	39.04%
7	300	40	7	2	1.4	1.02%	70.84%	28.14%
8	340	40	7	2	0.6	3.11%	80.23%	16.66%
9	300	20	4	4	0.6	2.89%	52.99%	44.12%
10	340	20	4	4	1.4	1.70%	37.46%	60.84%
11	300	40	4	4	1.4	0.99%	40.75%	58.26%
12	340	40	4	4	0.6	2.18%	59.75%	38.07%
13	300	20	7	4	1.4	1.22%	74.74%	24.04%
14	340	20	7	4	0.6	1.73%	77.33%	20.94%
15	300	40	7	4	0.6	1.59%	74.37%	24.04%
16	340	40	7	4	1.4	3.02%	73.19%	23.79%
17	280	30	5.5	3	1	2.28%	75.86%	21.86%
18	360	30	5.5	3	1	0.39%	61.90%	37.71%
19	320	10	5.5	3	1	2.35%	69.29%	28.36%
20	320	50	5.5	3	1	1.27%	71.28%	27.45%
21	320	30	2.5	3	1	0.93%	22.05%	77.02%
22	320	30	8.5	3	1	0.67%	61.21%	38.12%
23	320	30	5.5	1	1	0.54%	46.40%	53.06%
24	320	30	5.5	5	1	0.84%	89.29%	9.87%
25	320	30	5.5	3	0.2	0.25%	81.63%	18.12%
26	320	30	5.5	3	1.8	1.84%	47.92%	50.24%
27	320	30	5.5	3	1	1.81%	61.88%	36.31%
28	320	30	5.5	3	1	1.23%	60.04%	38.73%
29	320	30	5.5	3	1	0.53%	58.42%	41.05%
30	320	30	5.5	3	1	0.92%	59.43%	39.65%
31	320	30	5.5	3	1	0.63%	58.83%	40.54%
32	320	30	5.5	3	1	0.46%	59.47%	40.07%

Table S13. The yield of Ca in biocrude, hydro-char, and aqueous-phase products from HFCCD experiments.

No.	T (ºC)	t (min)	pH	Salt (wt%)	Cel/Lig	Ca yield		
						Biocrude (by diff)	Hydro-char	Aqueous-phase
1	300	20	4	2	1.4	0.82%	53.21%	45.97%
2	340	20	4	2	0.6	2.39%	82.11%	15.50%
3	300	40	4	2	0.6	0.87%	59.00%	40.13%
4	340	40	4	2	1.4	0.84%	52.57%	46.59%
5	300	20	7	2	0.6	1.81%	52.60%	45.59%
6	340	20	7	2	1.4	0.33%	46.54%	53.13%
7	300	40	7	2	1.4	2.72%	44.60%	52.68%
8	340	40	7	2	0.6	0.33%	38.46%	61.21%
9	300	20	4	4	0.6	1.83%	82.60%	15.57%
10	340	20	4	4	1.4	1.32%	57.84%	40.84%
11	300	40	4	4	1.4	2.11%	44.11%	53.78%
12	340	40	4	4	0.6	1.23%	71.87%	26.90%
13	300	20	7	4	1.4	0.29%	46.03%	53.68%
14	340	20	7	4	0.6	2.81%	44.40%	52.79%
15	300	40	7	4	0.6	1.25%	40.97%	57.78%
16	340	40	7	4	1.4	1.36%	40.44%	58.20%
17	280	30	5.5	3	1	0.25%	54.38%	45.37%
18	360	30	5.5	3	1	0.88%	42.44%	56.68%
19	320	10	5.5	3	1	0.32%	63.07%	36.61%
20	320	50	5.5	3	1	1.09%	57.79%	41.12%
21	320	30	2.5	3	1	1.24%	76.03%	22.73%
22	320	30	8.5	3	1	0.92%	53.71%	45.37%
23	320	30	5.5	1	1	0.94%	85.91%	13.15%
24	320	30	5.5	5	1	1.72%	44.43%	53.85%
25	320	30	5.5	3	0.2	2.31%	51.93%	45.76%
26	320	30	5.5	3	1.8	0.93%	46.33%	52.74%
27	320	30	5.5	3	1	1.22%	69.26%	29.52%
28	320	30	5.5	3	1	0.29%	46.01%	53.70%
29	320	30	5.5	3	1	1.11%	60.85%	38.04%
30	320	30	5.5	3	1	0.99%	61.16%	37.85%
31	320	30	5.5	3	1	1.30%	59.00%	39.70%
32	320	30	5.5	3	1	1.41%	56.06%	42.53%

Table S14. The yield of Mg in biocrude, hydro-char, and aqueous-phase products from HFCCD experiments.

No.	T (ºC)	t (min)	pH	Salt (wt%)	Cel/Lig	Mg yield		
						Biocrude (by diff)	Hydro-char	Aqueous-phase
1	300	20	4	2	1.4	0.84%	10.17%	88.99%
2	340	20	4	2	0.6	2.77%	8.76%	88.47%
3	300	40	4	2	0.6	3.11%	29.33%	67.56%
4	340	40	4	2	1.4	0.29%	6.03%	93.68%
5	300	20	7	2	0.6	3.18%	80.64%	16.18%
6	340	20	7	2	1.4	2.82%	82.67%	14.51%
7	300	40	7	2	1.4	0.76%	81.26%	17.98%
8	340	40	7	2	0.6	0.81%	88.87%	10.32%
9	300	20	4	4	0.6	1.03%	57.90%	41.07%
10	340	20	4	4	1.4	0.95%	68.04%	31.01%
11	300	40	4	4	1.4	0.85%	88.46%	10.69%
12	340	40	4	4	0.6	3.31%	68.85%	27.84%
13	300	20	7	4	1.4	1.26%	87.81%	10.93%
14	340	20	7	4	0.6	0.18%	94.21%	5.61%
15	300	40	7	4	0.6	5.19%	81.51%	13.30%
16	340	40	7	4	1.4	2.15%	90.47%	7.38%
17	280	30	5.5	3	1	3.11%	91.46%	5.43%
18	360	30	5.5	3	1	1.63%	78.81%	19.56%
19	320	10	5.5	3	1	0.65%	73.68%	25.67%
20	320	50	5.5	3	1	2.07%	60.81%	37.12%
21	320	30	2.5	3	1	3.66%	21.66%	74.68%
22	320	30	8.5	3	1	0.13%	85.68%	14.19%
23	320	30	5.5	1	1	0.89%	41.49%	57.62%
24	320	30	5.5	5	1	0.54%	58.77%	40.69%
25	320	30	5.5	3	0.2	0.83%	52.57%	46.60%
26	320	30	5.5	3	1.8	0.25%	45.75%	54.00%
27	320	30	5.5	3	1	2.28%	51.99%	45.73%
28	320	30	5.5	3	1	0.57%	53.70%	45.73%
29	320	30	5.5	3	1	0.99%	48.86%	50.15%
30	320	30	5.5	3	1	0.51%	53.13%	46.36%
31	320	30	5.5	3	1	0.72%	52.47%	46.81%
32	320	30	5.5	3	1	0.81%	46.64%	52.55%

Table S15. Statistics of heating time effects (X) on measured response variables

Term	$Y_{oil,daf}$ (%)		$C_{yield\text{-}oil}$ (%)		ER_{oil} (%)		ΔpH_{liq}	
	Coeff.	*p*	Coeff.	*p*	Coeff.	*p*	Coeff.	*p*
Constant	-28.3	0.732	-76	0.559	-77	0.537	-29	0.952
X	1.85	0.505	3.89	0.366	3.77	0.362	-0.8	0.963
X^2	-0.0131	0.558	-0.0269	0.443	-0.0253	0.509	0.009	0.946
R^2	5.57%		11.78%		15.09%		0.17%	
Term	$\%O_{oil\text{-}DWO}$		$\%O_{oil\text{-}DSO}$		$\%N_{oil\text{-}DWO}$		$\%N_{oil\text{-}DSO}$	
	Coeff.	*p*	Coeff.	*p*	Coeff.	*p*	Coeff.	*p*
Constant	122.2	0.507	32.6	0.237	-24.1	0.355	-9.46	0.363
X	-2.581	0.301	-0.168	0.853	0.907	0.678	0.375	0.642
X^2	0.0188	0.792	0.0003	0.971	-0.0074	0.609	-0.003	0.562
R^2	5.22%		11.07%		36.00%		19.41%	
Term	Ca_{AP} (%)		Mg_{AP} (%)		$NH_3\text{-}N_{AP}$ (%)		P_{AP} (%)	
	Coeff.	*p*	Coeff.	*p*	Coeff.	*p*	Coeff.	*p*
Constant	33.4	0.663	-165	0.152	36.1	0.404	-13	0.928
X	0.13	0.961	7.64	0.371	0.11	0.939	1.13	0.809
X^2	-0.0027	0.897	-0.0617	0.513	-0.0013	0.911	-0.0088	0.818
R^2	3.48%		12.85%		0.73%		0.27%	

Table S16. Statistics of total processing time (heating + reaction + cooling) effects (X) on measured response variables

Term	$Y_{oil,daf}$ (%)		$C_{yield\text{-}oil}$ (%)		ER_{oil} (%)		ΔpH_{liq}	
	Coeff.	*p*	Coeff.	*p*	Coeff.	*p*	Coeff.	*p*
Constant	0	0.999	6	0.982	34	0.893	284	0.766
X	0.4	0.875	0.45	0.911	-0.07	0.986	-5.3	0.716
X^2	-0.001	915	-0.0003	0.984	0.0018	0.901	0.0214	0.704
R^2	2.54%		7.72%		10.29%		0.75%	
Term	$\%O_{oil\text{-}DWO}$		$\%O_{oil\text{-}DSO}$		$\%N_{oil\text{-}DWO}$		$\%N_{oil\text{-}DSO}$	
	Coeff.	*p*	Coeff.	*p*	Coeff.	*p*	Coeff.	*p*
Constant	139.3	0.274	11.1	0.827	-42.6	0.697	-19.28	0.854
X	-1.385	0.877	0.317	0.684	0.702	0.772	0.324	0.772
X^2	0.0045	0.141	-0.0017	0.572	-0.0027	0.317	-0.0012	0.447
R^2	33.80%		20.22%		25.98%		17.57%	
Term	Ca_{AP} (%)		Mg_{AP} (%)		$NH_3\text{-}N_{AP}$ (%)		P_{AP} (%)	
	Coeff.	*p*	Coeff.	*p*	Coeff.	*p*	Coeff.	*p*
Constant	181	0.228	-213	0.362	66	0.422	59	823
X	-2.19	0.341	4.31	0.233	-0.32	0.797	-0.57	0.893
X^2	0.0079	0.37	-0.0165	0.234	0.0008	0.865	0.0022	0.891
R^2	5.74%		4.87%		7.03%		0.07%	

Table S17. Product yield distribution from each HFCCD run. The biocrude and hydrochar yields were directly measured, the gas yield was estimated by assuming carbon loss to the gas phase as CO_2, and the aqueous-phase product yield was calculated by difference.

No.	T (ºC)	t (min)	pH	Salt (wt%)	Cel/Lig	Product yield			
						Biocrude	Hydrochar	Aqueous-phase[b]	Gas[a]
1	300	20	4	2	1.4	45.32%	4.74%	46.83%	3.11%
2	340	20	4	2	0.6	50.90%	4.69%	40.85%	3.56%
3	300	40	4	2	0.6	45.19%	6.07%	47.62%	1.12%
4	340	40	4	2	1.4	49.32%	4.65%	45.85%	0.18%
5	300	20	7	2	0.6	28.18%	25.58%	39.58%	6.66%
6	340	20	7	2	1.4	43.53%	16.44%	36.37%	3.67%
7	300	40	7	2	1.4	33.34%	18.69%	41.07%	6.90%
8	340	40	7	2	0.6	32.67%	22.22%	37.76%	7.35%
9	300	20	4	4	0.6	38.52%	10.82%	47.09%	3.57%
10	340	20	4	4	1.4	45.54%	5.88%	47.03%	1.56%
11	300	40	4	4	1.4	37.69%	7.04%	53.38%	1.89%
12	340	40	4	4	0.6	45.16%	8.98%	43.41%	2.45%
13	300	20	7	4	1.4	26.70%	23.08%	42.93%	7.30%
14	340	20	7	4	0.6	25.43%	27.92%	38.87%	7.79%
15	300	40	7	4	0.6	19.70%	30.66%	42.26%	7.37%
16	340	40	7	4	1.4	30.70%	21.87%	41.35%	6.08%
17	280	30	5.5	3	1	35.31%	13.24%	45.17%	6.28%
18	360	30	5.5	3	1	52.04%	8.81%	36.75%	2.39%
19	320	10	5.5	3	1	51.20%	8.99%	36.62%	3.19%
20	320	50	5.5	3	1	48.64%	8.17%	40.27%	2.92%
21	320	30	2.5	3	1	30.16%	8.36%	57.58%	3.90%
22	320	30	8.5	3	1	7.03%	37.77%	48.84%	6.36%
23	320	30	5.5	1	1	55.88%	8.57%	33.60%	1.95%
24	320	30	5.5	5	1	38.78%	14.50%	40.98%	5.73%
25	320	30	5.5	3	0.2	46.89%	14.59%	35.48%	3.05%
26	320	30	5.5	3	1.8	47.81%	8.04%	40.98%	3.16%
27	320	30	5.5	3	1	46.00%	9.73%	39.93%	4.34%
28	320	30	5.5	3	1	47.27%	8.12%	40.54%	4.07%
29	320	30	5.5	3	1	48.10%	9.90%	38.74%	3.27%
30	320	30	5.5	3	1	45.48%	9.71%	40.73%	4.08%
31	320	30	5.5	3	1	48.30%	9.80%	37.93%	3.97%
32	320	30	5.5	3	1	46.20%	8.92%	41.06%	3.82%

[a] Y_{Gas} = (amount of carbon to the gas phase) × 44/12

[b] $Y_{HTL\text{-}AP} = 1 - Y_{Biocrude} - Y_{Hydrochar} - Y_{Gas}$

Figure S1. HTL Experimental Procedures using a 500-mL Parr 4575 SS316 reactor equipped with a Parr 4878 controller to control reaction temperature and stirrer speed (130 rpm).

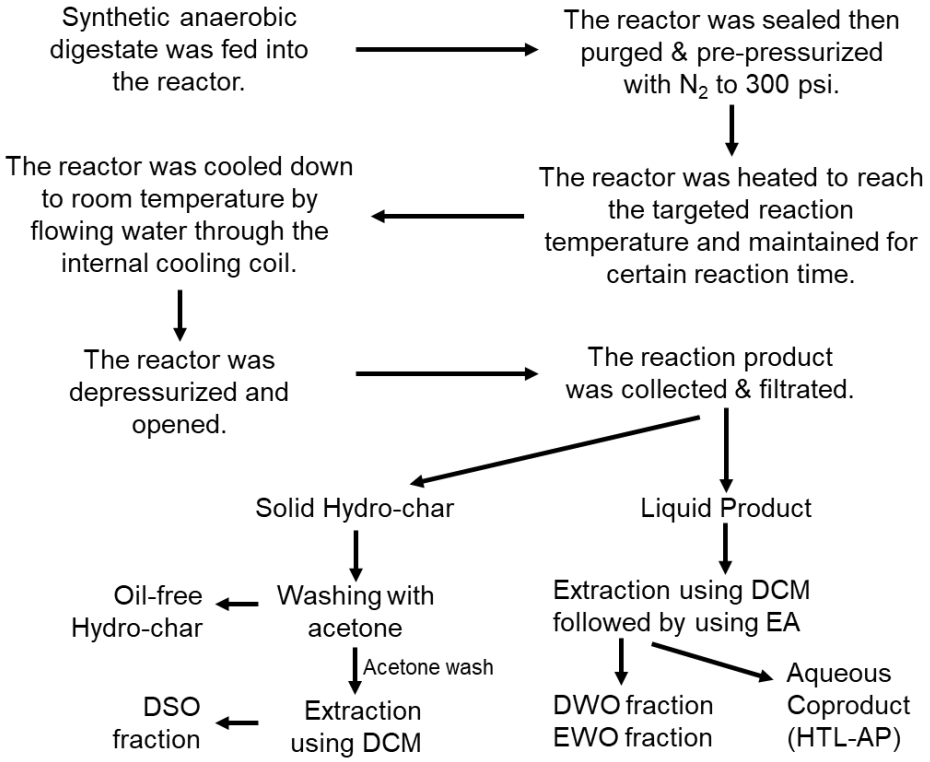


Figure S2. Contour plots for d.a.f. oil yield ($Y_{oil,daf}$)

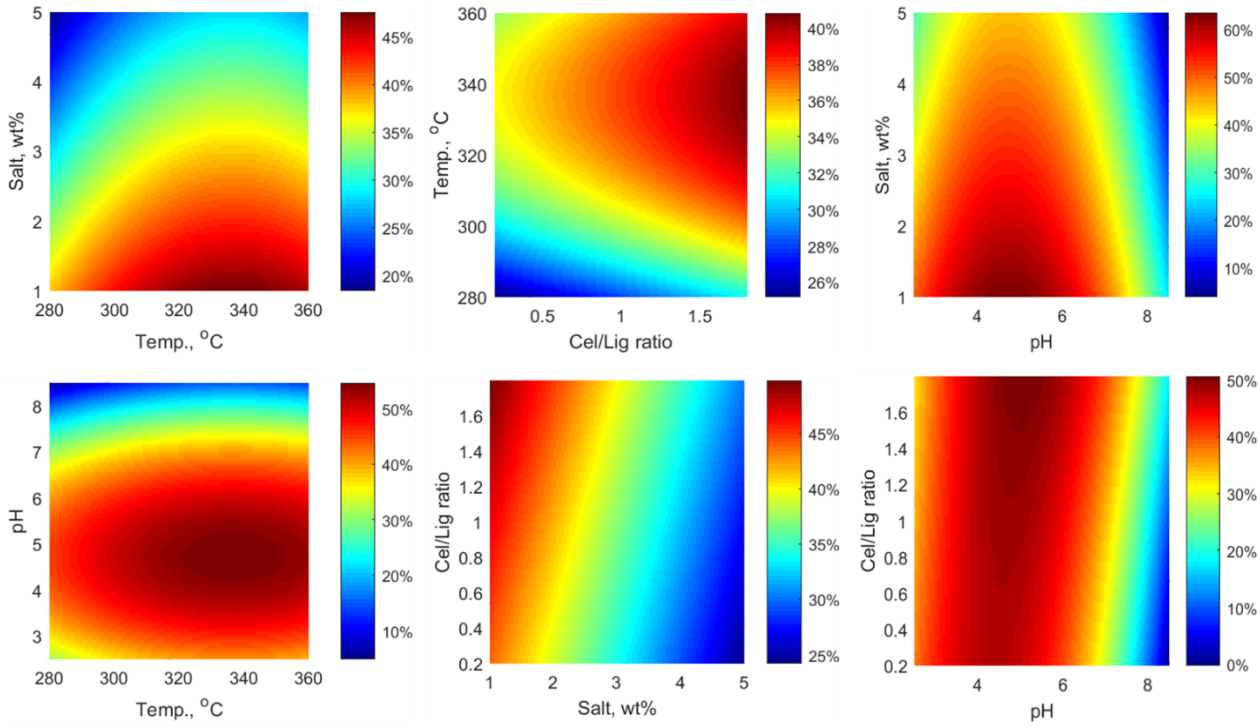


Figure S3. Contour plots for carbon yield in biocrude ($C_{yield\text{-}oil}$)

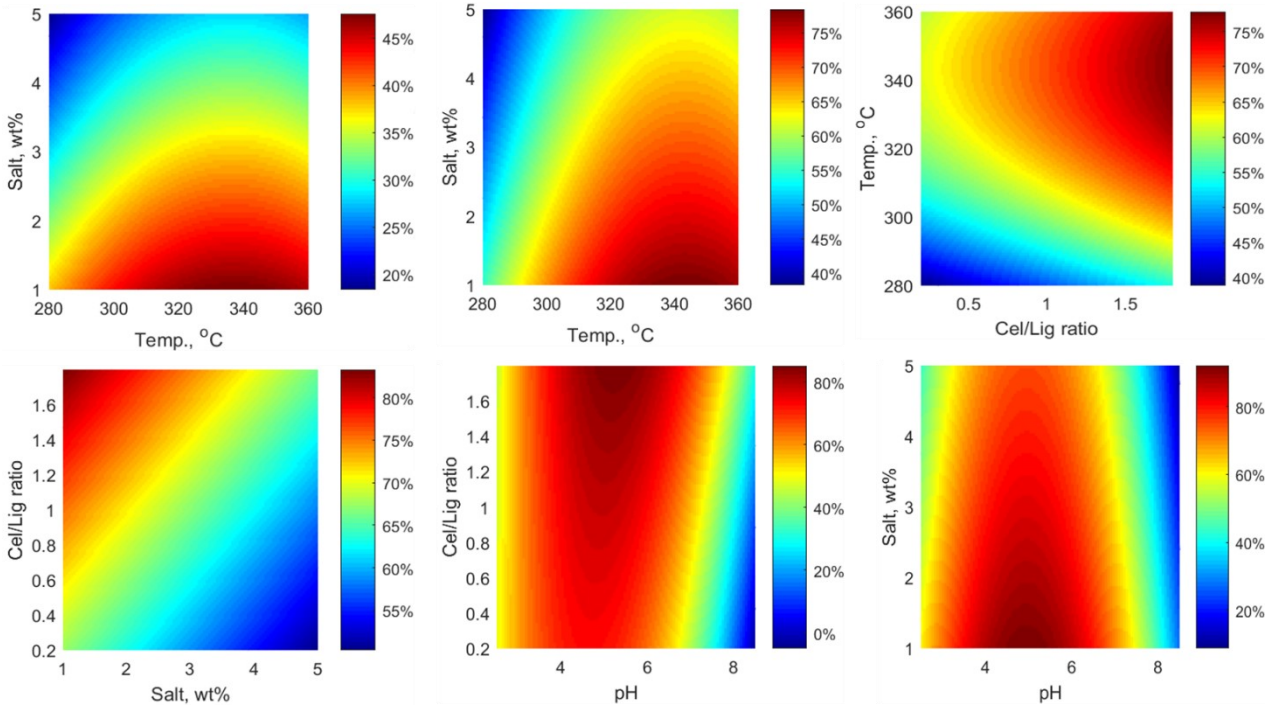


Figure S4. Contour plots for total energy recovery in biocrude (ER_{oil})

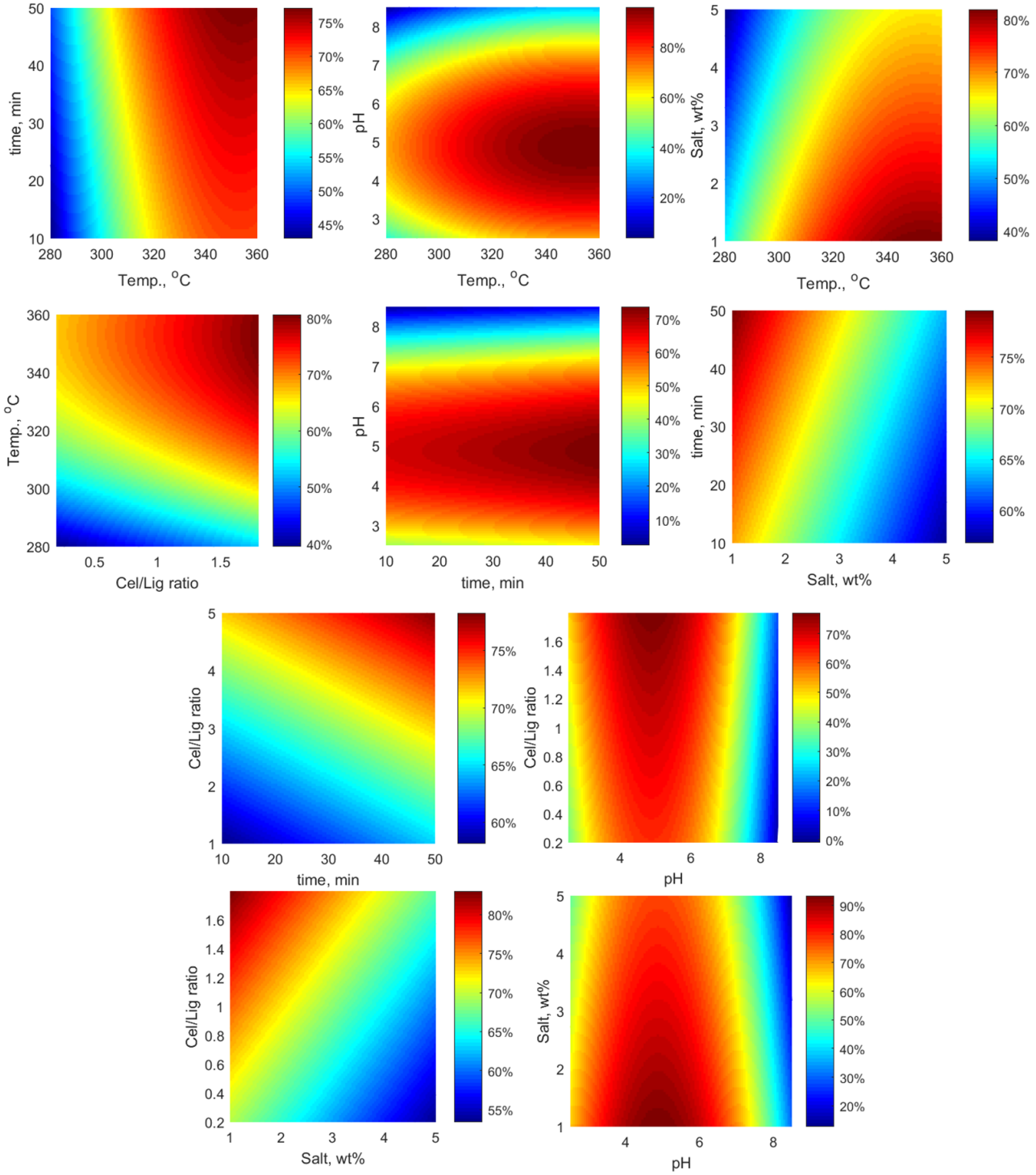


Figure S5. Contour plots for oxygen content in DWO fraction ($\%O_{oil\text{-}DWO}$)

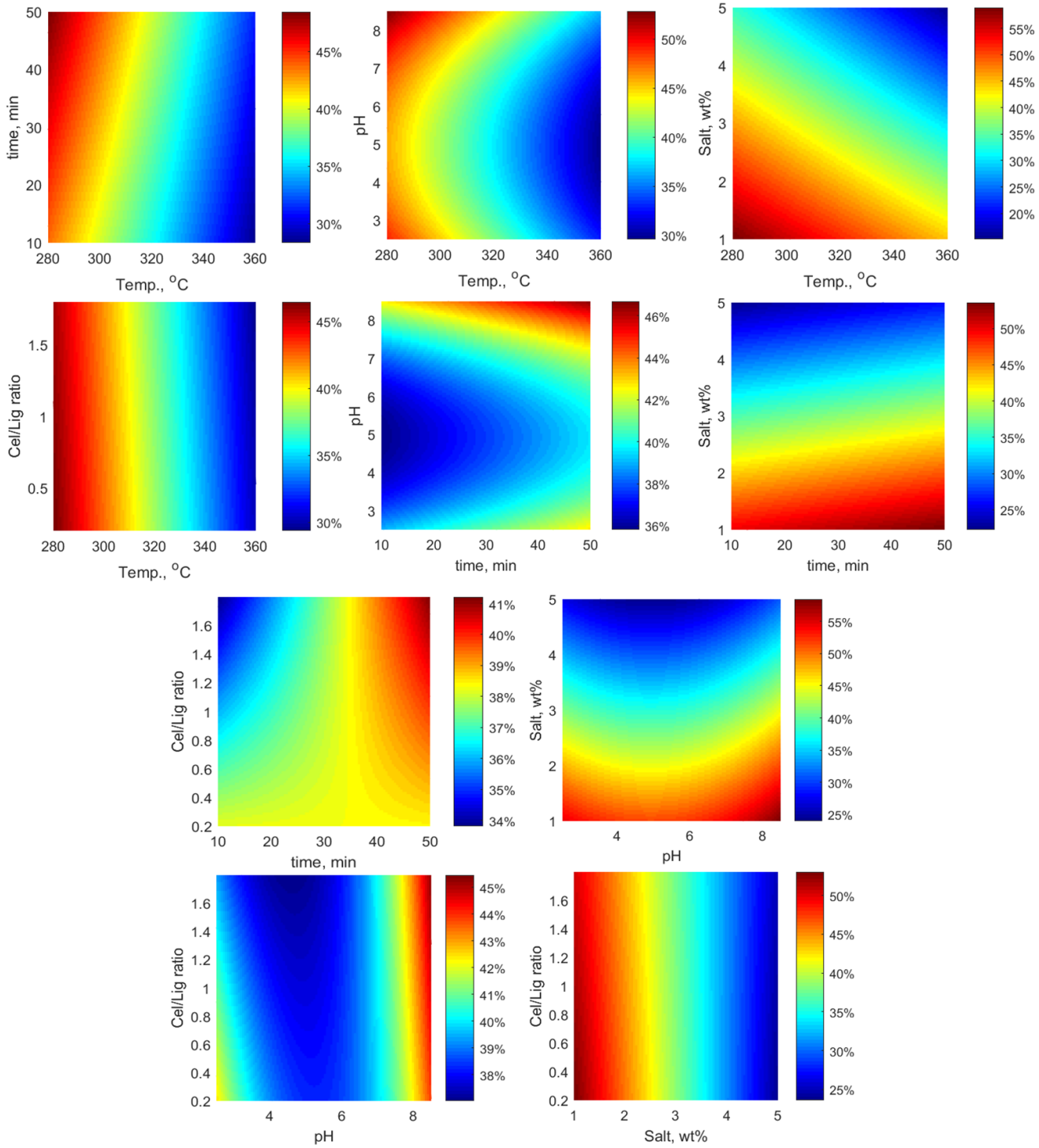


Figure S6. Contour plots for oxygen content in DSO fraction ($\%O_{oil\text{-}DSO}$)

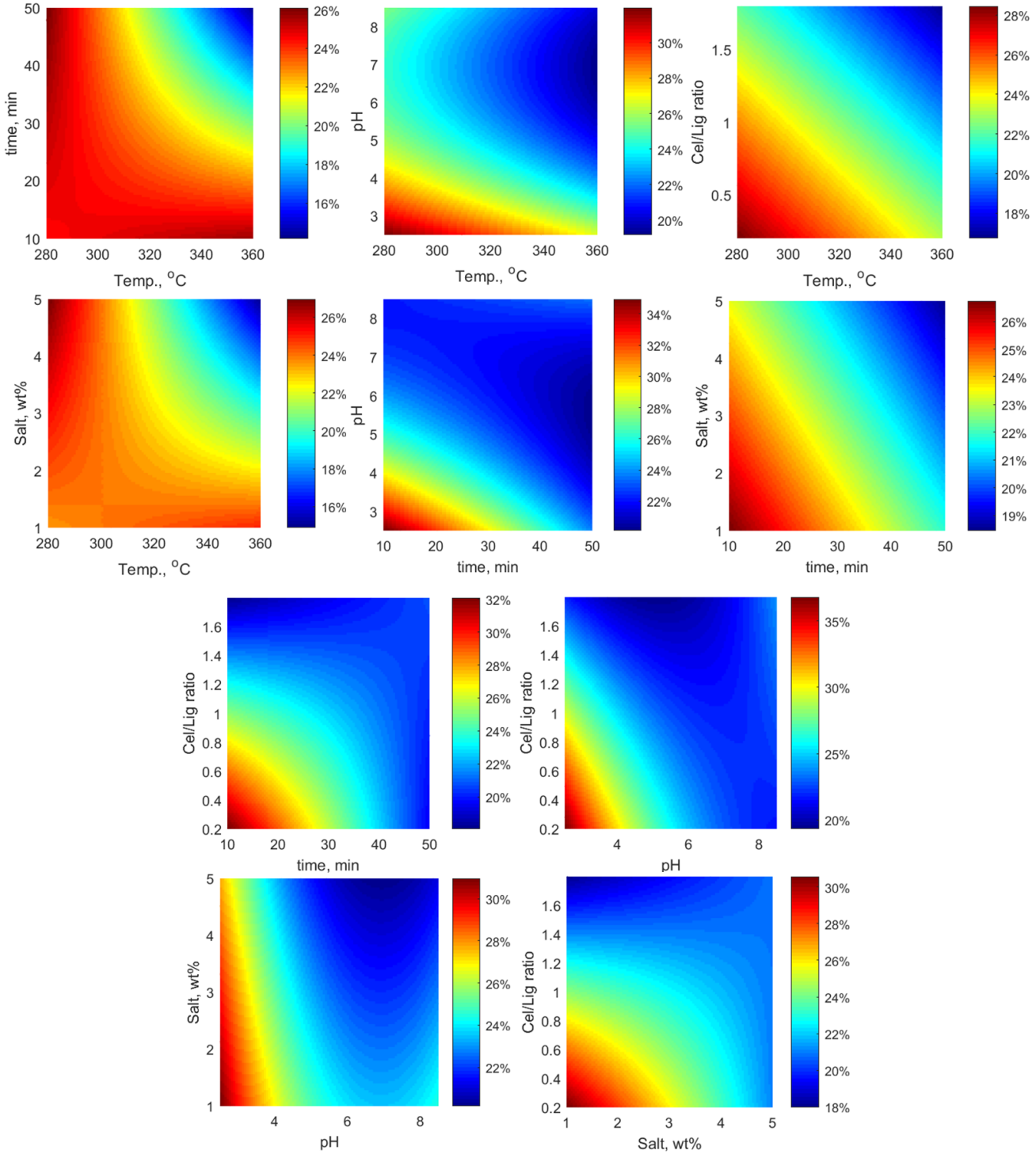


Figure S7. Contour plots for nitrogen content in DWO fraction ($\%N_{oil\text{-}DWO}$)

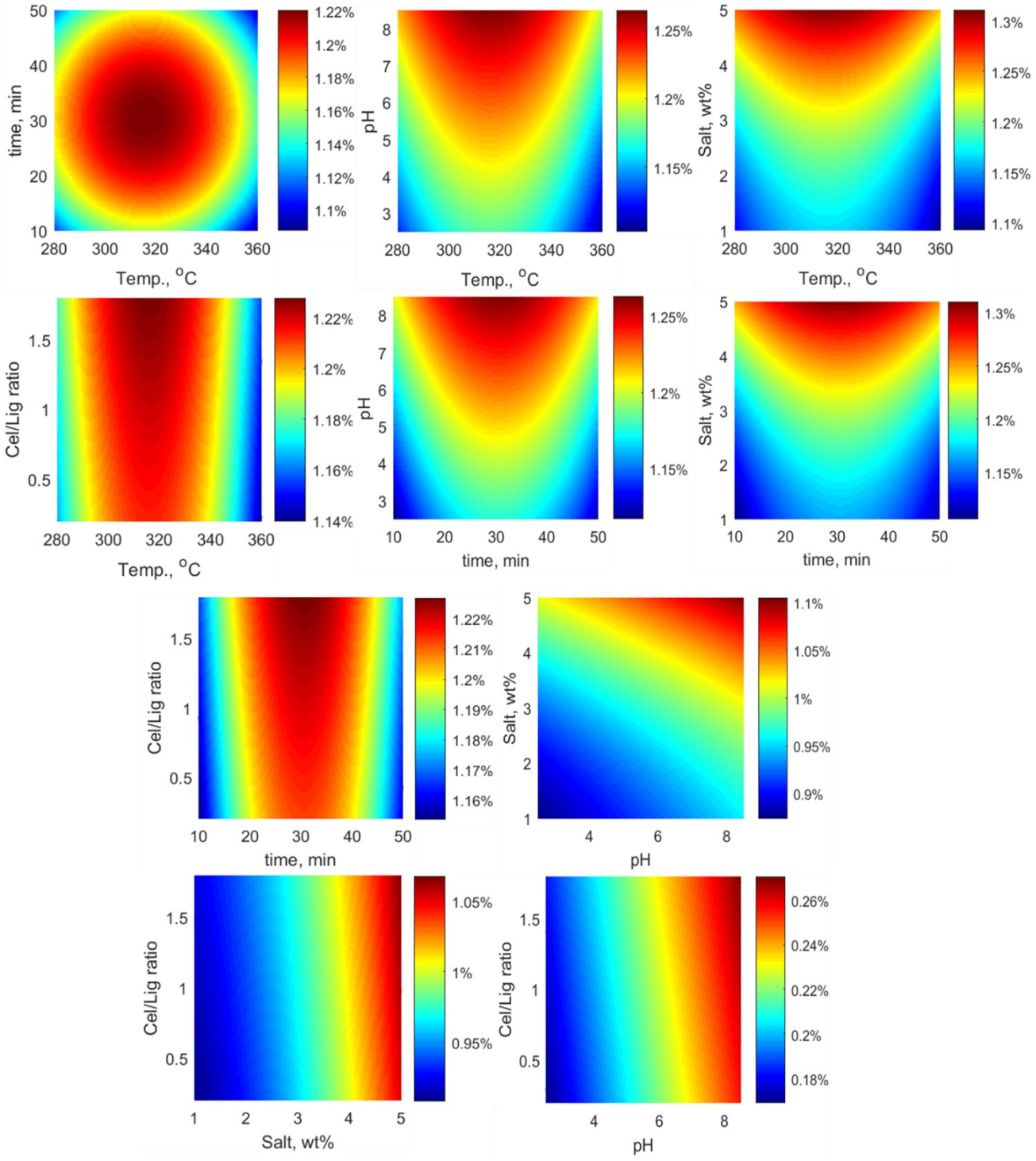


Figure S8. Contour plots for nitrogen content in DSO fraction ($\%N_{oil\text{-}DSO}$)

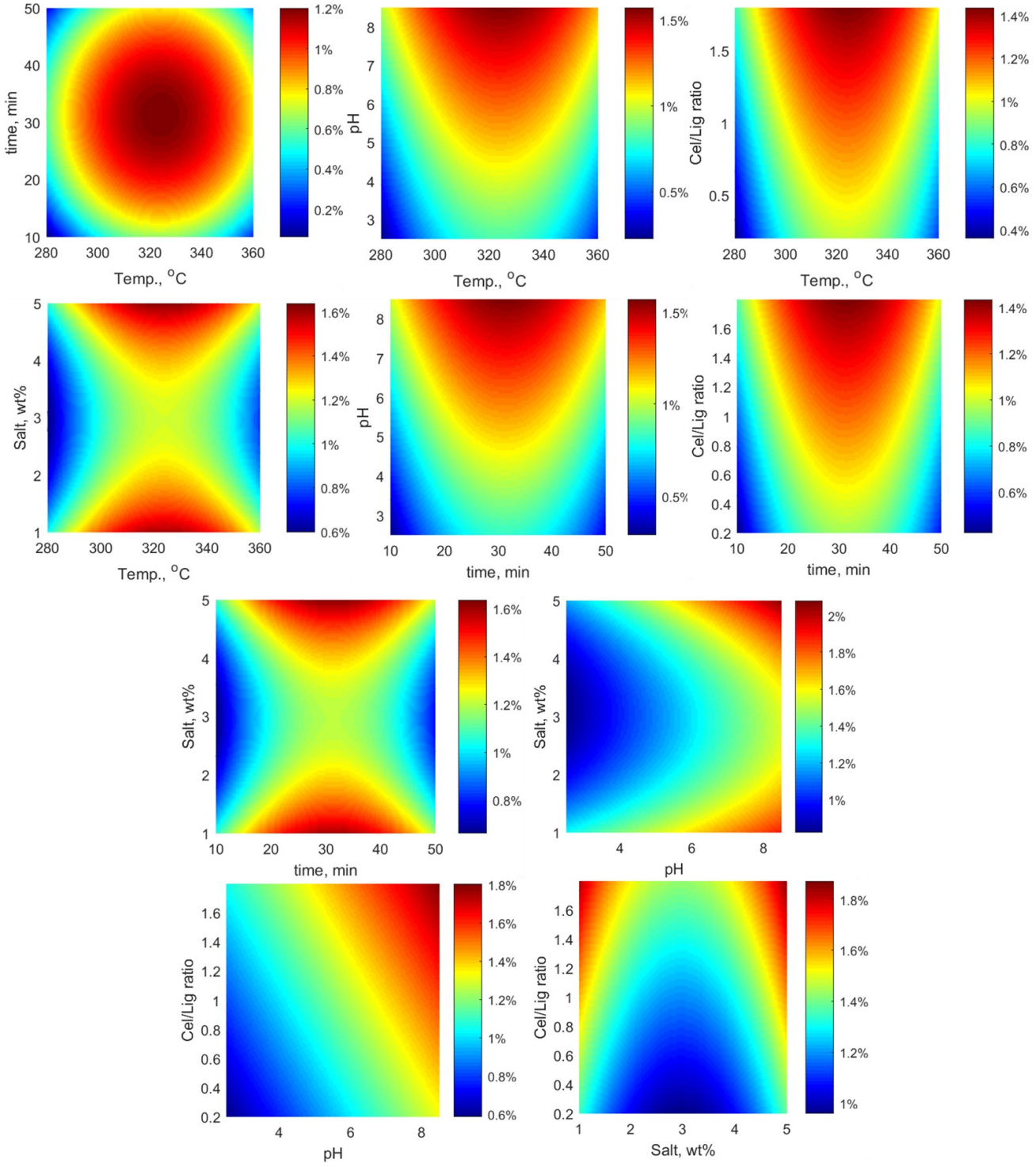


Figure S9. Contour plots for NH_3-N yield in HTL-AP (NH_3-N_{AP})

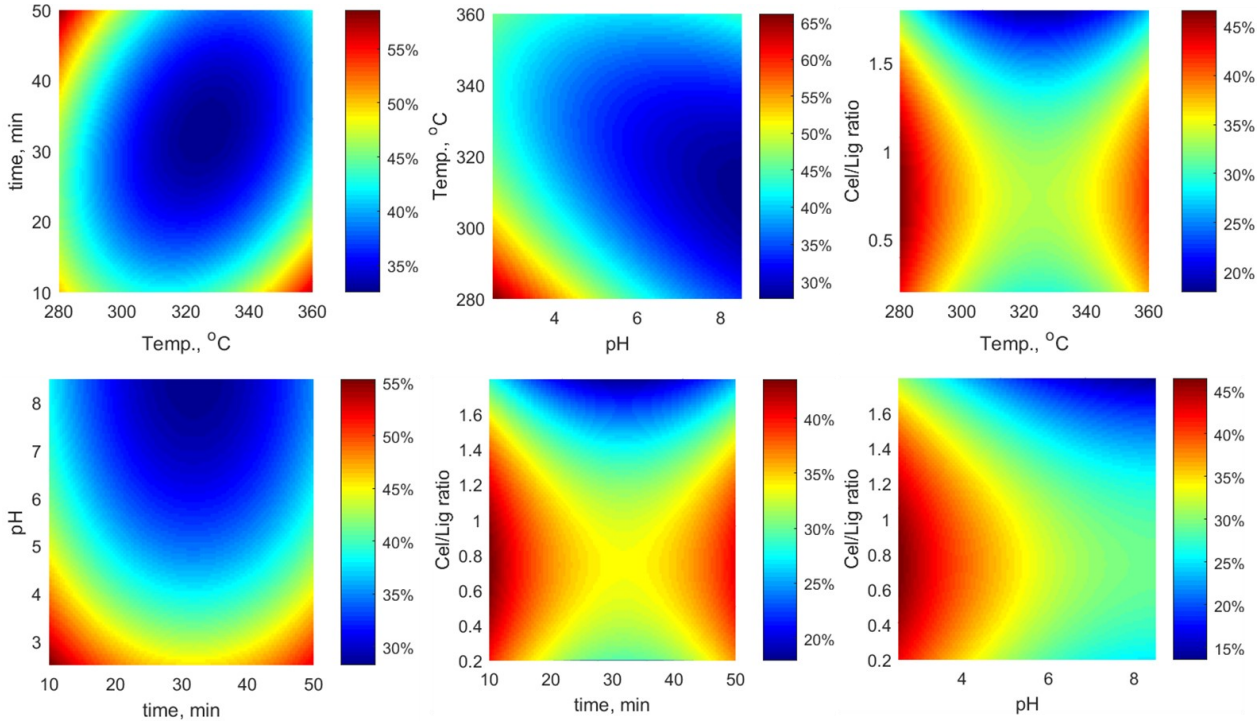


Figure S10. Contour plots for phosphorus yield in HTL-AP (P_{AP})

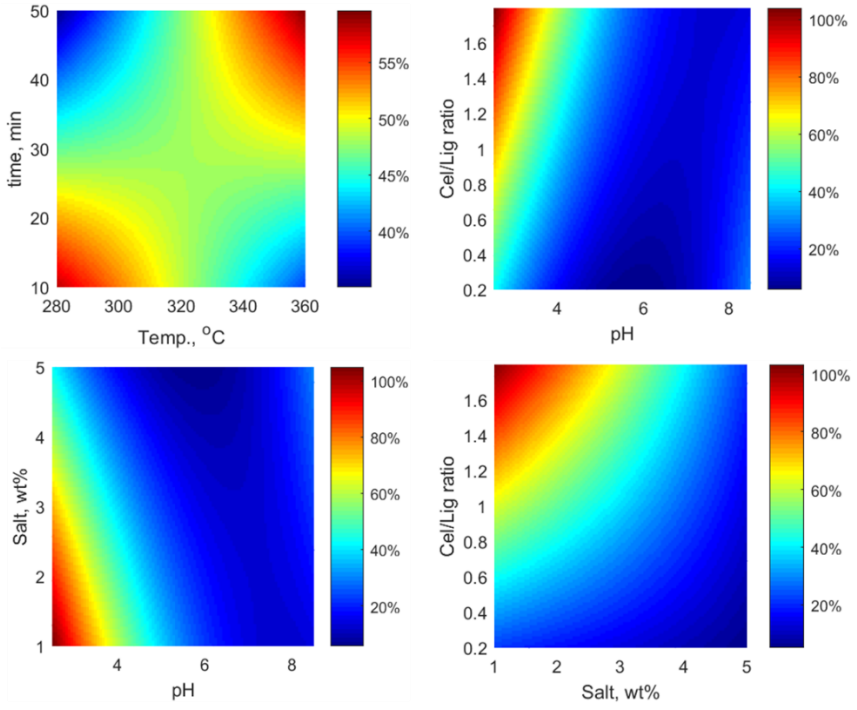


Figure S11. Contour plots for calcium yield in HTL-AP (Ca_{AP})

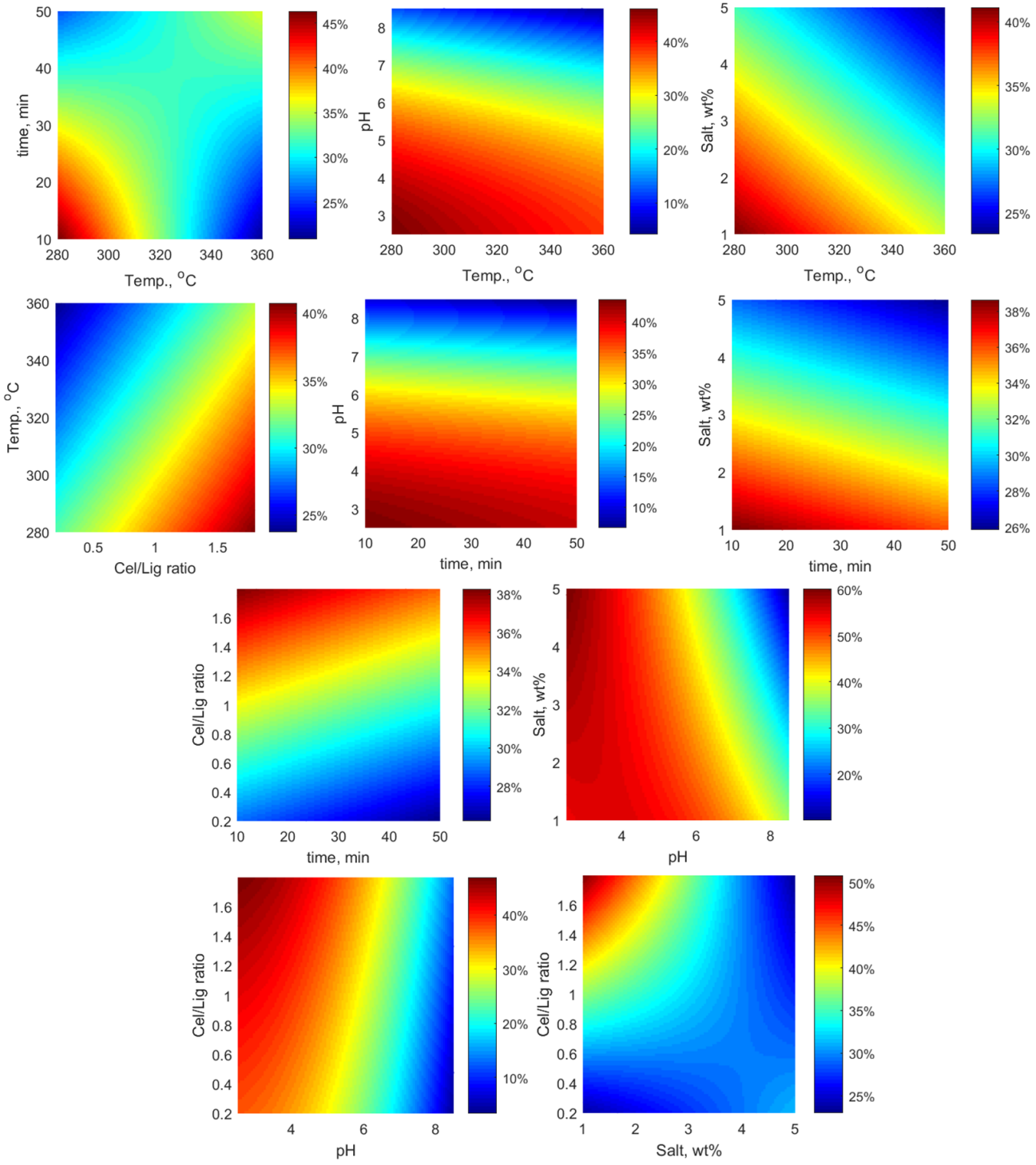


Figure S12. Contour plots for magnesium yield in HTL-AP (Mg_{AP})

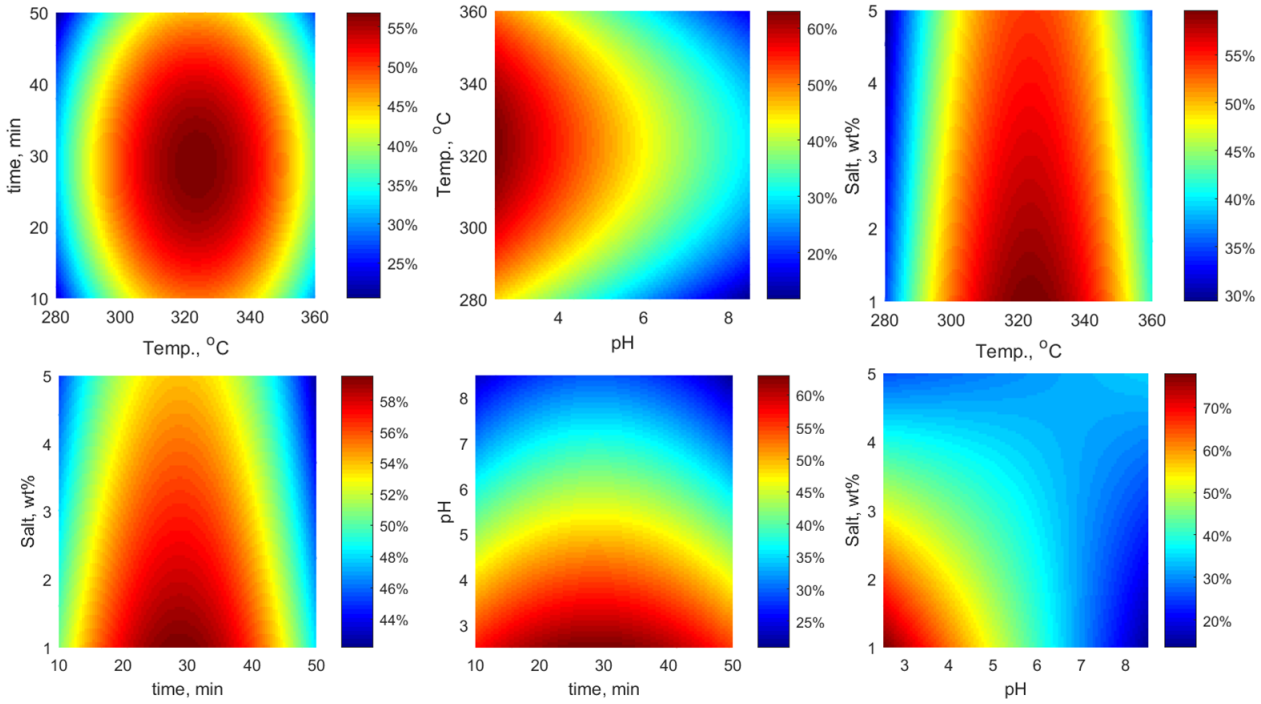


Figure S13. The Van Krevelen Diagram for DWO biocrudes to Demonstrate Major Deoxygenation Pathway

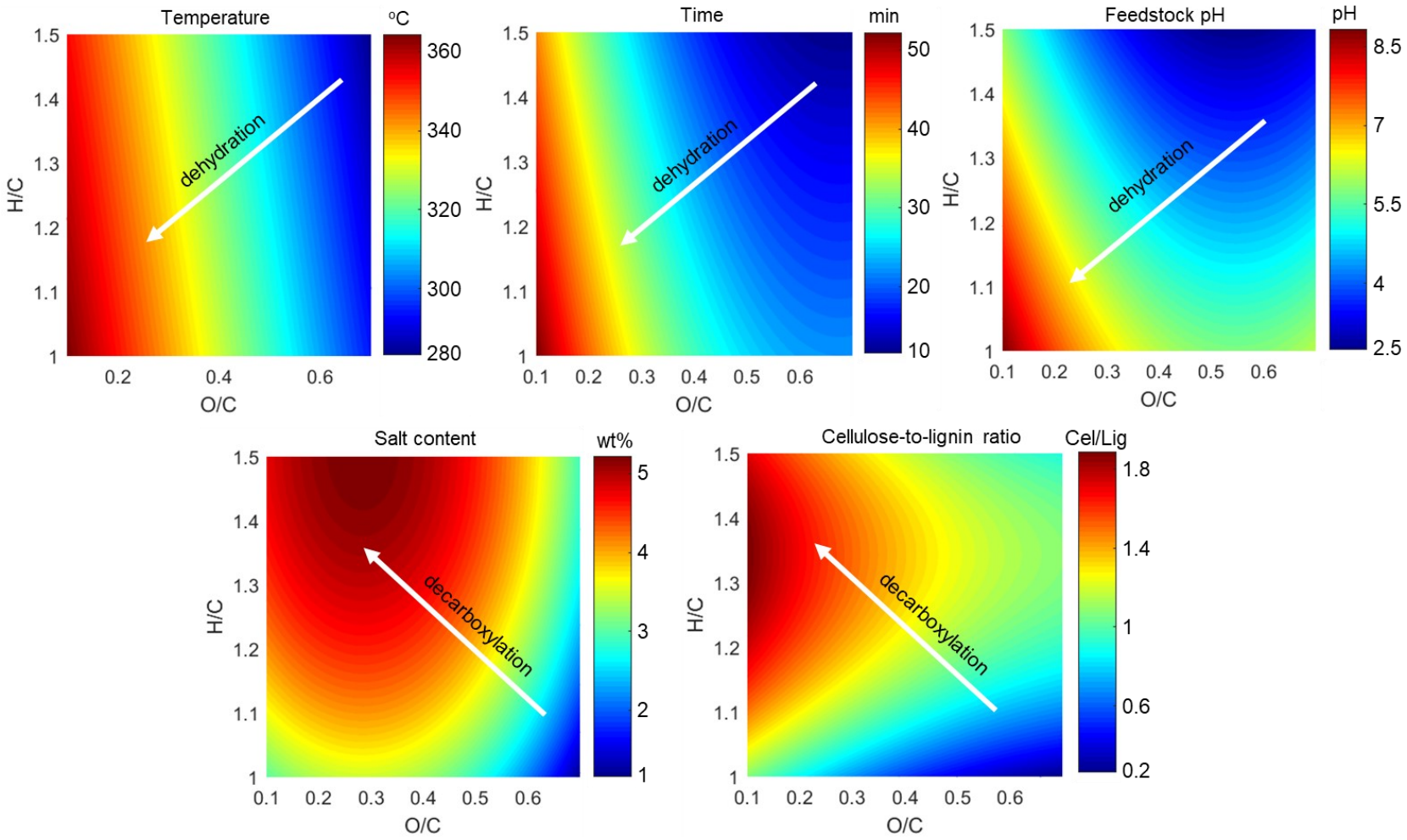


Figure S14. The Van Krevelen Diagram for DSO biocrudes to Demonstrate Major Deoxygenation Pathway

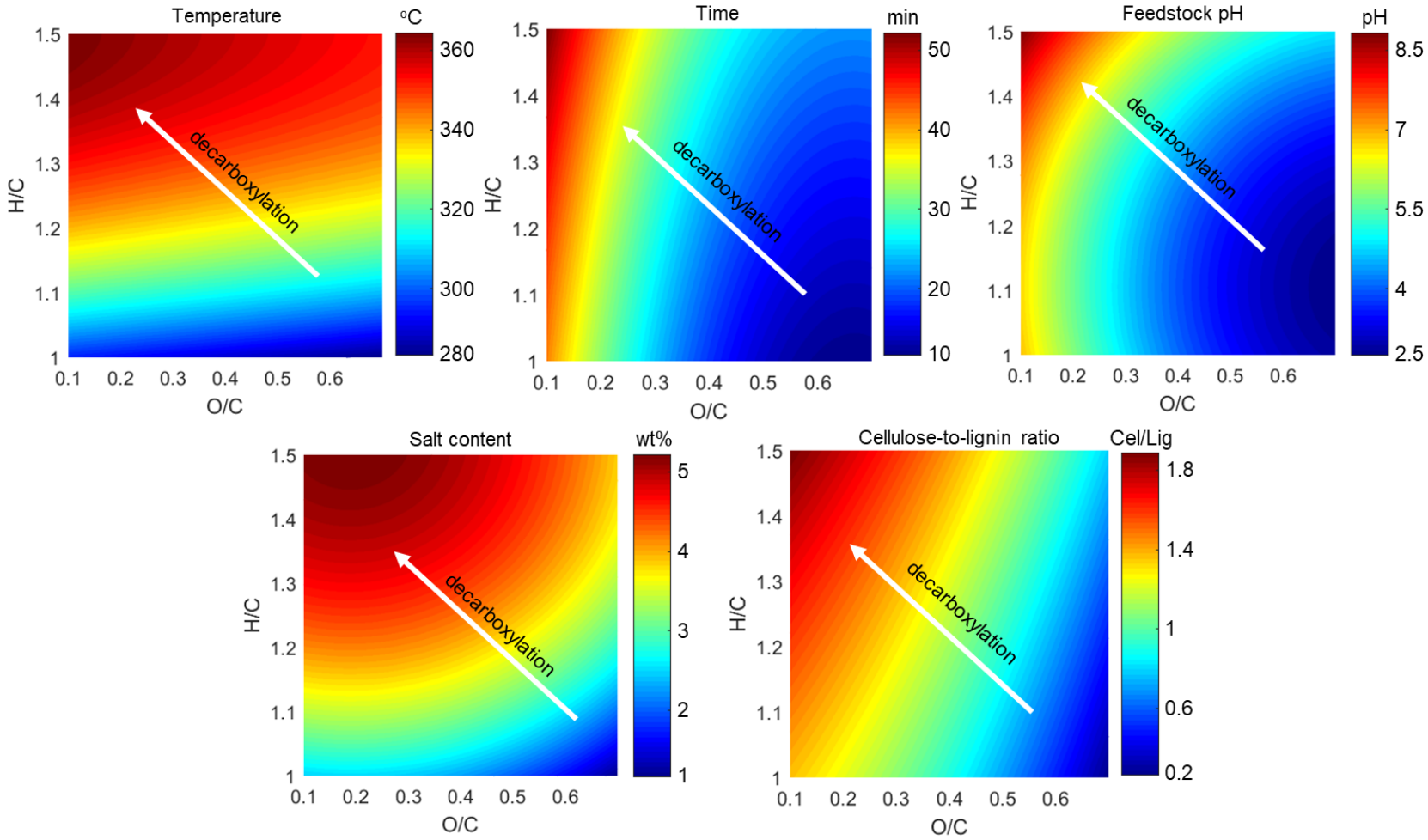
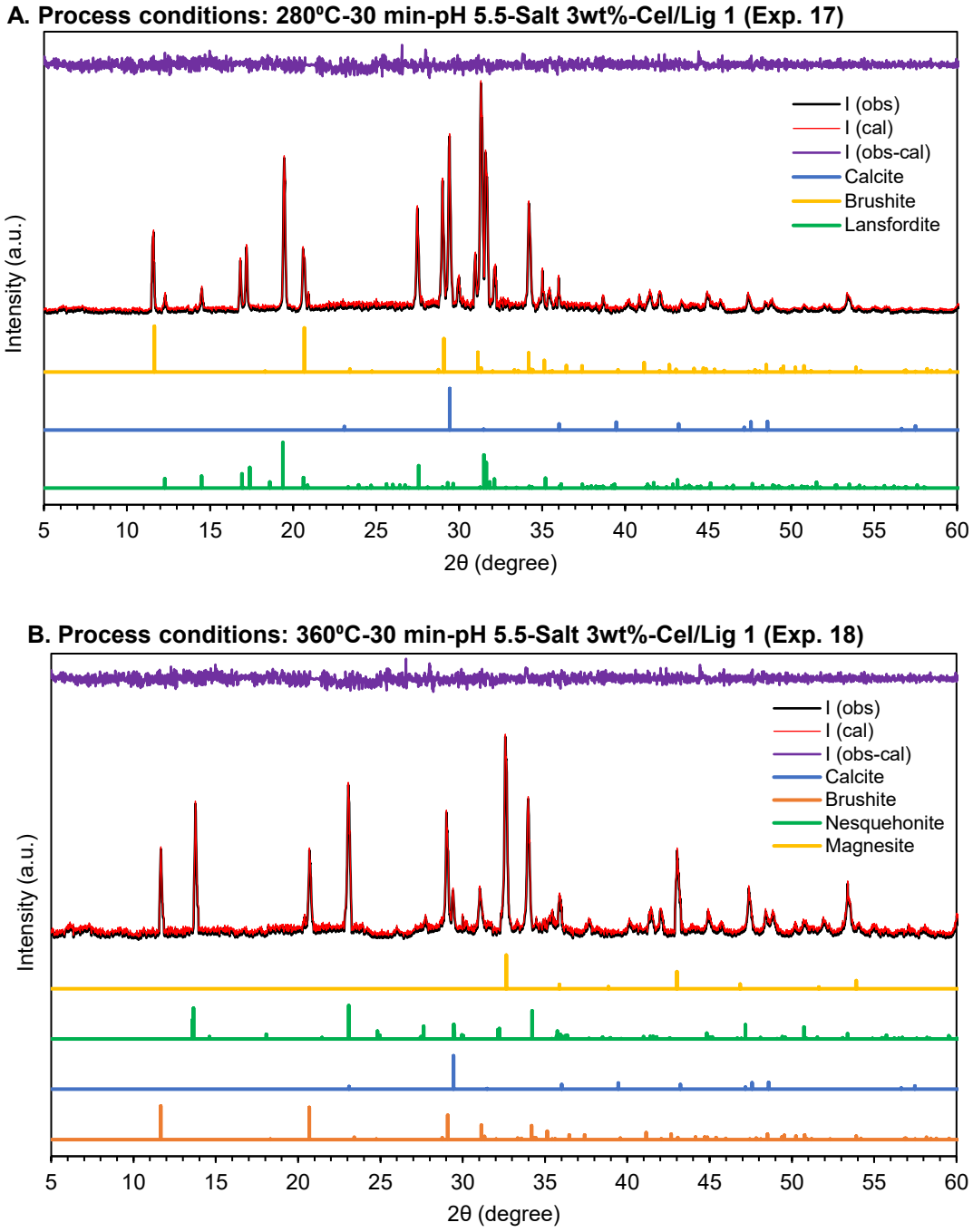
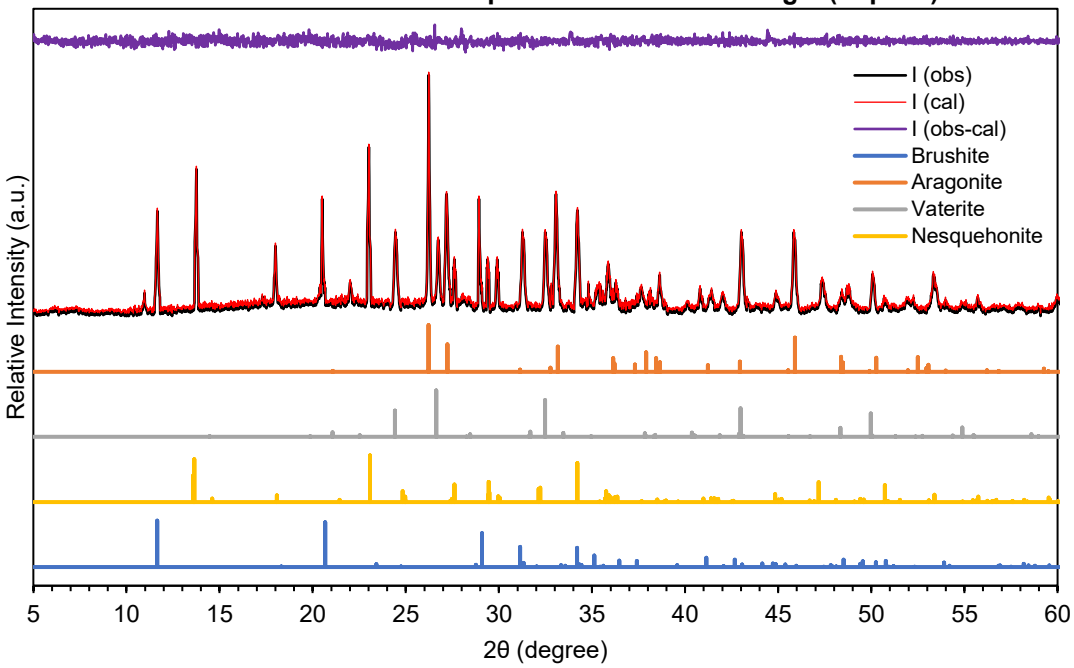


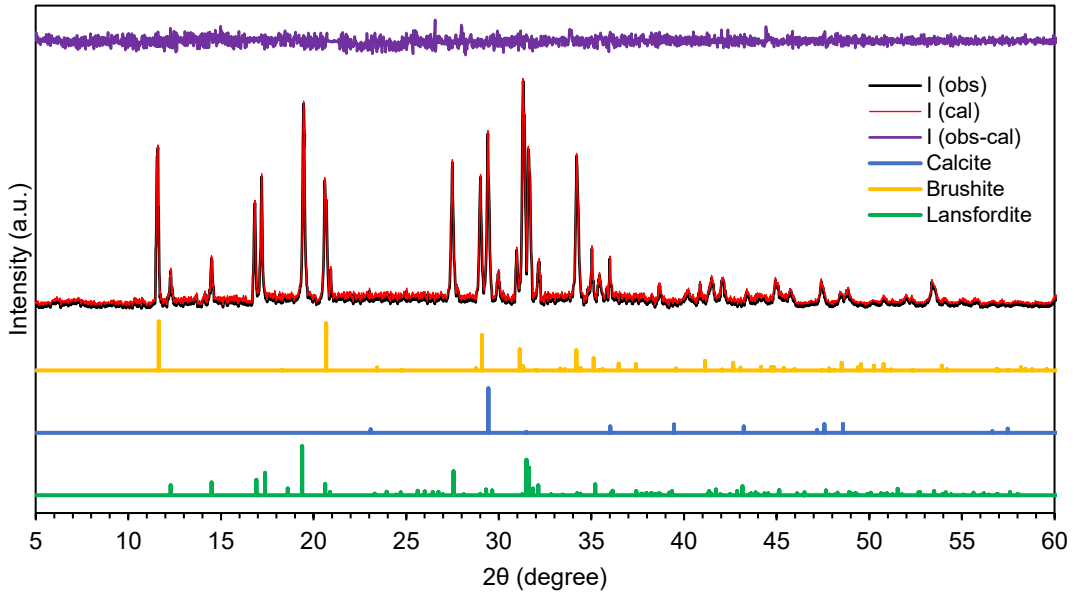
Figure S15. XRD results (with WPF and Rietveld refinement) for selected hydro-char samples: A). Produced from Exp. 17 (280ºC), B). Produced from Exp. 18 (360ºC), C). Produced from Exp. 20 (50 min), D). Produced from Exp. 27 (pH 5.5), and E). Produced from Exp. 22



C. Process conditions: 320ºC-50 min-pH 5.5-Salt 3wt%-Cel/Lig 1 (Exp. 20)



D. Process conditions: 320ºC-30 min-pH 5.5-Salt 3wt%-Cel/Lig 1 (Exp. 27)



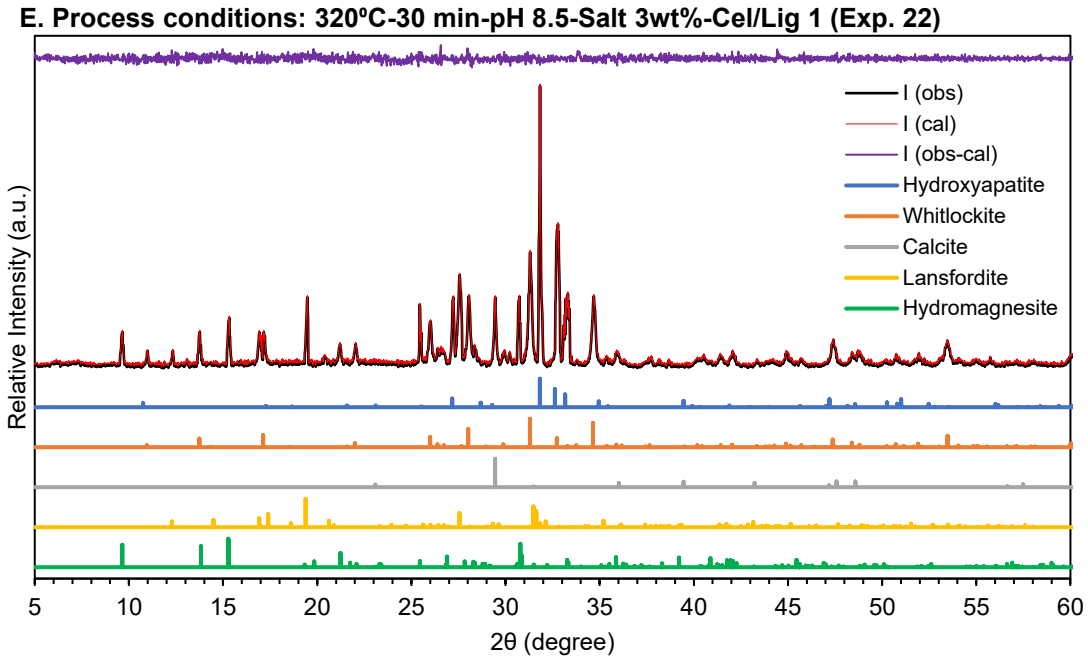


Figure S16. Contour Plot for Composite Desirability for Various Salt Contents & Cel/Lig Ratios

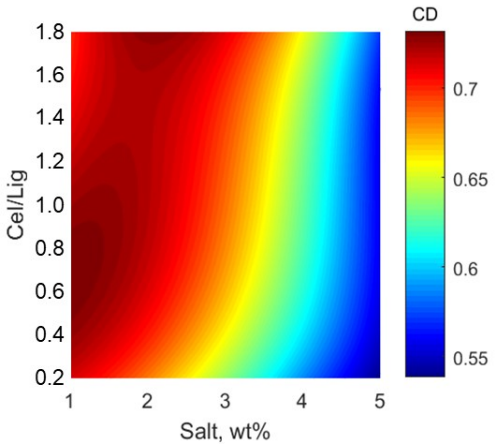


Figure S17. Contour Plots for Optimized Responses at Varying Salt Contents and Cel/Lig ratios

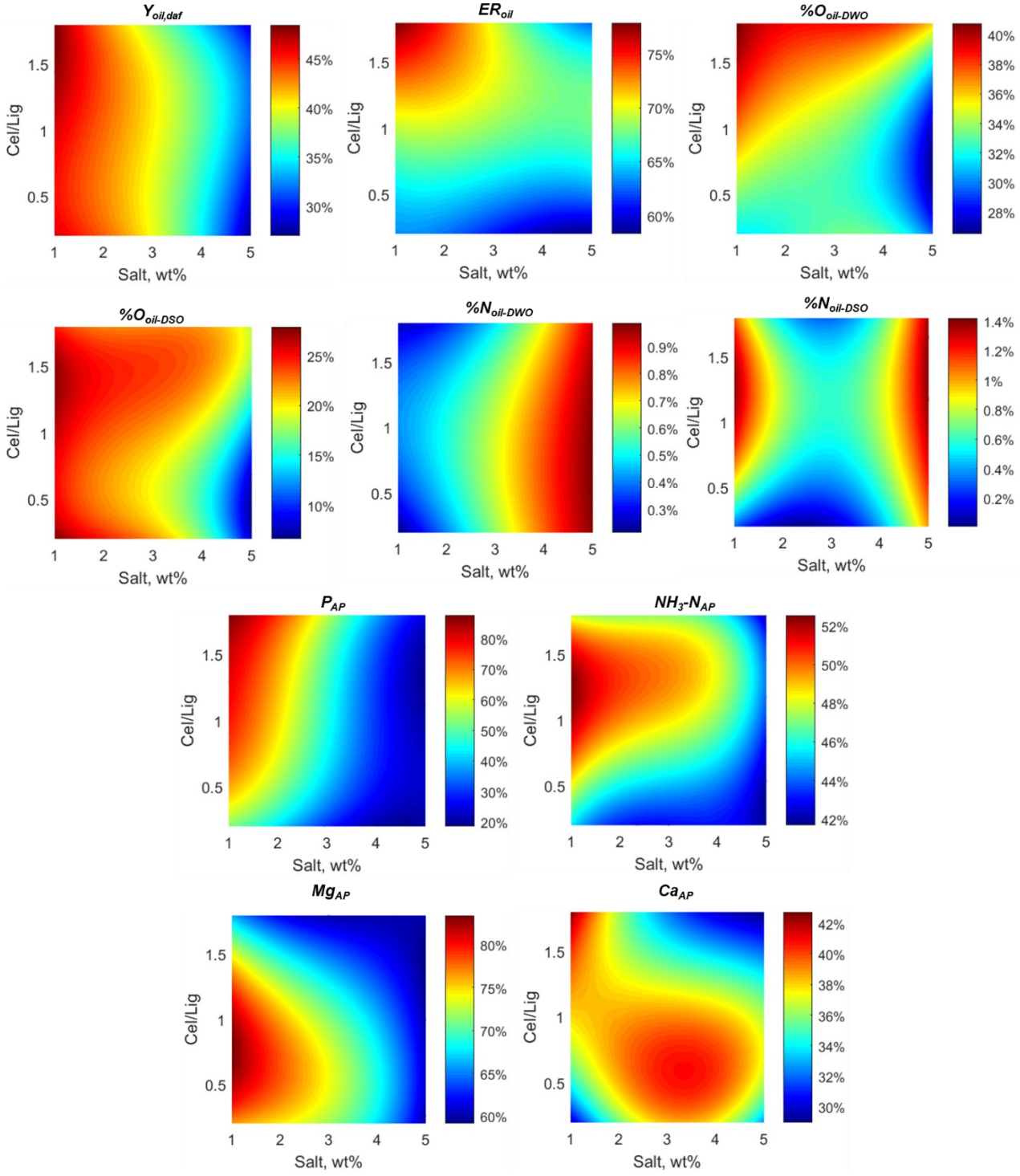
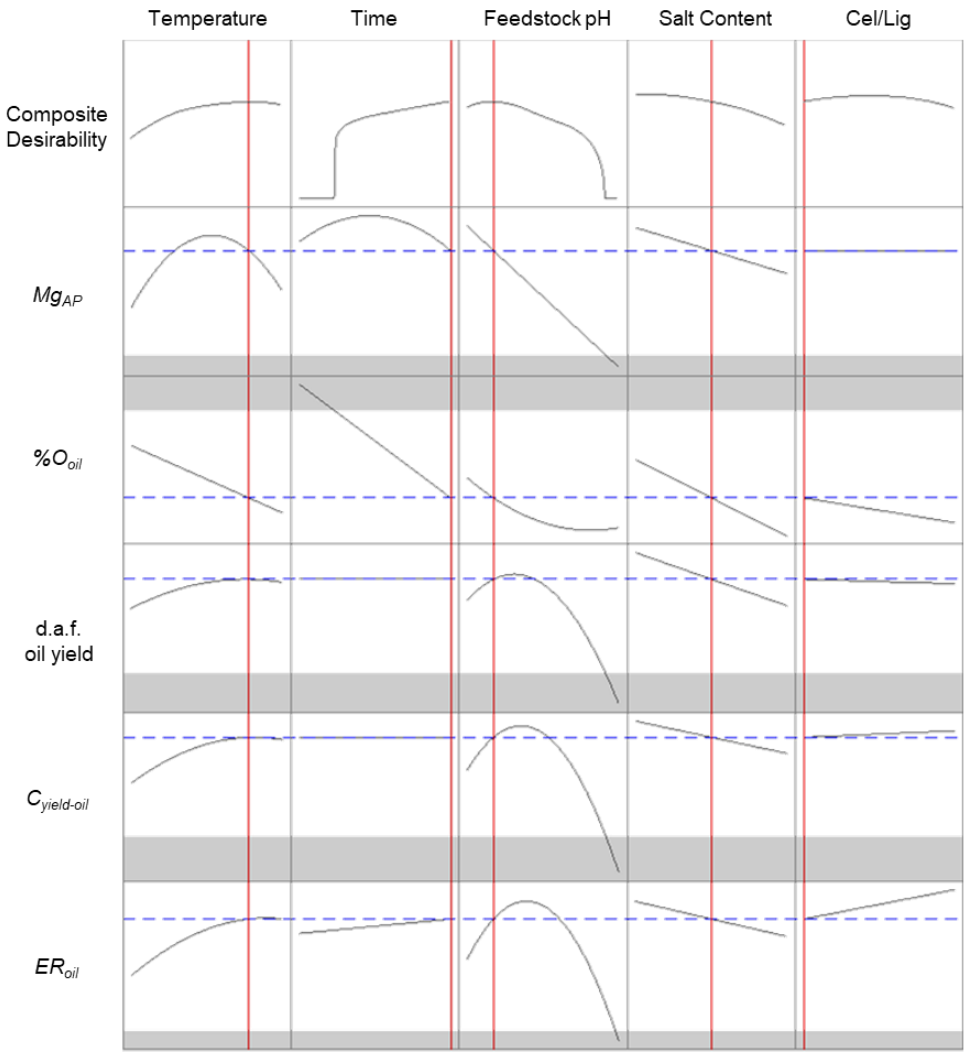


Figure S18. Individual Desirability Plots Generated from Minitab



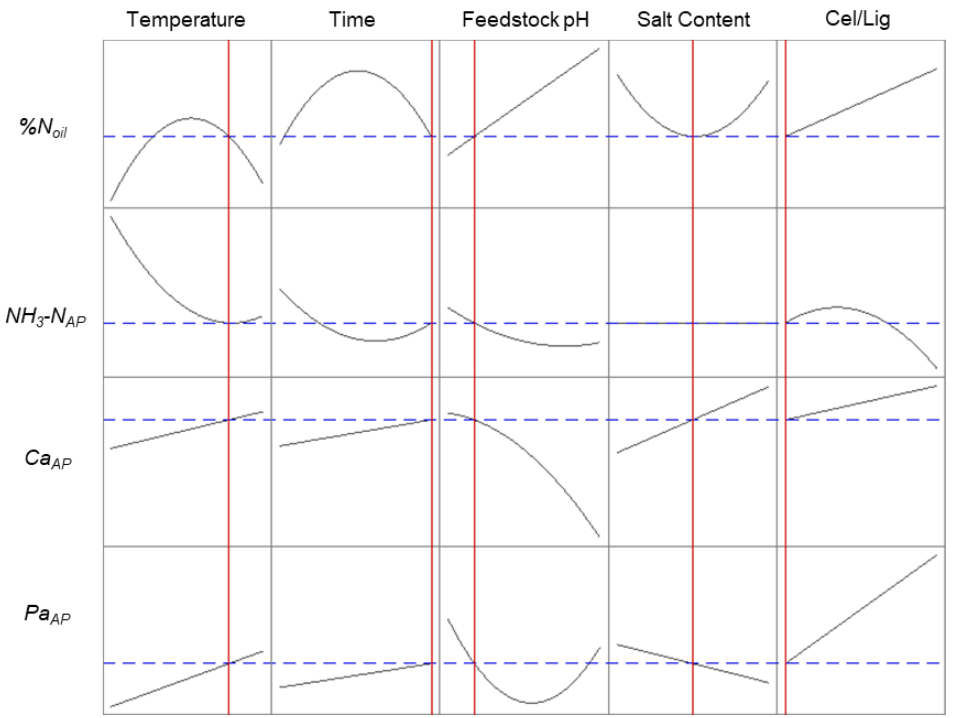


Figure S19. The heating and cooling time profile for the investigated reaction temperatures.

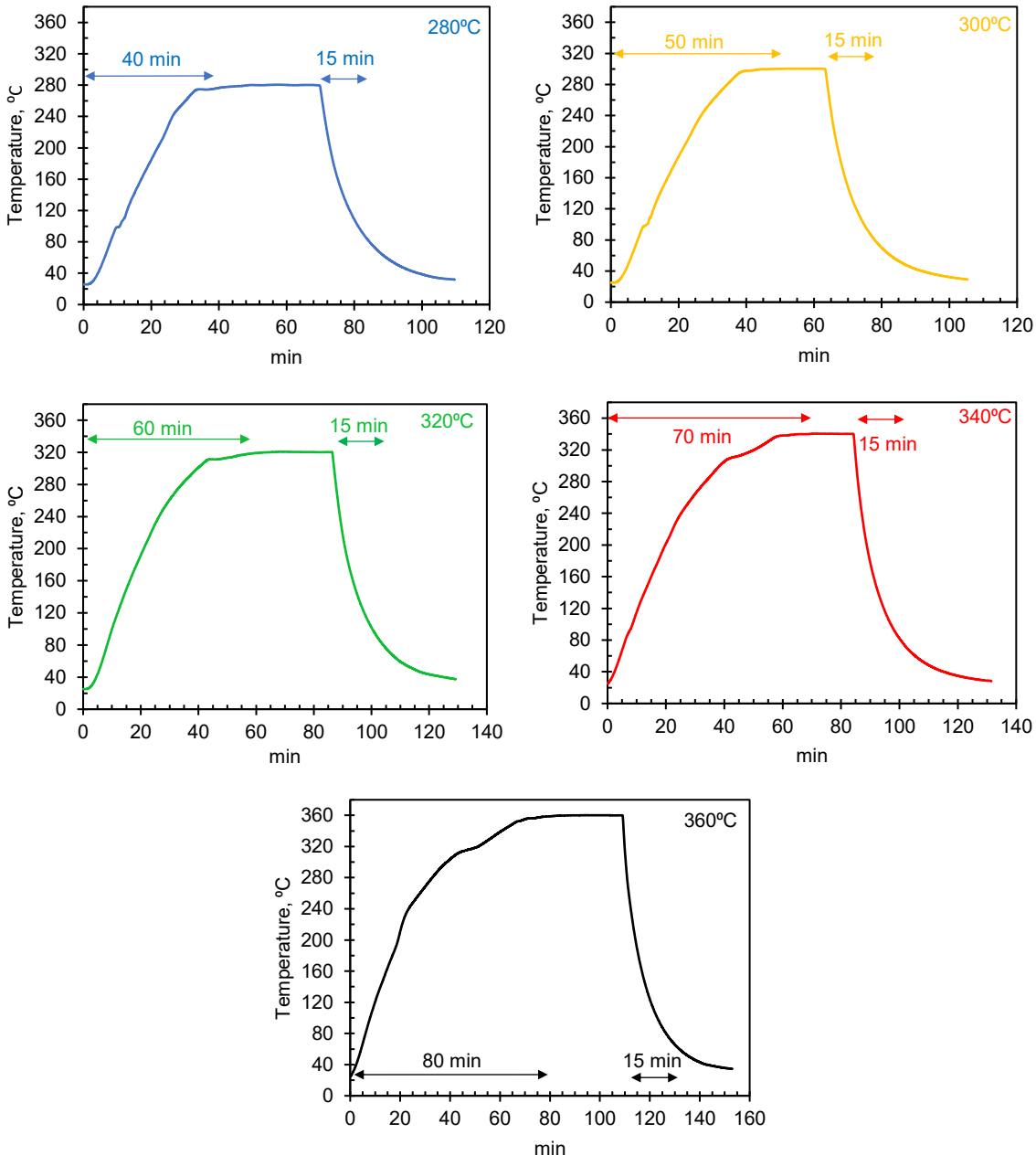


Figure S20. Thermogravimetric curves for dichloromethane-extracted water-soluble (DWO) and solid-bound (DSO) biocrudes produced from (A) pH 5.5 – Exp #27, (B) pH 8.5 – Exp # 22, (C) salt content 5 wt% - Exp #24, (D) 360ºC – Exp #18, (E) 50 min – Exp #20, and (F) Cel/Lig ratio 0.2 – Exp #25

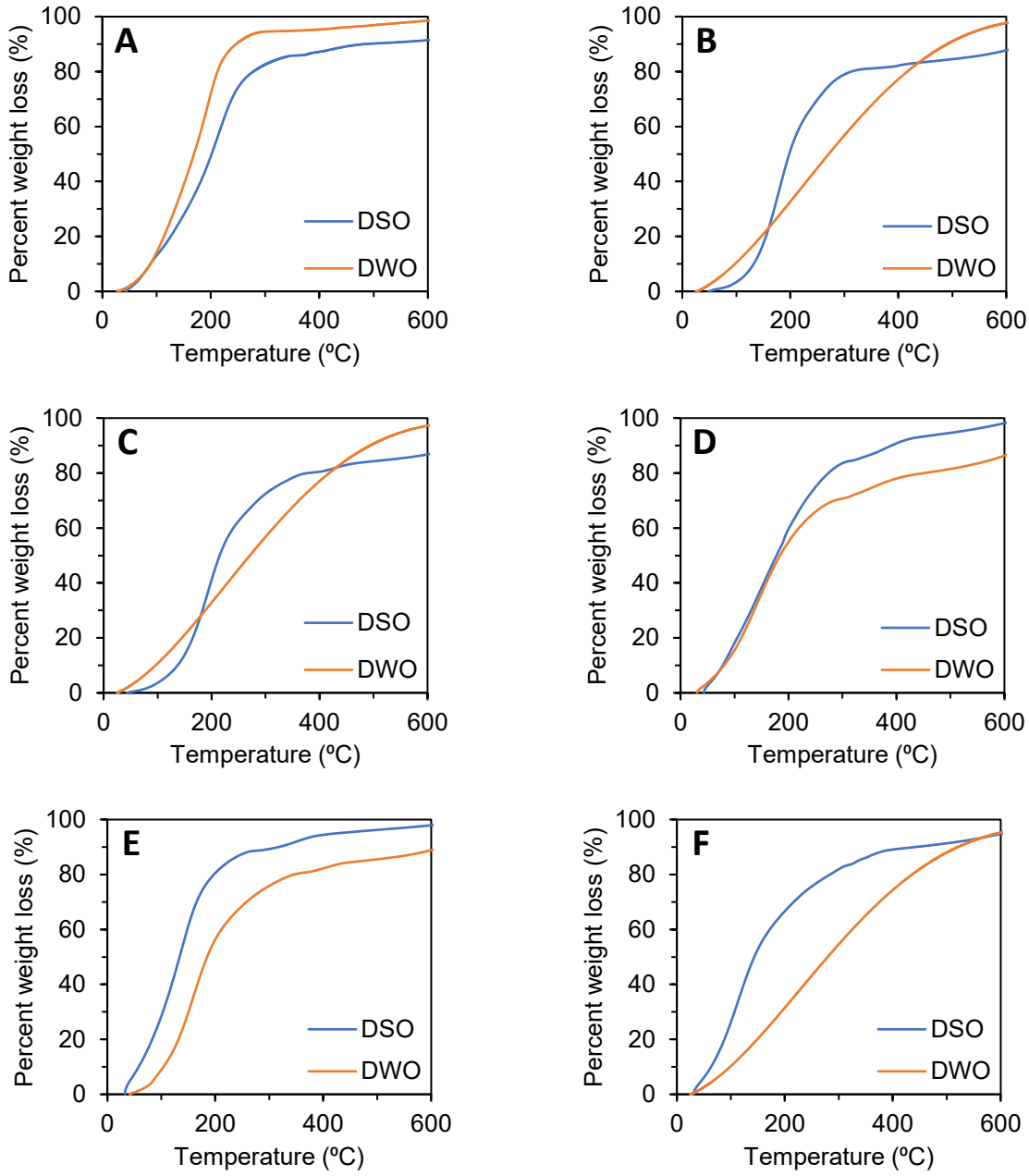


Figure S21. Thermogravimetric curves for the dichloromethane-extracted water-soluble (DWO) and solid-bound (DSO) biocrudes produced from the validation experiments at optimized HTL conditions: (A) digestate 1 – salt 2% and Cel/Lig 0.4, (B) digestate 2 – salt 2% and Cel/Lig 1.6, (C) digestate 3 – salt 4% and Cel/Lig 0.2, and (D) digestate 4 – salt 4% and Cel/Lig 1.6