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Integrated Extraction and Catalytic Upgrading of Biocrude Oil from Co-hydrothermal Liquefaction of Crude Glycerol and Algae

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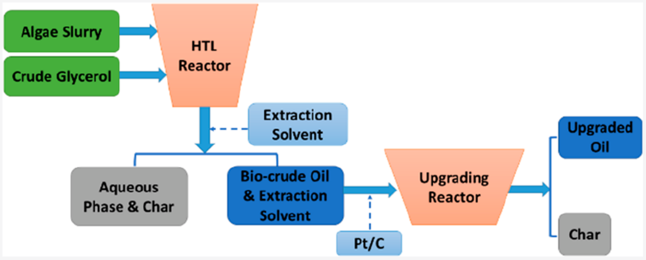

ABSTRACT: Co-hydrothermal liquefaction (HTL) of wastewater algae and crude glycerol has been shown to produce higher yields at lower costs compared to wastewater algae biomass conversion alone. The biocrude oil produced from co-HTL of wastewater algae and crude glycerol does, however, have a relatively high oxygen content (10−16 wt %) and relatively low energy content (34−36 MJ/kg). To upgrade the biocrude oil to high-quality biofuel and to simplify the overall process, several organic solvents were evaluated for their ability to extract biocrude oil from the HTL products and to donate hydrogen for biocrude oil upgrading. The solvent options tested were hexane, cyclohexane, ethyl acetate, and no solvent, in combination with effective heterogeneous upgrading catalysts: H-beta zeolite, Pt/C, and Raney Ni. Biocrude oil yields varied with the polarity of solvent; as expected, solvents with high polarity led to more extraction of biocrude oil albeit with lower quality. Pt/C was the most effective catalyst for upgrading, producing a light-colored, low-viscosity liquid with lower oxygen content (0.01 wt %) and higher energy content (44 MJ/kg). The choice of solvent had relatively little effect on upgrading outcomes compared to the selection of the catalyst. The no solvent with Pt/C and the ethyl acetate with Pt/C combinations were the most promising, resulting in an upgraded oil energy content similar to gasoline and a near complete removal of oxygen. The combination of ethyl acetate and Pt/C resulted in a higher energy recovery.

■ INTRODUCTION

Hydrothermal liquefaction (HTL) is a promising pathway to convert wet algal biomass into biofuels. Biocrude oil produced from HTL, however, is not suitable as a transportation fuel due to its high viscosity, high heteroatom content, and high emissions of nitrogen and sulfur oxides (NO_x and SO_x).[1] Biocrude oils obtained from algae HTL typically contain 10−15 wt % heteroatoms (mainly nitrogen-containing and oxygen-containing compounds), corresponding to 3−10 wt % nitrogen and 5−15 wt % oxygen contents.[2] Oxygen content decreases with longer residence times and higher temperatures, while nitrogen content increases because of the Maillard reaction between amines and carbohydrates.[3] These heteroatoms create challenges for refinement of biocrude oils into drop-in transportation fuels. The presence of oxygen decreases the biocrude oil heating value, while nitrogen and sulfur cause NO_x and SO_x air pollution during combustion. Biocrude oils, therefore, require upgrading to remove nitrogen and oxygen and to increase the H/C ratio.

After HTL, the standard laboratory practice is to add a nonpolar organic solvent into the product mixture to dissolve the biocrude oil in an organic phase to enable easy separation from the aqueous phase and char by filtration and decanting. The added solvent is then removed by evaporation; this process is simple at the lab scale but adds a nontrivial amount of complexity, energy, and cost at the commercial scale.[4] Many studies have examined the effects of extraction solvent on biocrude oil yield and properties; among the solvents studied have been hexane, decane, methyl tertbutyl ether, dichloromethane, and chloroform.[5−7] Watson et al. reported that the polarity, dipole−dipole interactions, hydrogen bonding, and chemical structure of the solvent all influence the chemical composition and energy recovery ratio of the oil product.[8] Jiang et al. reported that different solvents influenced the metal content distribution in the oil product and other fragments.[9]

Recent studies have investigated biocrude oil upgrading in supercritical fluids to take advantage of supercritical fluids' unique properties: faster rates of mass and heat transfer, liquid-like density, good dissolving power, gas-like flow, low viscosity, and homogeneous reaction conditions.[10] Upgrading of bio-oils produced from fast pyrolysis with supercritical ethanol and methanol resulted in removal of acids and aldehydes and an increase in esters.[11] Duan et al. upgraded biocrude oils in supercritical water over different catalysts to obtain oils with lower nitrogen and oxygen contents and high energy contents.[12] Peng et al. upgraded bio-oils in supercritical

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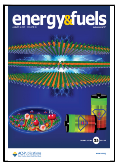

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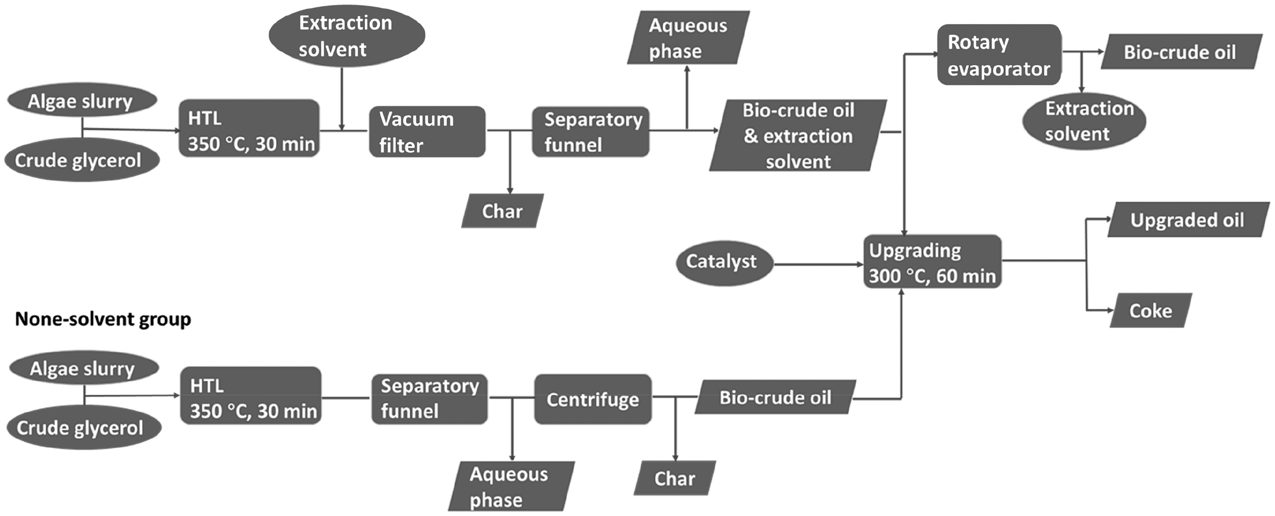

Figure 1. Process flowchart for co-HTL of algae and crude glycerol followed by catalytic biocrude oil upgrading.

ethanol over aluminum silicate without hydrogen; the contents of phenols, ketones, and aldehydes decreased, while esters increased.[13] Prajitno et al. observed hydrogen donation, alcoholysis, esterification, and cracking, leading to an increase in alcohol and ester species and a decrease in viscosity, when upgrading fast pyrolysis oil in supercritical ethanol without a catalyst or added hydrogen.[14] Many articles have reported on biocrude oil refining to hydrocarbons by catalytic hydrotreatment using large amounts of hydrogen gas to remove nitrogen and oxygen and to increase the H/C ratio. Some solvents, such as tetralin, cyclohexane, and hexane, have been shown to act as hydrogen donors for upgrading of heavy crude oil.[15] Cyclohexane forms hydrogen, cyclohexene, cyclohexadiene, and benzene over catalysts.[16] Hart et al. found that cyclohexane increased the upgraded oil yield and suppressed coke formation when upgrading heavy oil over Ni−Mo/Al_2O_3.[15] Hydrodeoxygenation in supercritical hexane over CoMo catalysts resulted in the conversion of phenols into aromatic hydrocarbons.[17] Alkanes (hexane, decane, dodecane) have been shown to serve as hydrogen donors in the presence of certain catalysts and provide good solubility for hydrogen gas in their supercritical states.[17,18]

To remove nitrogen and oxygen in biocrude oil, catalytic upgrading involves a reaction network of cracking, decarbonylation, decarboxylation, denitrogenation, and hydrogenation reactions.[19] For cracking, zeolites have shown good activity for biocrude oils due to their high surface areas and adsorption capacities.[20] Twaiq et al. found that differences in zeolite acidity, pore diameter, and surface area influenced the selectivity and reactivity toward certain final products when used for cracking fatty acids.[21] Compared to HZSM-5, H-beta zeolite has a larger pore size and medium acidity, which enables greater access for large biocrude oil molecules to the acid sites.[22] Large-pore systems can decrease deactivation by releasing fewer products.[23] Zhao et. al attributed the larger spaces and greater number of Bronsted acid sites on H-beta to higher selectivity for alkylation and deoxygenation of phenolics.[24] Metal catalysts are used widely in deoxygenation and denitrogenation processes due to their high catalytic activities and high reaction rates.[25,26] Noble metal catalysts, namely those with Ru, Pd, or Pt, have shown higher activity for deoxygenation than low-cost transition metal catalysts. Pt on activated carbon (Pt/C) showed better efficiency for hydrogenation and deoxygenation for upgrading biocrude oil from wastewater-grown algae[27] and bio-oil from pyrolysis of algae.[28] The oxygen and nitrogen contents of biocrude oil were reduced from 6.5 to 4.3 wt % and from 4.9 to 2.2 wt %, respectively, after upgrading over Pt/C in supercritical water.[29] Activated carbon as a catalyst support has high porosity as well as high surface area and is oxophilic, which can enhance the scission of C−O bonds within oxygen-containing compounds.[30] Pt/C was also effective for decarboxylation of fatty acids to remove O atoms with C atoms as CO_2 with no added hydrogen.[31] Guo et al. reported that Ni metal and Ni alloys with other noble metals opened the pyrrole ring of indoles.[32] Raney Ni can reduce nitro compounds to carbonyl derivatives in the presence of a hydrogen donor solvent.[33] Xu et al. used Raney Ni to promote in situ hydrogenation during upgrading of bio-oils over methanol, effectively converting ketones and aldehydes to alcohols.[34] Bai et al. found that Raney Ni resulted in the lowest nitrogen content (1.6 wt %) in upgraded oil from algal biocrude oil.[25]

The aim of this study was to simplify the HTL-to-upgrading process by identifying dual roles for the organic solvent: an extraction agent for biocrude oil recovery from the product mixture (where the hydrophilic portion of the biocrude oil is miscible with the aqueous phase and the hydrophobic portion attaches to the char surface) and a supercritical liquid medium for biocrude oil upgrading (to avoid extraction solvent removal and hydrogen donor addition steps). Co-HTL of *Galdieria sulphuraria* microalgae and crude glycerol were selected as a case study due to high biocrude oil yields obtained in a previous study and the desire to reduce oxygen- and nitrogen-containing compounds in the biocrude oil.[4] Hexane, cyclohexane, and ethyl acetate were selected as solvent candidates due to their low polarities, potential for hydrogen donation, and supercritical fluid state at the target upgrading conditions.[17,35] H-beta zeolite, Pt/C, and Raney Ni were selected as catalysts to identify potential synergistic effects between the catalysts and solvents during upgrading. The specific goals of this study were (1) to reduce the consumption of materials and energy for co-HTL through catalytic upgrading and (2) to quantify the effects of interactions

Table 1. Product Distributions from Co-HTL of Algae and Crude Glycerol and from Catalytic Upgrading of Biocrude Oils[a]

	co-HTL product yield, wt %				upgrading product yield, wt %		
extraction solvent	biocrude oil	nonvolatiles in aqueous phase	char	catalyst	upgraded oil	coke	overall upgraded oil yield, wt %
hexane	63.5	20.5	2.5	H-beta	64.0 ± 2.3	11.1 ± 0.3	40.6
				Raney Ni	47.5 ± 1.0	5.3 ± 0.2	30.2
				Pt/C	44.6 ± 0.8	24.1 ± 2.6	28.3
cyclohexane	59.8	25.2	2.4	H-beta	72.0 ± 0.5	7.6 ± 0.7	43.1
				Raney Ni	60.2 ± 2.3	28.8 ± 1.8	36.0
				Pt/C	47.4 ± 0.0	29.5 ± 0.0	28.3
ethyl acetate	77.6	19.2	2.0	H-beta	75.8 ± 2.1	7.8 ± 0.7	60.4
				Raney Ni	46.4 ± 0.1	3.4 ± 0.1	36.0
				Pt/C	53.8 ± 2.2	14.6 ± 1.0	41.8
none	72.7	20.4	2.1	H-beta	37.3 ± 1.3	14.1 ± 2.1	27.1
				Raney Ni	37.6 ± 2.0	12.1 ± 1.0	27.3
				Pt/C	40.3 ± 2.1	22.6 ± 1.0	29.3

[a] ± represents one standard deviation, where $n = 2$.

between catalysts and the supercritical solvents on upgrading without the addition of external hydrogen gas.

EXPERIMENTAL SECTION

G. sulphuraria was grown on media as described in Cheng et al.[36] Crude glycerol was obtained from Rio Valley Biofuels (El Paso, Taxes) and used as received. Hexane was reagent grade (Pharmco-Aaper, Shelbyville, KY). Cyclohexane (anhydrous, 99.5%) and ethyl acetate (ACS reagent, ≥99.5%) were purchased from Sigma-Aldrich (USA). Zeolite H-beta CP814C was purchased from Zeolyst (Kansas City, KS). Raney Ni and Pt/C (5 wt % loading, activated carbon support) catalysts were purchased from Sigma-Aldrich (USA).

Figure 1 shows the process of the co-HTL and catalytic upgrading experiments. Co-HTL experiments were performed in a 1.8-L Model 4572 stainless-steel batch reactor with a Model 4848B controller unit (Parr Instrument Co., Moline, IL). Feedstock (500 g) containing 5 wt % algae solids in crude glycerol was heated in the reactor at 350 °C for 30 min. After cooling, 400 mL of solvent (hexane, cyclohexane, or ethyl acetate) was added to the HTL products to separate the biocrude oil from the char and aqueous phase. After extraction, approximately 50 g of the biocrude oil/solvent mixture (BOS) was subjected to vacuum evaporation at the boiling point temperature of the extracting solvent to estimate a biocrude oil ratio (R_{BO}), as calculated by eq 1. The biocrude oil yield was calculated by eq 2.

$$R_{BO} = \frac{\text{mass of biocrude oil after evaporation}}{\text{mass of BOS before evaporation}} \quad (1)$$

$$\text{yield}_{\text{biocrude oil}} = \frac{M_{BOS} * R_{BO}}{M_{\text{algae}} + M_{CGLY}} * 100\% \quad (2)$$

where, M_{BOS}, M_{algae}, and M_{CGLY} are mass of the biocrude oil/solvent mixture, dry algae, and nonvolatile compounds in crude glycerol, respectively. The remaining BOS was stored in a refrigerator prior to catalytic upgrading. For the no-solvent control experiment, biocrude oil was recovered by spontaneous gravity separation for 20 min in a separatory funnel; the aqueous layer was removed from the bottom after separation. Char was separated from the no-solvent biocrude oil by centrifuge at 4000 rpm for 5 min by using a laboratory centrifuge (VWR International, LLC).

Before the upgrading experiments, the catalysts were reduced in a 50 mL/min flow rate of 94% N_2/6% H_2 at 600 °C for 3 h. The BOS was diluted to a biocrude oil/solvent ratio of 1:3 such that biocrude oil (5 g), extraction solvent (15 g), and catalyst (1.5 g; H-beta zeolite, Pt/C, or Raney Ni) were loaded into a 100 mL Model 4590 micro benchtop stainless-steel batch reactor with a Model 4843 controller unit (Parr Instrument Co., Moline, IL). This represents a 30 wt % catalyst loading. Prior to heating, the reactor was purged and pressurized to 1.38 MPa with nitrogen. Biocrude oil upgrading conditions were 300 °C for 60 min. After the reaction was complete, off gases were vented. The product mixture was transferred into centrifuge tubes and centrifuged at 4000 rpm for 5 min using the laboratory centrifuge to give an upgraded oil/solvent mixture supernatant and catalyst/coke solid. The supernatant was collected and the solvent was removed by vacuum evaporation at 40−50 °C using a rotary evaporator. The solid residue was dried at 65 °C overnight in a drying oven. Noncatalyst solid residue, defined as coke, was evaluated by subtracting the mass of catalyst from the total solid residue. The yield of each product was calculated by eq 3.

$$\text{yield of product i} = \frac{\text{mass of product i}}{\text{mass of biocrude oil added}} \quad (3)$$

where i represents the upgraded oil or the coke.

Elemental CHNS contents for algal feedstocks and HTL products were measured using a Series II 2400 elemental analyzer (PerkinElmer, Waltham, MA). Oxygen content was calculated by difference on a dry basis. The higher heating value (HHV) was determined using a Model 6725 semimicro bomb calorimeter (Parr Instrument Company, Moline, IL). Samples were analyzed in duplicate. Total N and total O reduction (wt %) between the upgraded oil and the corresponding biocrude oil were calculated by eqs 4 and 5, respectively.

$$\text{total N reduction, wt \%} = \frac{M_{BCO} \times N\% - M_{UO} \times N\%}{M_{BCO} \times N\%} \times 100\% \quad (4)$$

$$\text{total O reduction, wt \%} = \frac{M_{BCO} \times O\% - M_{UO} \times O\%}{M_{BCO} \times O\%} \times 100\% \quad (5)$$

where M_{BCO} and M_{UO} are mass of biocrude and upgraded oil, respectively. N % is nitrogen content and O % is oxygen content determined by elemental analysis.

Chemical functional groups within the biocrude and upgraded oil samples were characterized by Fourier transfer infrared spectroscopy (FT-IR) using a Spectrum Two FT-IR spectrophotometer (PerkinElmer, MA, USA) equipped with a crystal reflectance cell. Transmittance mode was used over a range of 4000−500 cm^{-1} at a resolution of 4 cm^{-1} with 10−30 scans. Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (TGA-Q500, TA Instruments, New Castle, DE) using platinum pans. Samples were heated from room temperature to 850 °C at 10 °C/min under N_2 (60 mL/min). Heteroatom compound distributions were analyzed using a custom-built 9.4 T Fourier transform ion cyclotron mass spectrometer (FT-ICR MS) (National High Magnetic Field Laboratory, Tallahassee, FL).[37] Sample preparation for positive-ion electrospray ionization (ESI), atmospheric pressure photoionization (APPI), data analysis,

Table 2. Elemental Distribution, Higher Heating Value (HHV), and Overall Energy Recovery for Extracted Biocrude Oils and Upgraded Oils from Catalytic Upgrading Using Different Solvent and Catalyst Combinations[a]

			elemental distribution, wt %								
oil type	solvent	catalyst	C	H	N	S	O	total N reduction, wt %	total O reduction, wt %	HHV, MJ/kg	energy recovery, %
biocrude oil	hexane	none	74.3 ± 0.0	10.3 ± 0.1	1.1 ± 0.1	3.2 ± 0.2	11.1 ± 0.0			34.7 ± 0.1	77.9
upgraded oil		H-beta	80.5 ± 0.0	10.8 ± 0.1	1.2 ± 0.1	2.9 ± 0.1	4.6 ± 0.1	31.8	73.6	40.2 ± 0.4	57.8
upgraded oil		Raney Ni	78.6 ± 0.1	10.8 ± 0.2	1.8 ± 0.1	3.7 ± 0.0	5.1 ± 0.1	24.5	78.1	39.8 ± 0.1	42.4
upgraded oil		Pt/C	82.6 ± 0.0	12.7 ± 0.0	0.9 ± 0.0	3.4 ± 0.2	0.4 ± 0.1	63.4	98.5	45.3 ± 0.8	45.4
biocrude oil	cyclohexane	none	75.4 ± 0.1	10.0 ± 0.0	1.3 ± 0.1	3.6 ± 0.3	9.7 ± 0.2			35.7 ± 0.5	75.5
upgraded oil		H-beta	75.7 ± 0.2	10.7 ± 0.1	1.2 ± 0.0	3.1 ± 0.0	9.4 ± 0.1	35.8	29.9	37.8 ± 0.0	57.6
upgraded oil		Raney Ni	76.6 ± 0.1	10.4 ± 0.2	1.6 ± 0.1	3.4 ± 0.1	8.2 ± 0.2	27.9	49.7	37.1 ± 0.7	47.2
upgraded oil		Pt/C	80.5 ± 0.5	12.5 ± 0.0	1.0 ± 0.0	2.8 ± 0.0	3.2 ± 0.3	62.5	84.4	39.6 ± 0.6	39.7
biocrude oil	ethyl acetate	none	68.9 ± 0.6	9.8 ± 0.1	1.4 ± 0.1	3.5 ± 0.5	16.5 ± 0.4			30.9 ± 0.5	84.8
upgraded oil		H-beta	74.5 ± 0.1	10.4 ± 0.0	1.0 ± 0.0	2.7 ± 0.1	11.4 ± 0.0	41.5	46.4	32.0 ± 0.2	68.5
upgraded oil		Raney Ni	73.4 ± 0.7	10.3 ± 0.1	0.9 ± 0.0	2.6 ± 0.1	12.8 ± 0.3	70.0	64.1	31.3 ± 0.8	40.4
upgraded oil		Pt/C	82.6 ± 0.0	12.5 ± 0.0	1.1 ± 0.0	3.5 ± 0.1	0.2 ± 0.1	55.8	99.3	43.1 ± 0.3	63.7
biocrude oil	no solvent	none	69.6 ± 0.4	10.0 ± 0.0	1.4 ± 0.1	4.0 ± 0.3	15.1 ± 0.2			33.9 ± 0.4	87.3
upgraded oil		H-beta	80.3 ± 0.1	10.1 ± 0.1	1.7 ± 0.1	4.3 ± 0.3	3.6 ± 0.2	54.9	91.1	39.4 ± 0.5	37.8
upgraded oil		Raney Ni	81.5 ± 0.1	12.0 ± 0.1	1.3 ± 0.0	2.9 ± 0.2	2.2 ± 0.1	63.9	94.4	38.9 ± 0.2	37.6
upgraded oil		Pt/C	82.9 ± 0.1	12.9 ± 0.1	0.9 ± 0.0	3.3 ± 0.2	0.00	73.1	100.0	44.9 ± 1.0	46.6

[a]± represents one standard deviation, where $n = 2$.

and visualization are described in Cui et al.[4] The hydrocarbon (HC) class was assigned by positive-ion APPI mode FT-MS.

RESULTS AND DISCUSSION

The product distribution from co-HTL of algae and crude glycerol varied with extraction solvent, as shown in Table 1. Extraction by ethyl acetate gave the highest biocrude oil yield (77.6 wt %), followed by gravity separation without solvent (72.6 wt %), hexane (63.5 wt %), and cyclohexane (59.8 wt %), respectively. Decreasing yields followed the decreasing polarity of the extraction solvents.[38] The HTL products to which no solvent was added separated spontaneously. The separation is attributed to the abundant fatty acids from the crude glycerol forming micelles around the algae-derived organic compounds.[4] The yield of nonvolatiles in the aqueous phase ranged from 19.4 to 25.2 wt % and increased with decreasing biocrude oil yield. The relative effect of biocrude oil partitioning between the oil phase and the aqueous phase when no solvent was added was intermediate between a moderately polar solvent and a nonpolar solvent.

Solvent polarity impacted the elemental composition of the HTL products (Table 2). Biocrude oils extracted with ethyl acetate and by gravity separation without solvents contained more O (15.1−16.5 vs 9.7−11.1 wt %) and more N (1.1−1.3 vs 1.4 wt %) as well as less C (68.9−69.6 vs 74.3−75.4 wt %) and H (9.8−10.0 vs 10.0−10.3 wt %) than the biocrude oils extracted with hexane and cyclohexane; these results were consistent with previous studies.[39,40] The higher oxygen content of the biocrude oils from ethyl acetate and gravity separation without solvent was consistent with their lower HHV compared to those from hexane and cyclohexane extraction, although the higher biocrude oil yield from ethyl acetate or no-solvent extraction still led to a higher overall energy recovery (Table 2).

FT-IR spectra of the four biocrude oils were similar, as shown in Figure 2(a). All four spectra had peaks at 2920 and 2850 cm^{-1} corresponding to aliphatic C−H stretching of methylene groups. The peak at 2950 cm^{-1} for methyl groups was not observed in a previous study of algal biocrude oil.[4] Biocrude oils from ethyl acetate and no-solvent extractions showed a broader and stronger peak at 3393 cm^{-1}, suggesting more N−H/O−H bonds. The biocrude oil from ethyl acetate extraction had more intense peaks at 1742, 1374, 1238, and 1042 cm^{-1}, which are associated with oxygen-containing esters, phenols, and ethers. The presence of these peaks is consistent with higher oxygen content. The peak around 850 cm^{-1} in biocrude oils from ethyl acetate and no-solvent extraction suggested that these two separation methods obtained more aromatic compounds.

The overall upgraded oil yield (on an HTL dry feedstock basis) varied with solvent and with catalyst, ranging from 60.4 wt % for ethyl acetate and H-beta to 27.1 wt % when H-beta was used without solvent (Table 2). In general, catalytic upgrading without solvent had the lowest yields. The appearance of the upgraded oils differed. Upgraded oils treated by Pt/C were noticeably lighter in color, clearer, and of lower viscosity. Compared with the biocrude oils, the HHVs of the upgraded oils were higher, and the oxygen contents were lower (Table 2). The combinations of hexane with Pt/C, ethyl acetate with Pt/C, and no solvent with Pt/C resulted in high

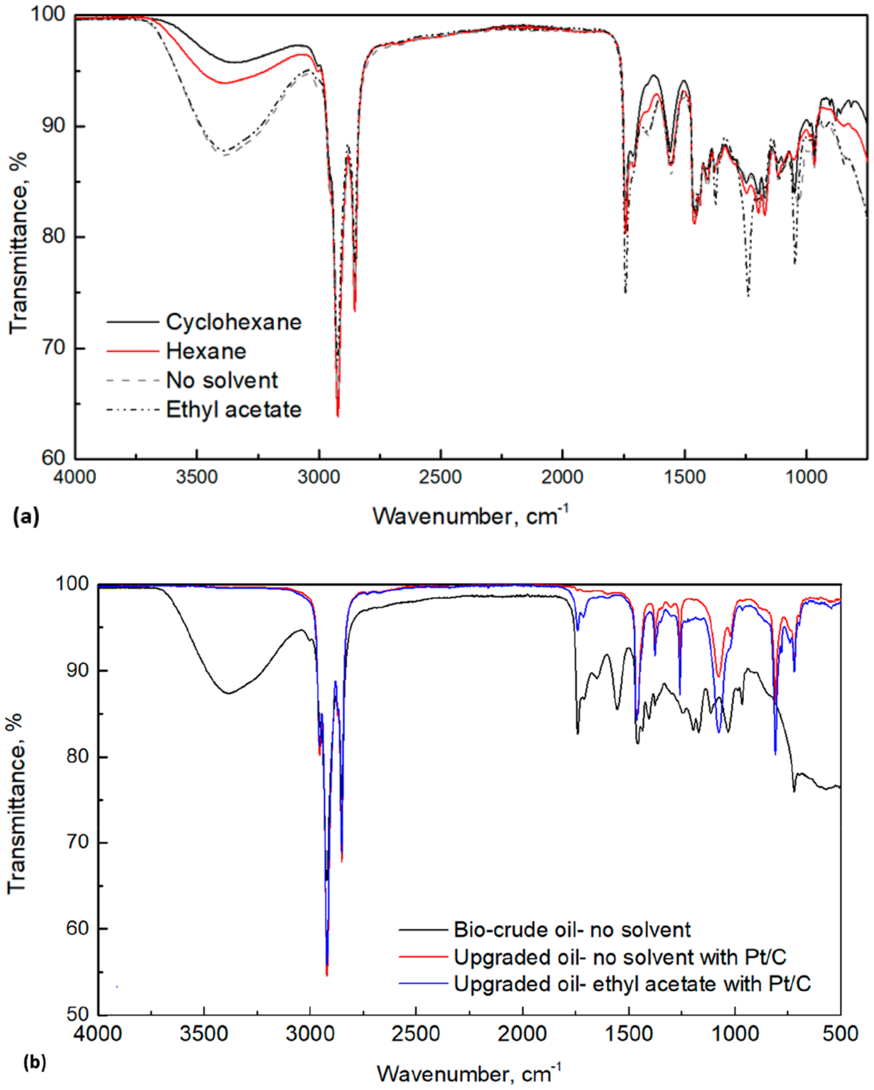

Figure 2. (a) FT-IR spectra of biocrude oils separated from HTL products by different extraction solvents. (b) FT-IR spectra of biocrude oil separated without solvent or with ethyl acetate and the upgraded oil after upgrading over Pt/C.

upgraded oil HHV (43.1−45.3 KJ/kg), which is similar to the energy content of gasoline and represent oxygen reduction rates close to 100%. Overall, Pt/C showed the highest activity for deoxygenation and denitrogenation (Table 2) and increase in HHV, regardless of the solvent. The combination of ethyl acetate and Raney Ni showed good denitrogenation activity (70%), which is consistent with results previously reported.[25] An interaction between ethyl acetate and Raney Ni in the hydrolysis of diphenyl ether has been shown.[41] The combination of ethyl acetate with Pt/C gave the highest energy recovery rate (63.7%), which exceeded the other solvent−catalyst combinations giving high-energy-content oils.

Differential thermogravimetry curves for representative biocrude oil and upgrade oil samples are shown in Figure 3. Curves for the four biocrude oils were very similar. The main weight loss regions for the no-solvent biocrude oil occurred at 223 and 460 °C, with smaller losses at 342 and 756 °C. The mass losses at temperatures over 460 °C are attributed to higher-boiling-point compounds from crude glycerol derivates.[4] All three upgraded oil samples over Pt/C showed only one sharp peak at 200 °C, indicating the ability of Pt/C to produce more low-boiling-point compounds, regardless of

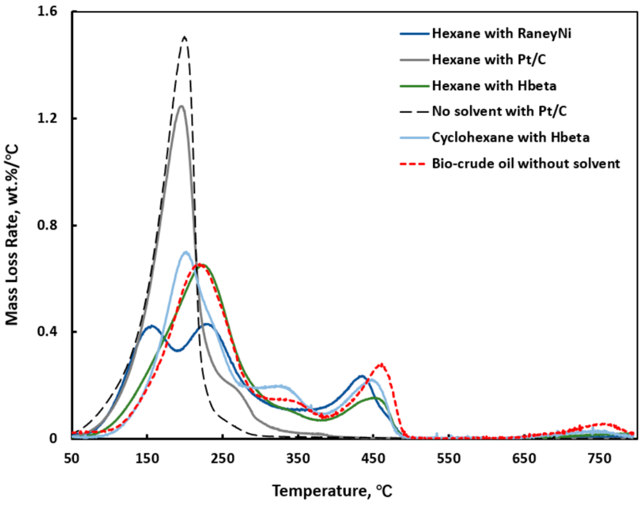

Figure 3. Differential thermogravimetry curves for biocrude oils and upgraded oils from reactions using different solvents and catalysts.

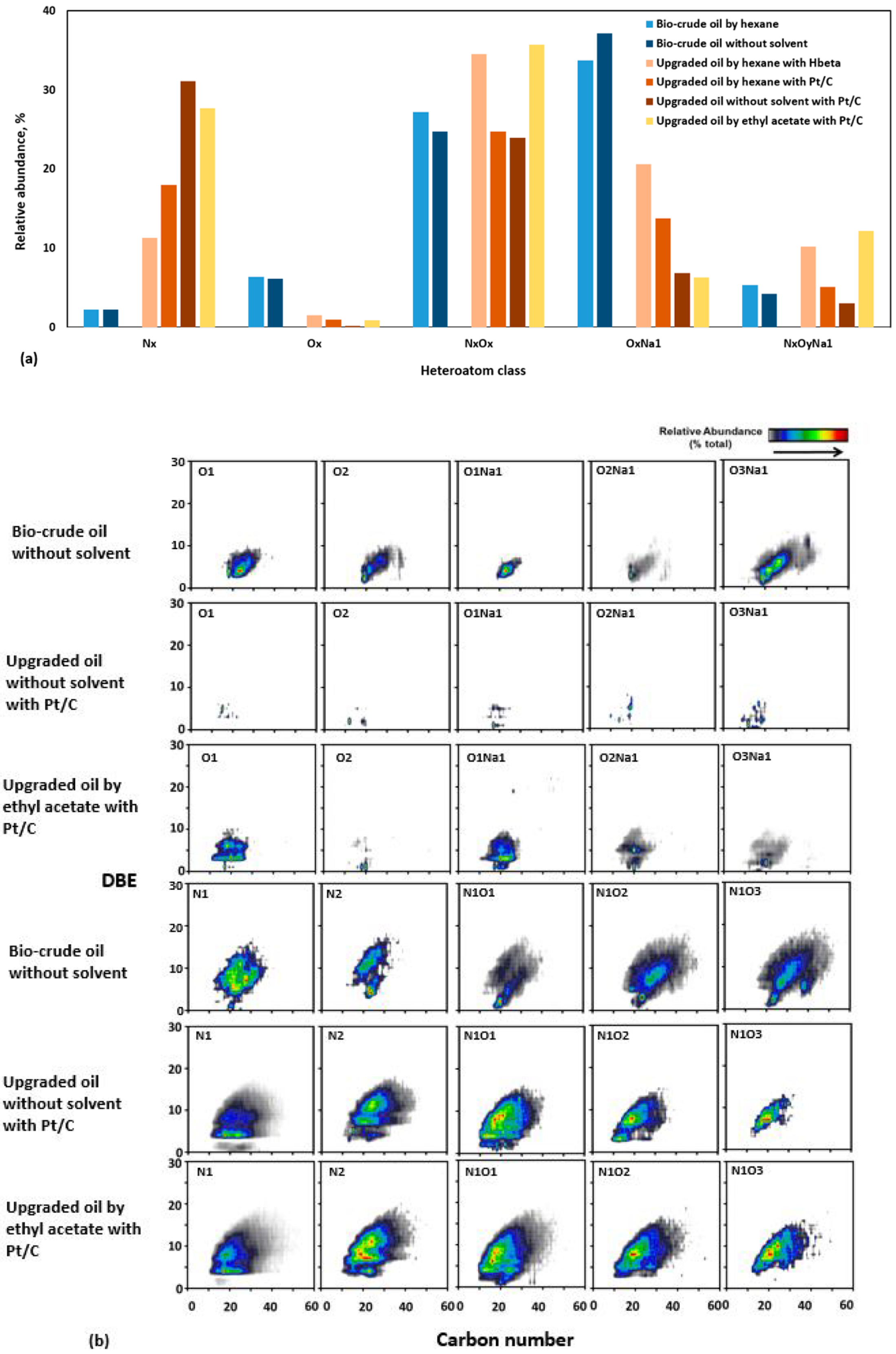

Figure 4. (a) Heteroatom class distributions of extracted biocrude oils and upgraded oils from extraction and/or upgrading with different solvents and catalysts; data derived from positive-ion ESI FT-ICR MS. (b) Color-coded abundance-contoured plots of double-bond equivalent (DBE) vs carbon number for heteroatom class of extracted biocrude oils and upgraded oils from extraction and/or upgrading with different solvents and catalysts; data derived from positive-ion ESI FT-ICR MS.

solvent type. For the other upgraded oils (Raney Ni with hexane, H-beta with hexane, and H-beta with cyclohexane), the shape of the curves was only slightly shifted toward lower volatilization temperatures from the biocrude oil curve. This indicates the relatively small degree of change in oil properties by upgrading, in agreement with the similarities in physical appearance and viscosity between these biocrude oils and upgraded oils.

Figure 2(b) shows the FT-IR spectra of the no-solvent biocrude oil and the corresponding upgraded oil after treatment with Pt/C. The upgraded oil had fewer but more distinctive peaks. The broad peaks at 3400−3100, 1740, and 1556 cm^{-1} were present in the biocrude oil but not in the upgraded oil, indicating the removal of N−H, O−H, and C=O, C=C stretching from amine, alcohol, and ester groups. The peaks from the biocrude oil spectrum that were retained in the upgraded oil were at 1469, 1378, 1260, 1077, 811, and 721 cm^{-1}. These remaining peaks are attributed to C−H bending, C−O stretching, =C−H out-of-plane bending, and C-(aromatic)−H out-of-plane bending and suggest that compounds with these structures exist in the upgraded oil. The upgraded oil from ethyl acetate with Pt/C had a similar curve to that of no solvent with Pt/C, but the peaks at 1740 and 1260 cm^{-1} were stronger, implying a lesser degree of C=O and C−O removal (Figure 2(b)).

The heteroatom class distribution of the biocrude oils, and their respective upgraded oils, derived from positive-ion ESI FT-ICR MS are presented in Figure 4(a). Our previous study has provided the reaction network of crude glycerol in HTL.[4] The fatty acids from crude glycerol contributed to biocrude oils, directly corresponding to the high relative abundance of O_x and ONa_1 species. And glycerol could react with the protein fragments through the Maillard reaction, resulting in more nitrogen-containing heteroatoms. Even with the reduction in oxygen content during upgrading, O- and N-heteroatom species (N_x, N_xO_y, O_x, ONa_1, and $N_xO_yNa_1$) are still easily observable in the upgraded oils. The relative abundance of O_x and O_xNa_1 classes decreased in the upgraded oils, supporting the occurrence of deoxygenation during upgrading. In all four upgraded oils, the abundance of the O_x classes was less than 2% compared to approximately 6% in the biocrude oils. For the O_x species, the biocrude oils have a higher relative abundance of compounds with more atoms of O per molecule ($O \geq 2$). Similar trends can be seen in the N_1O_x species, where N_1O_x species containing >2 O atoms per molecule are more abundant in the biocrude oils. After upgrading, there is a higher relative abundance of species with less oxygen content ($O < 2$). This shift away from higher-oxygen-containing species is indicative of deoxygenation reactions. The abundance of the O_xNa_1 classes in oils upgraded over H-beta and over Pt/C was 20.6 and 13.8%, respectively, compared to 33.8% in the hexane-extracted biocrude oil. For the biocrude oil separated without solvent, the O_xNa_1 classes in the oil upgraded over Pt/C decreased from 37.2 to 6.9%. In a previous study, the abundant O_xNa_1 compounds were derived from crude glycerol.[4] However, here, there was an increase in relative abundance of higher-oxygen-containing, Na adducts ($O > 10$) when hexane and Pt/C were used, which suggests unfavorable polymerization reactions occur with the use of this catalyst. More details about the distribution of each heteroatom class are provided in the Supporting Information.

When analyzing the changes that occur for nitrogen-containing species, there is an apparent increase in the relative abundance of the N_x species upon upgrading. The relative abundance in upgraded oils was ∼12−32% while only ∼2% in biocrude oils, which indicated more of these species were generated through deoxygenation reactions. Although the overall relative abundance of the N_xO_x species does not change substantially from sample to sample, the trends between the different classes are indicative of deoxygenation and polymerization reactions. The N_1O_1 class had the highest abundance (∼20%) among the N_xO_y classes in the biocrude oil derived from HTL of wastewater treatment algae.[42] Previously, the diversity of the N_xO_y classes in the biocrude oils from co-HTL was higher and more frequently contained multiple O atoms (2−4), indicating the interactions between algae and crude glycerol during co-HTL. For the N_1O_x species, there is a decrease in species with higher oxygen content ($O > 2$) in the biocrude oils and a subsequent increase in species with lower oxygen content ($O < 2$) in the upgraded oils, indicative of deoxygenation reactions. The upgraded oils (by hexane with Pt/C or H-beta and by ethyl acetate with Pt/C), unfortunately, show a higher relative abundance of species with higher N content ($N > 2$) compared to the biocrude oils, most likely due to polymerization reactions. These higher-heteroatom-containing classes ($N_{3-4}O_{0-6}$) were more prevalent when hexane with Pt/C was used. These results indicate that the use of hexane or ethyl acetate with Pt/C leads to the generation new compounds through polymerization reactions, which can have unfavorable consequences during later processing/use (e.g., catalyst fouling, equipment plugging, higher NO_x emissions).

The color-coded abundance-contoured plots of double-bond equivalent (DBE) vs carbon number derived from the positive-ion ESI FT-ICR mass spectra show how the heteroatom species in the biocrude oil changed during upgrading over Pt/C (Figure 4(b)). For the upgraded oil without solvent over Pt/C, the compositional spaces of the O_x classes and O_xNa_1 classes for the upgraded oils were narrower. For the N_1O_2 and N_1O_3 classes, the compositional spaces in the upgraded oil are narrower and contain lower-carbon-number species compared to the biocrude oil. The compositional spaces for the N_{1-2} and N_1O_1 classes in the upgraded oil show an increase in compositional space (carbon number and DBE) and relative abundance compared to those of the biocrude oil. The reduction of species with more O atoms ($O \geq 2$), along with the concurrent increase in the diversity and relative abundance of species that contain fewer heteroatoms ($N \leq 1$ and $O \leq 1$), was attributed to Pt/C removing O atoms from multiple-heteroatom-containing compounds and producing new species with fewer heteroatoms. At the same time, the trace amounts of higher heteroatoms ($N = 4$, $O \geq 2$) observed in the upgraded oils from ethyl acetate or no solvent with Pt/C indicated that some heteroatoms partially polymerized to the higher-heteroatom species.

Further evidence of the deoxygenation reactions resulting in the generation of new species with fewer heteroatoms can be seen within the hydrocarbon (HC) classes. Since positive-ion ESI has a substantially reduced ability to ionize hydrocarbons, positive-ion APPI was utilized. The HC class in the upgraded oils from hexane with H-beta, hexane with Pt/C, ethyl acetate with Pt/C, and no solvent with Pt/C had relative abundances of 6.3, 12.9, 13.5 and 17.4% (Figure 5(a)); the HC class was not present within the untreated biocrude oils. Color-doped abundance-contoured plots of DBE vs carbon number for the HC class derived from the positive-ion APPI mass spectra of

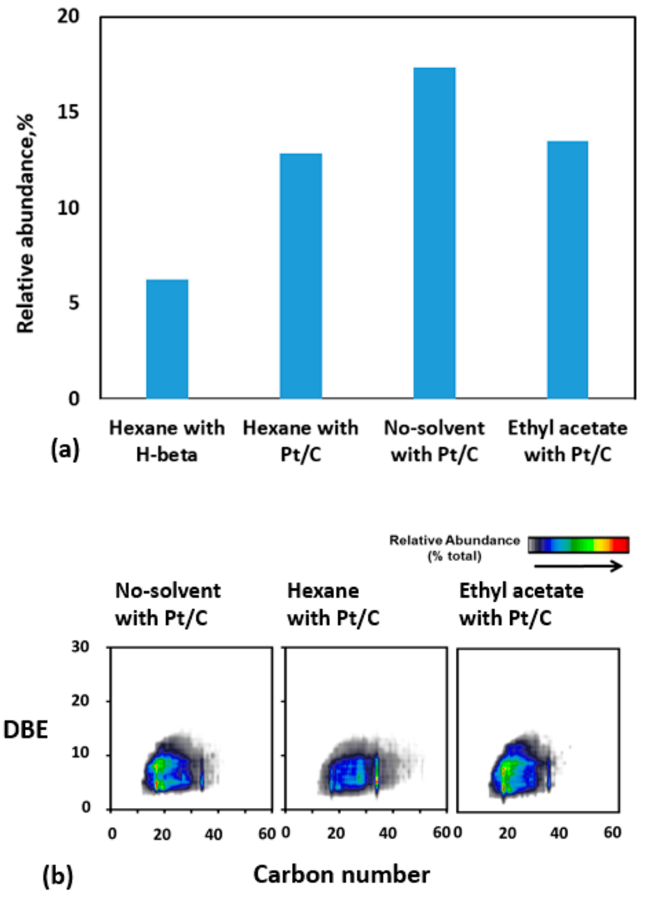

Figure 5. (a) Hydrocarbon class distribution of upgraded oils separated with different solvents over Pt/C; data derived from positive-ion APPI FT-MS. (b) Color-coded abundance-contoured plots of double-bond equivalent (DBE) vs carbon number for hydrocarbon class (HC) of upgraded oils separated with different solvents over Pt/C; data derived from positive-ion APPI FT-MS.

oils upgraded over Pt/C are shown in Figure 5(b). In the previous study, GC−MS analysis of the oil from no-solvent upgrading over Pt/C contained substantial amounts of heptadecane ($C_{17}H_{36}$), pentadecene ($C_{15}H_{30}$), and other small hydrocarbons, which came from the same pathway and used the materials from the same sources with the one in this study.[43] The space area of the three oil samples was similar, but the upgraded oil from hexane with Pt/C contained compounds with carbon numbers >40. The "hot-spot" of each upgraded oil sample was also different. Oils from no solvent with Pt/C and ethyl acetate with Pt/C had "hot-spots" around carbon numbers of 20, while the upgraded oil from hexane with Pt/C had a "hot-spot" around carbon numbers of 34. The presence of hydrocarbons within the upgraded oils was attributed to deoxygenation of oxygen-containing species present within the biocrude oils. Additionally, more hydrocarbons were generated with the use of Pt/C catalyst compared to the H-beta catalyst, regardless of solvent.

Based on the compositional results from biocrude oil upgrading, Pt/C was the most effective catalyst but with the trade-off of lower overall yields (28.3−41.8 wt %). The apparent lack of solvent effect might be attributed to the need in previous experiments for the solvent to have good H_2 solubility.[16−18] With no hydrogen used in this study, any advantages with respect to that function would not be observed. For oils upgraded over Pt/C, the elemental analysis and FT-IR results showed that deoxygenation correlated to the removal of alcohol and ester groups. The FT-ICR MS also indicated the removal of O atoms from multiple-heteroatom-containing compounds ($O \geq 2$) and the increase in low-heteroatom-containing compounds ($N \leq 1$ and $O \leq 1$). Although the oils upgraded over Pt/C provide a clear and low-viscosity liquid fuel with low oxygen content and an HHV similar to current transportation fuels, additional strategies will be needed in the future to increase the share of hydrocarbons and to decrease the content of nitrogen- and heteroatom-containing compounds in the target oil product.

■ CONCLUSIONS

Biocrude oils from the co-HTL of algae and crude glycerol varied in composition with the use of an extraction solvent and the polarity of that solvent. Biocrude oil was observed to spontaneously separate into aqueous and organic fractions. Compared to Raney Ni and H-beta zeolite catalysts, Pt/C catalyst was more effective for upgrading biocrude oil at mild conditions (300 °C), for all of the solvents tested, producing a clear, light-colored, low-viscosity oil with reduced oxygen content and higher energy content. The combinations of no solvent with Pt/C and ethyl acetate with Pt/C resulted in high energy contents and near complete oxygen removal, while the combination of ethyl acetate with Pt/C provided a higher energy recovery. The upgraded oils from the promising solvent−catalyst combinations did show the presence of nitrogen-containing and polymerized compounds, which will require additional care to address. The impact of ethyl acetate on separation and upgrading of lipid-poor biomass HTL products bears further investigation, especially to compare the costs and benefits of ethyl acetate for HTL extraction and upgrading relative to a no-solvent extraction pathway in future large-scale HTL processes.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.1c01336.

Additional FT-ICR MS data (PDF)

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Notes

The authors declare no competing financial interest.

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