Supporting Information for Desalting Biocrude for Improved Downstream Processing toward Marine Fuel Application

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Experimental

High-performance liquid chromatography (HPLC) analyses of samples were carried out using HPLC equipped with a Waters 2414 refractive index detector. A Bio-Rad Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm) was used for analyte separation. Sulfuric acid (0.005 M) was used as eluent at a flow rate of 0.55 mL/min. **Inductively coupled plasma (ICP)** analyses were conducted using a Perkin Elmer Optima 7300-DV ICP-OES equipped with a cyclonic spray chamber and a Meinhard nebulizer. Calibration was performed with certified reference standards. **Gas chromatography–mass spectrometry (GC-MS)** analyses of aqueous samples were carried out using an Agilent 5795C GCMS. The column was an Agilent HP-5MS with a 30 m × 0.25 mm × 0.25 μm film thickness and a carrier gas of helium at 1.0 mL/min. Oven temperature was initially held for 0.1 min at 35 °C, then ramped at 6 °C/min with a final temperature of 325 °C. A final oven hold of 1 minute was used. The inlet was heated at 270 °C, and 1 μL of sample was injected using a splitless injection. **Ion chromatography** samples were analyzed using a Dionex ICS-3000 equipped with a Dionex AS11-AC (4.0 × 250 mm) column and a conductivity detector. Aqueous samples were diluted as necessary to fall within the calibration range. Detection limits range from 1.0 to 100 ppm. Analytes included fluoride, bromide, nitrate, chloride, sulfate, and phosphate. **Nitrogen, ammonia (NH_3-N), and chemical oxygen demand (COD) analyses** were carried out using a HACH DR2800 following the manufacturer's recommended methods. **Carbon, hydrogen, nitrogen, and sulfur (CHNS) analyses** were carried out using an Elementar Vario Macro Cube. Combustion and reduction tubes were packed accordingly to analyze CHNS. The combustion tube was heated to 1,150 °C and the reduction tube to 850 °C. Helium was used as the carrier gas. All sample data are reported as-is or as-received (not on a dry basis). For **oxygen content**, samples were analyzed using an Elementar Rapid Oxy-Cube. The combustion tube was packed according to manufacturer specifications. The combustion tube was heated to 1,450 °C. Helium was used as the carrier gas.

Table S1. Representative ICP Data for Biocrudes

	High Moisture UWBC[a]	Low Moisture UWBC[a]	Scaleup UWBC
Element	***ppm***	***ppm***	***ppm***
Al	15	18	15
Ca	22	50	49
Fe	192	317	250
K	1063	626	745
Mg	16	28	31
Mn	15	11	BDL
Na	3184	1086	1274
Si	365	12	127
S	1125	1814	1655

[a]*Differences in the composition of the biocrudes between are attributed to the design of the biocrude recovery tank. The product tank is static and the biocrudes were recovered at different depths in the tank.*

High-moisture biocrudes > 20% water, as assessed by KF titration

Low-moisture biocrude ~7% water as assessed by KF titration

Table S2. Representative CHNS For Biocrudes

	High Moisture UWBC[a]	Low Moisture UWBC[a]	Scaleup UWBC
Element	***wt%***	***wt%***	***wt%***
N	3.1	3.5	3.2
C	58.8	74.0	71.8
H	11.3	11.7	11.2
S	0.1	0.1	0.1

[a]*Differences in the composition of the biocrudes between are attributed to the design of the biocrude recovery tank. The product tank is static and the biocrudes were recovered at different depths in the tank.*

Table S3. Initial Additive Screening and Observations. 1:1 UWBC to water. 80°C. 1 hour.

Additive	Weight% Added (% of Aqueous)	Phase Separation After Heating?
None		Limited
Ethylene Glycol	10%	No
Formic Acid	10%	Yes
Acetic Acid	10%	Yes
Citric Acid	10%	Yes
EDTA	3.3%	Yes
Formic Acid	4.8%	Yes
Acetic Acid	4.8%	Yes
Citric Acid	4.8%	Yes
Malic Acid	4.8%	Yes
HDTA Br	4.8%	Yes
Fumaric Acid	1%	Yes
Glycolic Acid	1%	Yes
Succinic Acid	1%	Yes
Formic Acid	1%	Yes
Sulfuric Acid	0.7%	Partial

Table S4. Mass% metals extracted from unwashed biocrude (UWBC) at various formic acid concentrations with different additives.

	Percent Mass of Element Transferred to Aqueous Phase				
Element	Formic Acid[1]	Acetic Acid[1]	Citric Acid[1]	EDTA[2]	Malic Acid[1]
Al	92%	15%	86%	71%	87%
Ca	>99%	>99%	>99%	>99%	>99%
Fe	>99%	33%	71%	81%	66%
K	>99%	97%	>99%	>99%	>99%
Na	94%	69%	64%	79%	73%
Zn	>99%	16%	>99%	>99%	85%
Mo	<18%	<18%	<18%	18%	19%
S	7%	4%	7%	3%	5%

1: 4.8 wt%. 2: 1.6 wt%

Figure S5. Mass metals extracted from unwashed biocrude (UWBC) at various temperatures in early screening experiments. Concentrations in aqueous phase (left) and Washed Biocrude (right).

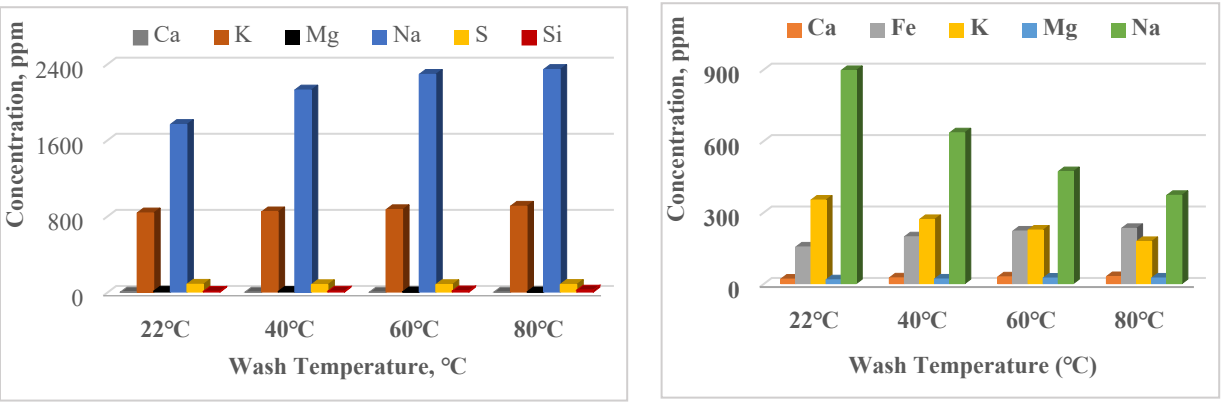


Table S6. Mass% metals extracted from unwashed biocrude (UWBC) at various formic acid concentrations.

	Metal Removal, wt% (Aqueous, ICP Basis)				
Formic Acid wt% of Total	Al	K	Mg	Na	S
0.05 Wt%	0.0%	40.9%	0.0%	38.1%	1.8%
0.14 Wt%	16.8%	42.8%	0.0%	40.5%	2.6%
0.3 Wt%	20.54%	58.2%	0.0%	65.7%	1.0%
0.5 Wt%	28.09%	76.1%	10.8%	85.3%	0.9%

Figure S7. Mass% metals extracted from unwashed biocrude (UWBC) at various formic acid concentrations.

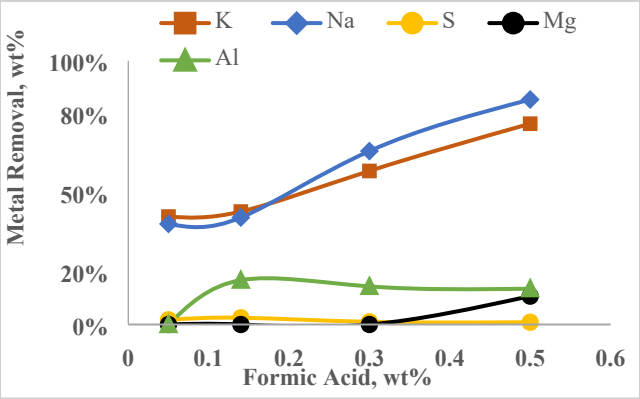


Table S8. Metals Concentration in Recovered Aqueous. High-Moisture UWBC treated at various formic acid concentrations.

FA/Total, wt%	Al	Fe	K	Mg (oil)	Na
0.87	4.42	0.35	91.29	46.21	90.77
1.51	11.63	14.13	96.66	46.30	96.17
2.40	20.54	44.93	95.49	46.49	93.17
3.15	28.09	52.06	96.74	46.30	93.47
5.07	29.14	68.09	92.62	42.49	90.71
7.36	37.62	74.83	97.54	44.21	96.61

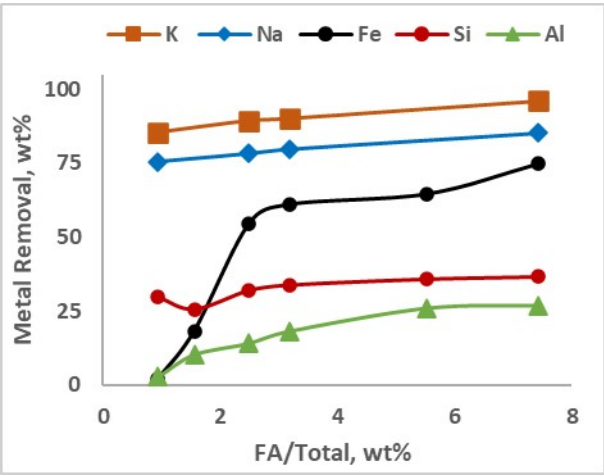


Figure S9. Mass% metals extracted from unwashed low-moisture biocrude (UWBC) at various formic acid concentrations

Figure S10. Percent of various elements removed from high-moisture biocrude washed at various UWBC to water mass ratios (1 weight% of unwashed biocrude, 80℃, 1 hour)

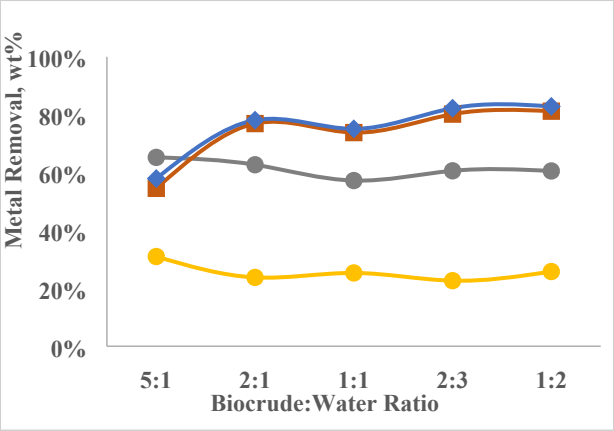


Figure S11. Metal removal from low-moisture UWBC at various UWBC to water mass ratios at 80℃, 0.7 weight% formic acid.

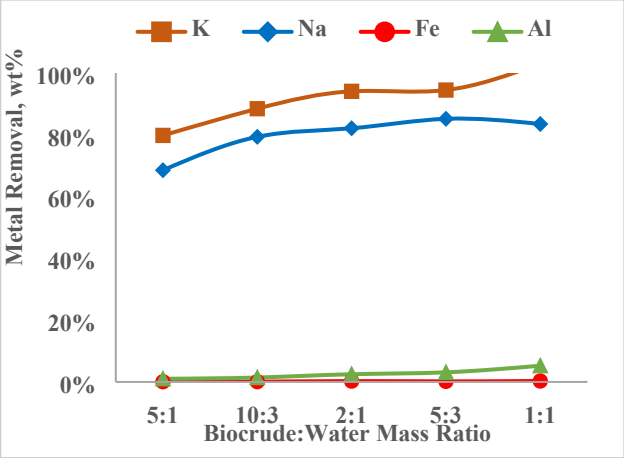


Table S12. Percent of various elements removed from high- and low-moisture biocrudes washed with aqueous solutions of formic acid (0.7 weight% of UWBC , 80 °C, 1 hour)

High-Moisture UWBC Middle Oil	Metal Transferred to Aqueous, wt% (ICP)				
UWBC:Water Mass Ratio	Al	Fe	K	Mg	Na
5:1	1.91	0.15	66.77	35.91	66.56
10:3	3.17	0.25	100	81.0	98
5:2	3.60	0.29	89.08	55.74	89.36
2:1	4.35	0.35	94.04	58.75	91.61
5:3	5.80	0.47	95.63	53.25	96.90
1:1	7.34	0.59	104	55.00	103
Low-Moisture UWBC	**Metal Extracted into Aqueous, wt% (ICP)**				
UWBC:Water Mass Ratio	Al	Fe	K	Mg	Na
5:1	1.0	0.06	79.8	91.5	68.5
10:3	1.4	0.08	88.4	99.99	79.3
5:2	2.2	0.10	100.39	118.59	89.4
2:1	2.5	0.26	94.1	107.43	82.1
5:3	3.1	0.18	94.5	106.7	85.2
1:1	5.3	0.30	103.07	105.75	83.5

Figure S13. Metal removal from low-moisture (top) and high moisture UWBC at various wash times at 80C, 0.7 weight% formic acid.

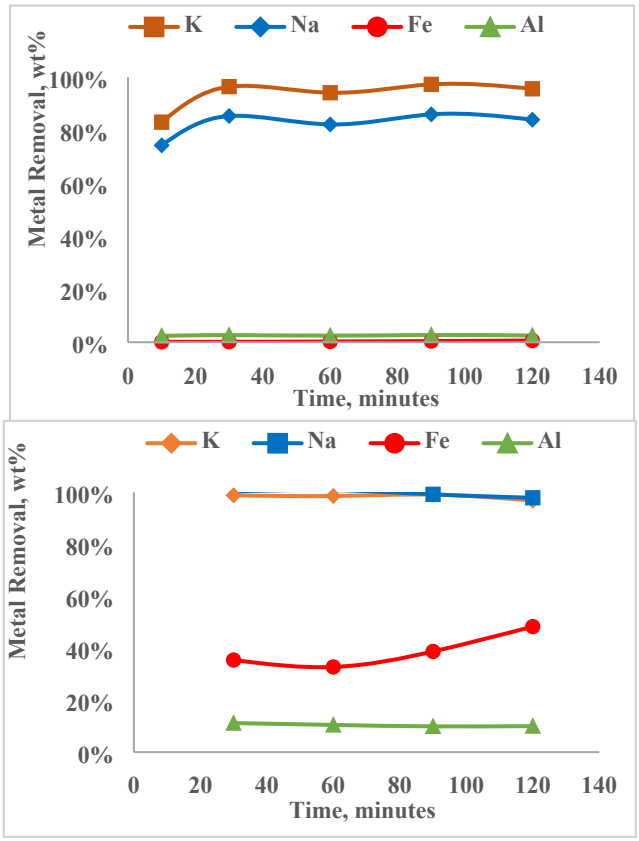


Table S14. Compounds Identified by HPLC in Recovered Aqueous in Scaled Up Washes

Peak Name	Wt%	Mass
Glycolic Acid	0.002	0.002
Glycerol	0.031	0.033
Formic Acid	**0.905**	0.970
Acetic Acid	0.017	0.018
Ethylene Glycol	0.003	0.003
Propylene Glycol	0.002	0.002
1,3-propanediol	0.006	0.006
Propanoic Acid	0.004	0.004
1,2-butanediol	0.001	0.001
Ethanol	**0.163**	0.175
Butanoic Acid	0.003	0.003
Acetone	0.03	0.032
tert-Butanol	0.008	0.009
1-propanol	0.012	0.013
MEK (2-butanone)	0.019	0.020
2-butanol	0.004	0.004
2-methyl-1-propanol	0.007	0.008
3-methyl-2-butanone	0.01	0.011
1-butanol	0.018	0.019
2-pentanone	0.002	0.002
2-cyclopenten-1-one	0.001	0.001
3-methyl-2-(5H)-furanone	0.002	0.002
2-methylcyclopentanone	0.012	0.013
3-hexanone	0.008	0.009
Phenol	0.004	0.004
3-methyl-2-cyclopentene-1-one	0.015	0.016
o-Cresol	0.003	0.003
m-Cresol	0.008	0.009
p-Cresol	0.009	0.010
Total	**1.309**	1.403
Total – Formate	**0.404**	0.433

Table S15. Compounds identified in Recovered Aqueous by GC-MS.

Compound	
Ethanol	2-methyl-2-Cyclopenten-1-one
Acetone	1-ethyl-2,5-Pyrrolidinedione
2-amino-1-Propanol	1,3-Diazine
1-Propanol	L-Alanine, ethyl ester
2-Butanamine	methyl-Pyrazine
dihydro-2-methyl-Furanone	5-methyl-2-Hexanamine
sec-Butylamine	2,6-dimethyl-Pyrazine

Table S16. Metal Content Removed from Biocrude after Washing.

Analyte Name	*Average PPM in WBC*
Al	15
Fe	271
Ca	52
K	50
P	<12
Mg	22
Na	110
Si	175
Zn	<12

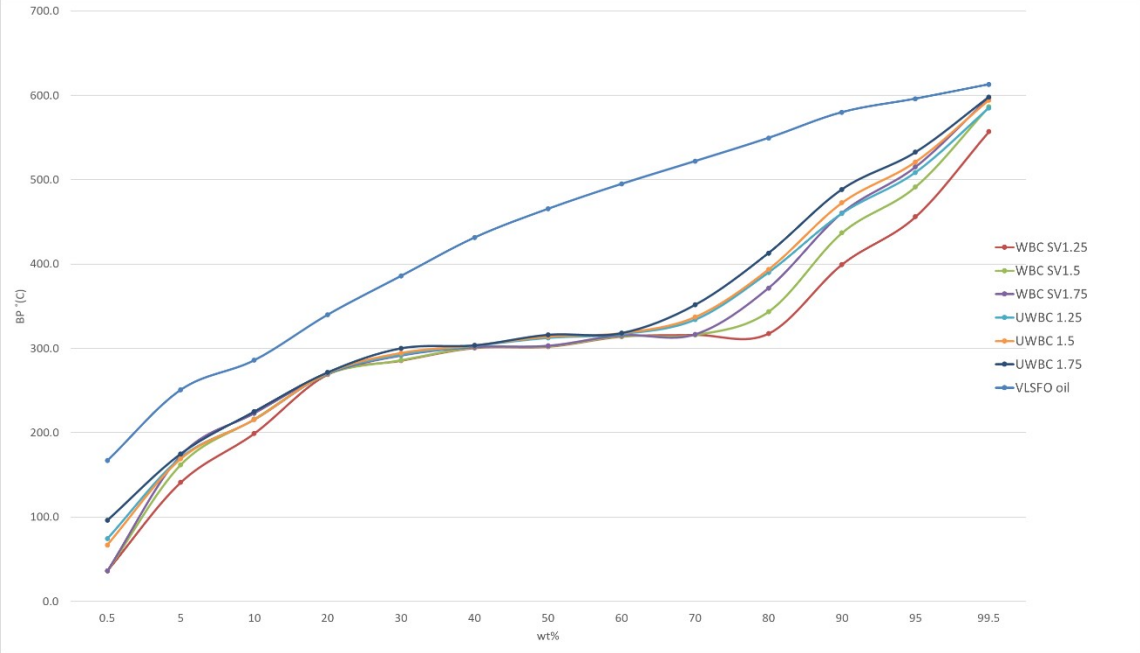
Table S17. Metals Removed from Biocrude after Washing. 0.75 weight% formic acid

Analyte Name	*% Removal from UWBC*
Al	5%
Fe	2%
K	87%
Mg	21%
Na	84%
Si	8%

Table S18. Hydrotreating Yield Data

	HT1-WBC	HT2-WBC	HT3-WBC	HT1-UWBC	HT2-UWBC	HT3-UWBC
WHSV (H-1)	1.25	1.5	1.75	1.25	1.5	1.75
YIELDS ANALYSIS (DRY-BASIS)						
OIL YIELD (G/G FEED)	0.827	0.859	0.949	0.827	0.870	0.850
AQ YIELD (G/G FEED)	0.116	0.097	0.011	0.129	0.087	0.115
GAS YIELD (G/G FEED)	0.058	0.043	0.040	0.044	0.043	0.035
H_2 CONSUMPTION (G/G FEED)	0.032	0.024	0.029	0.028	0.030	0.032

Figure S19. SIMDIST of the hydrotreated product versus fuel oil



S20. Process description of wet waste hydrothermal liquefaction (HTL) without a water wash process

In the base case, the HTL plant processes 1,000 dry metric tons of sludge a day and the sludge cost at the gate of the HTL plant is assumed to be zero. Sludge is dewatered to 25% solid content and then pumped into the HTL reactor. HTL reactor operating conditions are near the subcritical water status, which results in high solubility of organic compounds. To reach such operating conditions, the feed slurry is first pumped to 20 MPa and then heated in the heat exchanger and trim heater to 350 ℃. The HTL reactor has a shell-and-tube structure, with feed slurry on the tube side and hot heating oil on the shell side. After the reaction, the wet waste is converted into biocrude, an aqueous phase, and a small number of solids and gases. In a solid-liquid-gas three-phase separator, the solid and gas are separated from the liquid, and the liquid effluents are then cooled for further aqueous–biocrude phase separation. The gas combined with natural gas is sent to a burner for generating heat to supply the HTL heating requirements via the hot oil system. The aqueous phase needs a series of treatment steps before recycling back to the wastewater treatment (WWT) plant. Specifically, it is first treated with quicklime to raise the pH to ~11 and then stripped with air to remove ammonia and volatile organics (VOCs) from the aqueous stream. The ammonia and VOCs can be destroyed in a thermal oxidizer (THROX) with the help of natural gas and a catalyst. At the same time, the liquid at the bottom of the stripper is further treated to decrease COD before recycling back to WWT plants.

Table S21 summarizes the primary economic assumptions for the “nth-plant” method employed in this study. This method does not account for special financing, equipment redundancies, large contingencies, and long start-up times because it assumes that several plants have already been built and are operating.

Table S21. Key assumptions for the technoeconomic analysis.

Assumption Description	Assumed Value
Cost year	2016 $
Internal rate of return (IRR)	10%
Plant financing debt/equity	60% / 40% of total capital investment (TCI)
Plant life	30 years
Income tax rate	21%
Interest rate for debt financing	8.0% annually
Term for debt financing	10 years
Working capital cost	5.0% of fixed capital investment (excluding land)
Depreciation schedule	7-year MACRSschedule [a]
Construction period	3 years (8% 1st yr, 60% 2nd yr, 32% 3rd yr)
Plant salvage value	No value
Start-up time	6 months
Revenue and costs during start-up	Revenue = 50% of normal Variable costs = 75% of normal Fixed costs = 100% of normal
On-stream factor	90% (7,920 operating hours per year)

[a] Modified accelerated cost recovery system