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Understanding the Upgrading of Sewage Sludge-Derived Hydrothermal Liquefaction Biocrude via Advanced Characterization

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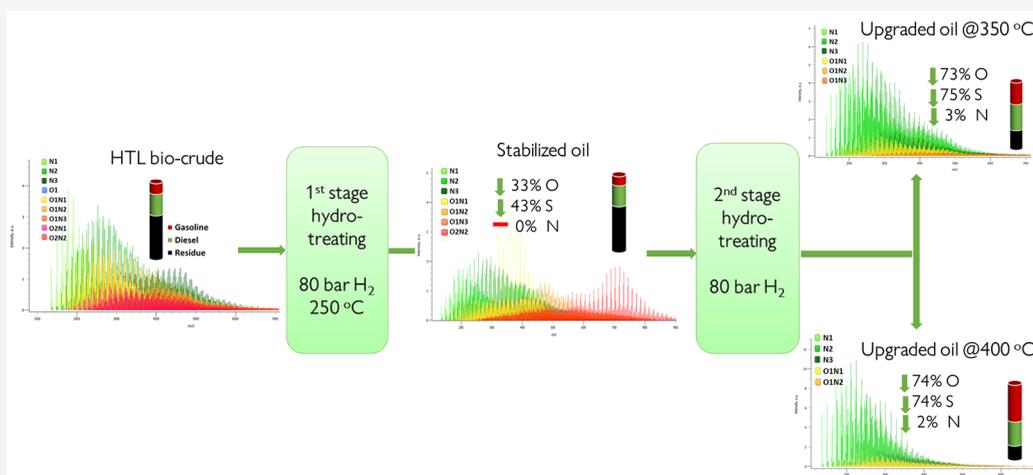
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ABSTRACT: Hydrothermal liquefaction (HTL) can thermochemically transform sewage sludge into a biocrude with high energy content, high chemical complexity, and high O and N content. The development of an efficient upgrading process for such complex feedstocks necessitates detailed knowledge of the molecular composition and the specific heteroatom-containing compounds to understand and optimize the hydrotreating reactions. In this study, we present the upgrading of sewage sludge-derived HTL biocrude via a two-stage hydrotreatment process and perform advanced chemical characterization of the feedstock, intermediate, and final upgraded products with gas chromatography−mass spectrometry (GC−MS) and Fourier transform ion cyclotron resonance mass spectrometry (FTICR−MS). We show that hydrotreatment significantly improves the quality of the oil, primarily succeeding in cracking the heavy molecules and removing the sulfur- and oxygen-containing components. FTICR−MS analysis shows that the HTL biocrude has a high concentration of fatty acid amides that readily lose their oxygen and nitrogen during hydrotreating and are converted into saturated hydrocarbons, whereas the aromatic OxNy compounds are converted into N1 and N2 classes, which are more resistant to hydrotreating. We also demonstrate that the upgraded HTL oil can be successfully blended with intermediate refinery streams, such as vacuum gas oil (VGO), for further co-processing to in-spec fuels in conventional processes. This provides an alternative route to introduce renewable carbon in existing fossil-based refineries.

1. INTRODUCTION

Hydrothermal liquefaction (HTL) is a high-temperature, high-pressure process that can thermochemically transform a wide variety of renewable feedstocks to a high energy content liquid. However, HTL oil is typically a complex mixture of thousands of organic compounds with properties that differ significantly from petroleum-derived fuels. Its chemical composition and physical properties can vary substantially primarily depending upon the type of feedstock, but also the HTL reaction conditions (temperature, pressure, use of solvent, reaction time, etc.).[1] HTL oil is usually dark-colored, relatively viscous, and with a high total acid number and high ash and oxygen content. High levels of nitrogen (up to 10%) have also been reported for biocrudes produced from municipal solid waste, manure, wastewater sludge, and algae, as a result of the protein content of the feedstock.[2] These properties make HTL oil difficult to use as transportation fuel, and further upgrading is

required to reduce the heteroatom content and meet current road transport fuel specifications.

Catalytic hydrotreating is the technology that has been most widely studied for the upgrading of bio-derived oils. The hydroprocessing of bio-oils generated by pyrolysis and HTL has been reviewed by Elliott[3] and more recently by Yeh et al.[4] and Ramirez et al.[2] The majority of the reviewed literature concerns the upgrading of pyrolysis oil, with work on HTL oil treatment being more limited. Early work demonstrated the catalytic hydroprocessing of wood-derived HTL oil on sulfided NiMo and CoMo catalysts at 350−400 °C and 100−150 bar in a continuous-flow, fixed catalyst bed reactor system operated in an upflow configuration. High yields of high-quality gasoline were produced from biomass-derived oils; however, high hydrogen consumption and low space velocities were required, negatively impacting process economics. Catalyst deactivation as a result of deposition of alkali metals on the catalyst surface was also reported.[5,6] Subramaniam et al.[7] recently reported the stable hydrotreating of HTL biocrudes from food waste and sewage sludge in a continuous fixed bed reactor unit for over 1500 h with minimal catalyst deactivation and a high overall yield of 85%.

The upgrading challenges are closely linked to the type of feedstock used for the HTL oil production. The high concentration of nitrogen in waste- and algae-derived HTL oil requires more severe hydrotreating conditions and leads to higher H_2 consumption as a result of the resilience of the nitrogenated compounds.[8] On the other hand, higher temperatures enhance the formation of higher molecular weight compounds as a result of polymerization and condensation reactions of oxygenated compounds, leading to increased coking and reactor clogging issues. Castello et al. investigated the hydrotreatment of HTL oils from *Miscanthus*, microalga *Spirulina*, and primary sewage sludge over a standard NiMo/Al_2O_3 catalyst and highlighted the feedstock-specific upgrading challenges.[9] Lignocellulosic-based HTL oil produced gasoline-range hydrocarbons, with a high aromatic content, whereas sewage sludge and algae oil produced straight-chain hydrocarbons in the diesel range. Complete oxygen removal was readily achieved; on the contrary, nitrogen removal was found to be challenging and dependent upon the specific feedstock, as a function of the specific nitrogen-containing compounds in each biocrude. In a similar work by Jarvis et al.,[10] raw and upgraded HTL biocrudes from sewage sludge, microalgae, and pine were characterized in detail with ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR−MS) analysis. The HTL biocrude from pine contained Ox species predominantly, whereas microalgae and sewage sludge biocrudes primarily comprised of NxOy species. After hydrotreatment, the higher (>2) heteroatom-containing species were converted to a variety of hydrocarbon and lower heteroatom-containing species.

The above highlight that the development of an efficient upgrading process for such complex feedstocks necessitates detailed knowledge of the molecular composition and the specific heteroatom-containing compounds to understand and optimize the hydrotreating reactions. In this study, we complement previous literature and attempt to shed light on upgrading HTL biocrude from sewage sludge via basic and advanced characterization with gas chromatography−mass spectrometry (GC−MS) and FTICR−MS. HTL oil from non-digested sewage sludge produced via supercritical HTL was hydrotreated in two stages in a high-pressure batch reactor

over a commercial pre-sulfided NiMo-based catalyst: a first stabilization step at 250 °C and a final hydrotreating step at 350 or 400 °C. The raw feedstock and the upgraded products at all conditions were analyzed in detail to obtain insight into the reaction pathways and the required upgrading conditions. Moreover, the miscibility of the upgraded HTL oil with fossil vacuum gas oil (VGO) was investigated with the aim of determining the feasibility of further co-processing to in-spec fuels in conventional refinery processes.

2. EXPERIMENTAL SECTION

2.1. Feedstocks and Catalyst. The HTL biocrude was produced in a continuous HTL research facility at Aalborg University in Denmark, designed and built by Steeper Energy, from non-digested sewage sludge. The sewage sludge was converted to biocrude, water, and gas via HTL at water supercritical conditions (∼400 °C and ∼320 bar).[11] Dewatering and demineralization of the biocrude was performed prior to hydrotreating stages. For the blending tests, a typical refinery low-sulfur VGO fraction was used. Both the HTL biocrude and VGO feedstock were extensively characterized to determine their physicochemical properties and chemical composition. The characterization results are presented and discussed in detail in the Results and Discussion of this paper.

The upgrading tests were performed with a commercial NiMo/Al_2O_3 hydrotreating catalyst provided by Haldør Topsoe. Prior to use, the catalyst was crushed and sieved to a particle size of 150−300 μm. The catalyst was activated *ex situ* in a continuous fixed bed reactor unit by reduction and sulfidation with 4.5 wt % dimethyl disulfide (DMDS)/n-C$_{16}$ in H_2 at 350 °C.

2.2. Experimental Setup and Testing Procedure. The HTL biocrude was upgraded by hydrotreating in a laboratory-scale micro bench top reactor system. The experimental unit consists of a system of two identical Parr 4590 micro bench top reactors. Each autoclave is a stirred mini batch reactor made of Hastelloy C-276, with a volume of 50 cm^3, designed for a temperature range up to 500 °C and a pressure range up to 345 bar. A heating jacket is applied externally to each reactor, while a Parr model 4848 reactor controller is used to control the temperature inside the reactor. Uniform heating and temperature, as well as homogeneous composition of the reaction mixture, are ensured by the use of a propeller-type magnetic agitator. A rupture disk is installed in the seal of the reactor to ensure the safety of the system. An external auxiliary flow of air is also used to rapidly cool the reactor when necessary.

For each test, the reactor was loaded with about 20−25 cm^3 of HTL biocrude and the appropriate amount of pre-sulfided catalyst (catalyst loading of 0.25 g/g$_{oil}$). After loading, the reactor was sealed and flushed with H_2 to remove residual air. The system was then pressurized with H_2 and heated to the desired temperature. The reactor was stirred at 500 rpm throughout the experiment. Hydrotreating was performed in two stages, comprising of a first, mild treatment to stabilize the oil, followed by a second step at more severe conditions. The stabilization step was performed at 250 °C and 80 bar of H_2 for 4 h of reaction time. After that, the system was further heated to 350 or 400 °C, without intermediate cooling, and was retained at the final temperature for another 4 h of reaction time. During both steps, the reactor was repressurized with H_2 as necessary to compensate for hydrogen consumption and maintain the system pressure constant at 80 bar. At the end of each test, the reactor was quenched with air and the gas and liquid products were collected. The upgraded liquid was separated from the catalyst through filtration.

2.3. Product Characterization. The gaseous products of the upgrading experiments were analyzed with gas chromatography, on a Hewlett-Packard 5890 series II GC, equipped with a 10-port gas sampling valve and a 6-port column isolation valve, a split/spitless injector, thermal conductivity detector (TCD)/flame ionization detector (FID), and four columns.

The HTL biocrude feedstock and the upgraded final products were extensively characterized with various methods to determine

physicochemical properties and chemical composition. The density of the liquids was measured at 60 °C following the ASTM D4052 analytical procedure. Elemental analysis (C, H, and N content) was conducted on an elemental CHN LECO-628 analyzer, following the ASTM D5291 and ASTM D4629 methods. The ASTM D4294 method was followed for the determination of the S content, while the O content was calculated by difference. The heating value was determined by burning a pre-weighed sample in an oxygen bomb calorimeter (Parr 1261) under controlled conditions (ASTM D4809). The water content was determined by Karl Fischer titration according to ASTM E203-08. The total ash content was measured by combustion. In the presence of ambient air, the temperature was raised to 750 °C, where it was maintained for 3 h. The ash content was calculated on the basis of the weight difference of the initial and final sample weights, according to the EN 14775/ISO 18122 method. The micro carbon residue (MCR) was determined with the ASTM D4530 method. The acidity was assessed by measuring the total acid number (TAN). TAN was determined with potentiometric titration with tetrabutyl ammonium hydroxide on a 751 Titrino Metrohm analyzer, following the ASTM D664 procedure. According to the method, a 50 vol % toluene, 49.5 vol % isopropanol, and 0.5 vol % distilled water solution was prepared for the analysis. Then, 0.2 g of the liquid was mixed with 100 mL of the prepared solution, and the mixture was added to the analyzer. Determination of the liquid product distribution (gasoline, diesel, and heavy fractions) was determined by simulated distillation (SIMDIS), according to ASTM D6352, assuming a cut-off point of 216 °C for gasoline and 343 °C for diesel.

The chemical composition of the HTL bio-oil and upgraded products was determined by GC–MS and FTICR–MS. GC–MS analysis was performed on an Agilent 7890A/5975C gas chromatograph–mass spectrometer system (helium flow rate, 0.7 mL/min; column, HP-5MS 30 m × 0.25 mm inner diameter × 0.25 μm). The samples were diluted with CH_2Cl_2 and were then injected into the gas chromatograph, analyzed to their components, and ionized, giving the unique mass spectra for each compound. The identification was performed automatically by the mass spectra libraries (NIST05) of the system software.

FTICR–MS analysis of the liquid samples in the atmospheric pressure chemical ionization (APCI) positive ion mode was performed by employing a Petroleomic approach.[12] The samples were diluted in 1:10 $CHCl_3$/acetonitrile and infused at a flow rate of 50 μL/min by a syringe pump into the APCI ion source. The final concentration of the solution in the APCI ion source was around 0.4–0.6 mg/mL. Typical APCI(+) conditions were as follows: source heater, 360 °C; source voltage, 5 kV; capillary voltage, 7 V; tube lens voltage, 60 V; capillary temperature, 275 °C; sheath gas, 60 arbitrary units; and auxiliary gas, 10 arbitrary units. The mass spectra were acquired in positive mode with a mass range of m/z 100–1000. The resolution was set to 400 000 (at m/z 400). The ion accumulation time was defined by the automatic gain control (AGC), which was set to 10^6. A total of 360 scans were acquired for each analysis to improve the signal-to-noise ratio using the Booster Elite system (Spectroswiss), which allowed for the registration of the transient data directly. Transients were then processed by the software Peak-by-Peak Petroleomic (Spectroswiss). The 360 transients were first of all averaged and Fourier-transformed into a single averaged mass spectrum. The resulting spectrum was then further processed to remove the noise (thresholding set to 6σ of the background noise) and internally recalibrated through the unwrapping method.[13] Around 8000–12 000 different peaks were then obtained. The final attribution of these peaks was obtained using the composing function of peak by peak with the error limit of ±2 ppm. The molecular formulas were categorized according to different parameters, such as the number of heteroatoms (N, O, and S) and the number of unsaturation expressed as double bond equivalent (DBE). According to the heteroatoms present, specific classes were determined and their relative abundance was used for building class distribution plots.

3. RESULTS AND DISCUSSION

3.1. Hydrotreating Test Results. The sewage sludge-derived HTL biocrude was hydrotreated in two stages in a high-pressure batch reactor over a commercial sulfided NiMo-based catalyst. The first stabilization step was performed at 250 °C and 80 bar H_2 for 4 h. With the other operating conditions kept constant (P, 80 bar; reaction time, 4 h), the second step was conducted at 350 and 400 °C to investigate the effect of the hydrotreating temperature on the heteroatom removal and the properties of the upgraded liquid product. The two stages were conducted sequentially, without intermediate cooling or fresh catalyst loading. The stabilization step was also performed individually, and the reaction was stopped after 4 h to collect stabilized oil for analysis reasons.

The upgrading of the HTL oil results in the formation of an organic liquid phase, gases, and heavy tars, solids, and coke. No separate aqueous liquid phase is produced. The total mass balance closure varies between 83 and 88 wt %. The yields to the different products, normalized to 100 wt %, are shown in Table 1 for the first stabilization stage at 250 °C and the two-

Table 1. Normalized Product Yields of HTL Biocrude Hydrotreating Experiments

product yield (wt %)	first stage	second stage	second stage
	$T = 250$ °C	$T = 250$ and 350 °C	$T = 250$ and 400 °C
gases	0.9	4.7	10.4
organic liquid	66.7	55.8	44.4
heavy tars, solids, and coke	32.2	39.4	45.1
total	100.0	100.0	100.0

stage hydrotreating tests at final temperatures of 350 and 400 °C. The results clearly show that the progressive increase of the hydrotreating temperature from 250 to 400 °C leads to a gradual decrease of the organic oil yield from ∼67 to 44 wt %, respectively, with considerable increase in the formation of gases. The normalized composition of the gases, with and without H_2, is presented in Table 2. The majority of the gases consist of C_1– C_5 light alkanes, evidencing the occurrence of cracking reactions. The extent of cracking increases with the severity of the hydrotreating conditions. There is also significant formation of CO_2, produced from the decarboxylation reactions of the O-containing molecules in the HTL biocrude. The concentration of CO_2, after excluding H_2, decreases with the reaction temperature, suggesting that oxygen is primarily removed at the first stabilization stage at 250 °C. Oxygen elimination through decarbonylation is only observed at 400 °C, however at a very small degree as evidenced by the low CO concentration in the gases.

The upgrading process also results in the substantial production of heavy tars, char (solids), and coke deposited on the catalyst. It is experimentally very difficult to further break down this fraction to its individual constituents, because it forms a hard deposit on the bottom of the reactor. The amount of solids/coke increases with the hydrotreatment temperature, suggesting that it results from a combination of thermal degradation and condensation/oligomerization reactions of the heavy molecules in the HTL biocrude to large polynuclear aromatic molecules.

It should be noted that the experimental conditions applied in this work, i.e., use of crushed catalyst in batch reactor, are

**Table 2. Composition of Gaseous Products in HTL Biocrude Hydrotreating Experiments**

composition (vol %)	first stage T = 250 °C	second stage T = 250 and 350 °C	second stage T = 250 and 400 °C
		Normalized	
H_2	94.7	66.7	45.6
CH_4	2.3	18.3	32.3
C_2H_6	0.7	5.9	9.3
C_3H_8	0.3	2.3	4.0
C_4H_{10}	0.4	1.5	1.6
C_5H_{12}	0.1	0.2	0.3
CO	0.0	0.0	0.4
CO_2	1.6	5.0	6.4
total	100.0	100.0	100.0
		Normalized H_2-Free	
CH_4	42.6	55.0	59.5
C_2H_6	12.5	17.8	17.1
C_3H_8	5.0	6.8	7.4
C_4H_{10}	7.9	4.6	2.9
C_5H_{12}	2.1	0.7	0.6
CO	0.0	0.0	0.7
CO_2	29.9	15.1	11.8
total	100.0	100.0	100.0

not optimal for the commercial application of the process. It was recently highlighted that catalyst crushing can change the pore diffusion properties, as well as the wetting and channeling properties, thus affecting product yields.[14] Investigation of the hydrotreating of HTL oil in continuous flow reactors with the use of catalyst extrudates is currently on-going to establish industrially relevant catalyst performance and operating conditions.

3.2. Physicochemical Properties and Elemental Composition of HTL Oils. The upgraded HTL liquids from the stabilization stage at 250 °C and the two-stage hydrotreating tests at final temperatures of 350 and 400 °C were thoroughly characterized to determine their physicochemical properties and elemental composition. The results, including the corresponding data for the HTL biocrude feedstock, are presented in Table 3. As shown by the MCR analysis results, the sewage sludge-derived feedstock displays high coking tendency and high acidity. The latter is, as discussed in detail later, due to the presence of carboxylic and phenolic compounds. This is also mirrored in the oxygen content that lies in the 10 wt % dry basis (db) range. What is

also notable is the high nitrogen content (2.3 wt % db), originating from the sewage sludge feedstock. High levels of nitrogen have been reported for biocrudes produced from municipal solid waste, manure, wastewater sludge, and algae as a result of the protein and amino acid content of the feedstock.[2]

The characterization of the HTL upgraded products shows that the hydrotreating temperature increase improves the fuel quality, as evidenced by the lower density, higher heating value, lower coking tendency, and decreasing acidity. With regard to heteroatom removal, Figure 1 presents the hydrodenitrogena-
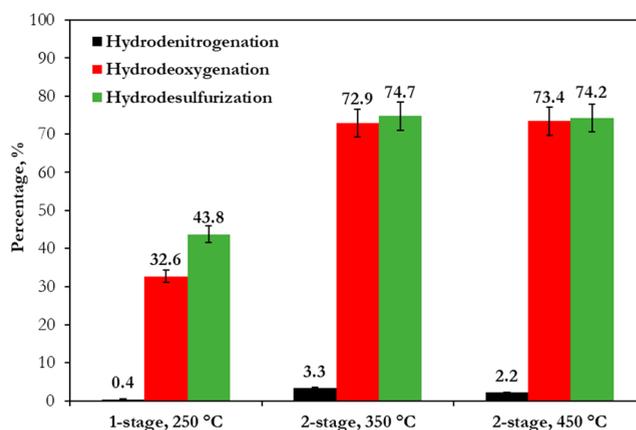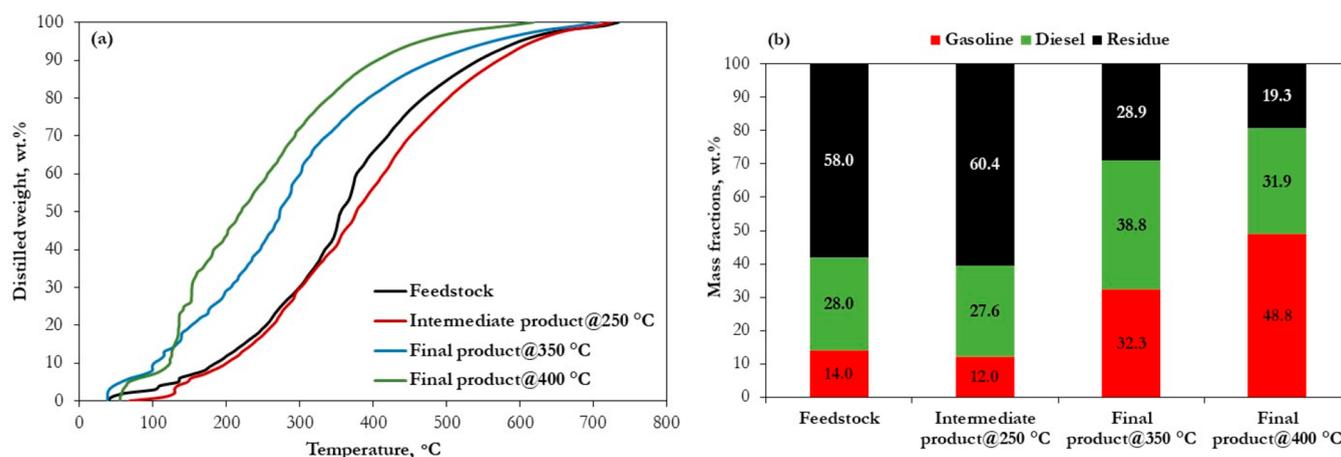

Figure 1. HDN, HDO, and HDS degrees attained at different hydrotreating conditions.

tion (HDN), hydrodeoxygenation (HDO), and hydrodesulfurization (HDS) degrees achieved at the different hydrotreating temperatures. The stabilization step at 250 °C manages to remove a substantial amount of the oxygenated and sulfur-containing compounds present in the HTL oil. Subsequent hydrotreatment at higher temperatures considerably increases the HDO and HDS levels to 73−74%. On the other hand, the nitrogen-containing compounds appear extremely resilient, and only negligible nitrogen removal is achieved at all investigated conditions. The results obtained at 350 and 400 °C are very similar, suggesting that the more severe temperature conditions do not achieve further conversion of the heteroatom compounds.

The HTL oil samples were also subjected to high-temperature simulated distillation to compare the boiling point distribution. The simulated distillation curves are

Table 3. Physicochemical Properties and Elemental Composition of HTL Oils

property	feedstock	first stage T = 250 °C	second stage T = 250 and 350 °C	second stage T = 250 and 400 °C
density at 60 °C (g/cm^3)	0.97	0.93	0.88	0.85
heating value (MJ/kg)	37.3	39.7	41.6	41.9
MCRT (wt %)	12.1	9.8	9.4	5.6
TAN (mg of KOH/g)	103.7	23.5	3.7	2.8
H_2O content (wt %)	1.0	1.3	1.1	0.3
		Elemental Analysis (wt %, db)		
carbon	77.7	79.9	83.7	84.1
hydrogen	9.7	11.0	11.3	11.0
nitrogen	2.3	2.3	2.2	2.2
sulfur	0.7	0.4	0.2	0.2
oxygen (by difference)	9.6	6.4	2.6	2.5

Figure 2. (a) Simulated distillation curves and (b) gasoline-range (cut-off point 216 °C), diesel-range (cut-off point 343 °C), and residue fractions of HTL oils.

presented in Figure 2a, together with the simulated weight fractions in the gasoline range (cut-off point 216 °C), diesel range (cut-off point 343 °C), and heavy compounds (>343 °C) (Figure 2b). The HTL biocrude has a high percentage of heavy boiling fractions, but also gasoline- and diesel-range components. Interestingly, the distillation curve of the partially upgraded oil at 250 °C demonstrates an increase in the molecules that boil off in the 400–600 °C range and a slightly higher residual fraction than in the original feed. Further treatment at higher temperature hydrocracks the oil to significantly lighter fractions, with both the gasoline- and diesel-range fractions substantially increasing compared to the feedstock. The upgraded product at 400 °C is the lightest, containing more than 82 wt % gasoline- and diesel-range molecules.

3.3. Chemical Composition of HTL Oils. *3.3.1. GC–MS Analysis.* GC–MS analysis was employed to identify and classify the specific molecular compounds present in the HTL oils, both feedstock and upgraded products. Figure 3 reports the results of the GC–MS analysis, in terms of families of
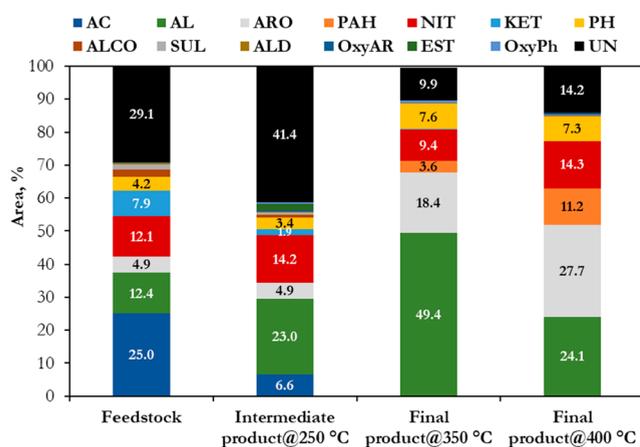

Figure 3. Semi-quantitative composition of HTL oils by GC–MS (legend: AC, acids; AL, aliphatics; ARO, aromatics; PAH, polyaromatic hydrocarbons; NIT, N-containing compounds; KET, ketones; PH, phenols; ALCO, alcohols; SUL, S-containing compounds; ALD, aldehydes; OxyAR, oxy-aromatics; EST, esters; OxyPH, oxy-phenols; and UN, unidentified).

compounds present in the samples based on the respective chromatogram areas. These findings correspond to the CH_2Cl_2-soluble, volatile fraction of the oils with boiling point <500 °C, which, according to the simulated distillation curves, represents more than 85% of all analyzed liquid samples. The largest compound class in the HTL biocrude is carboxylic acids, consistent with its high TAN (Table 3). The most abundant species in this category are long-chain, saturated, and monounsaturated fatty acids with C_{12}–C_{18} carbon atoms, namely, dodecanoic (lauric) acid, tetradecanoic (myristic) acid, pentadecanoic (pentadecylic) acid, hexadecanoic (palmitic) acid, hexadecenoic (palmitoleic) acid, octadecanoic (stearic) acid, and octadecenoic (oleic) acid. The concentration of lipids (cellular lipids, free fatty acids, wax, and gum) in sludges from wastewater treatment plants has been reported to be high, accounting for approximately 20% of the organic matter.[15] Other important family classes in the feedstock are long-chain aliphatics, carbonyls (ketones), and nitrogen-containing compounds, mainly C_{12}–C_{18} linear, saturated amides and heterocyclic nitrogenated compounds (pyridine, indole, and pyrrole) with various alkyl substitutions. These products are the result of amidation reactions of proteins with fatty acids, producing fatty acid amides,[16] and Maillard reactions with carbohydrates, forming *N*-hetero-cycles.[17]

The stabilization treatment at 250 °C brings about a formidable decrease in the acidic compounds, in line with the great decrease of the TAN of this sample. This is accompanied by a concurrent increase of the aliphatic molecules, consisting mainly of saturated, long-chain alkanes in the C_{14}–C_{18} range. The long-chain fatty acids are thus easily converted to the corresponding paraffins, even at mild temperature conditions, leading to the observed reduction in the oxygen content of the oil. Similar results have been reported by other studies on the upgrading of HTL biocrudes from sewage sludge and algae.[9] The deoxygenation of the fatty acids probably occurs via both decarboxylation and dehydration routes, as evidenced by the formation of both CO_2 and H_2O in the reaction products (see Tables 2 and 3). Another noticeable change in the chemical composition of the oil after the first stage treatment is the drastic elimination of the ketones in the oil. Carbonyl compounds, mainly aldehydes and ketones, are highly reactive and tend to polymerize very easily to larger molecules via aldol condensation reactions.[18,19] Ketones have been reported to be
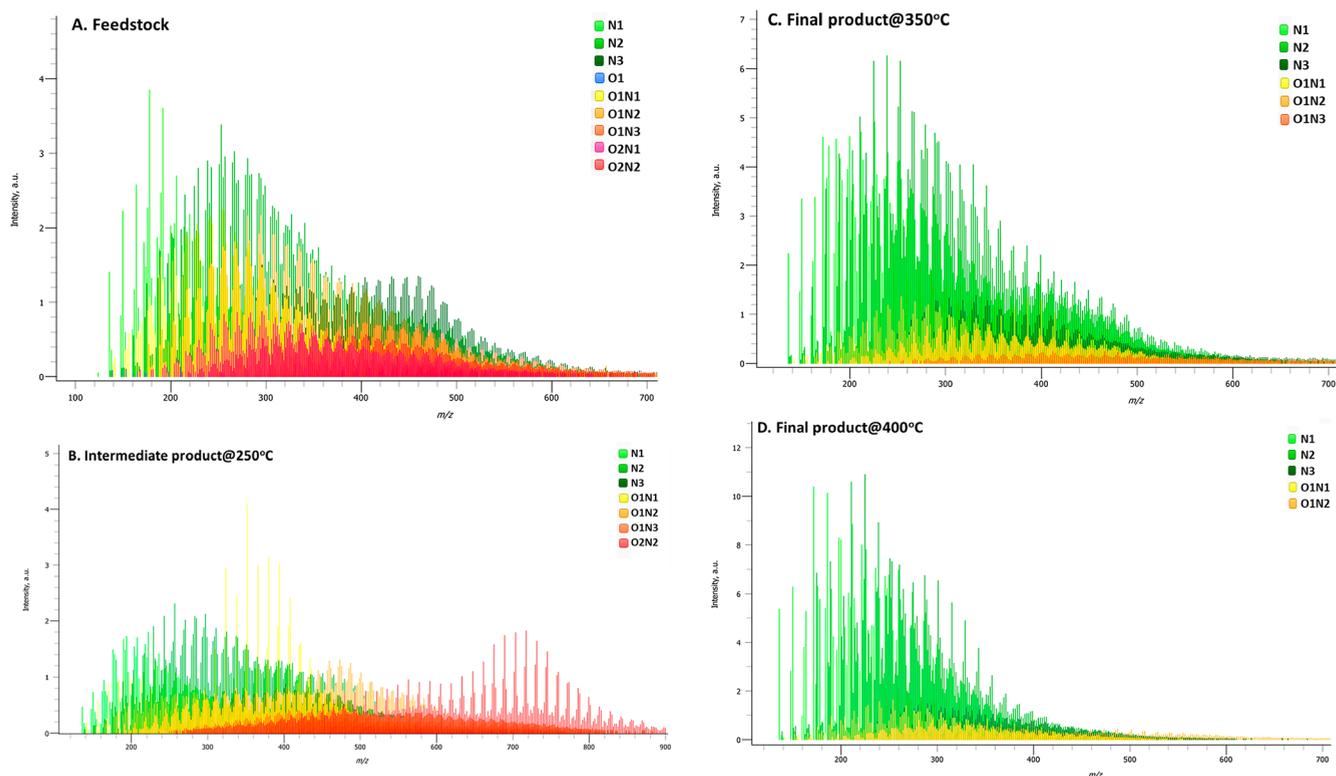
Figure 4. APCI(+) FTICR fingerprint mass spectra of the (A) HTL feedstock, (B) intermediate product at 250 °C, (C) final product at 350 °C, and (D) final product at 400 °C.
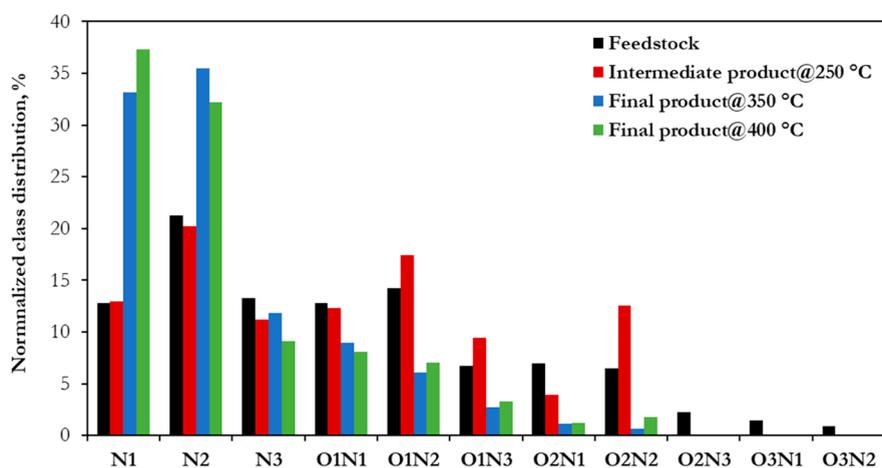
Figure 5. Normalized distribution of the compound classes identified in the HTL oils by APCI(+) FTICR−MS.

mainly responsible for the instability of bio-oils, which represents the biggest challenge in hydrotreating, because the polymerization of the oil can cause blockage of the reactor and deactivation of the upgrading catalysts.[20] Therefore, this mild hydrogenation step appears to be required to reduce extensive coking under the more severe hydrotreating conditions.

The second stage hydrotreatment under more severe conditions significantly changes the composition of the oils. At 350 °C, the majority of the peaks (∼50% area) correspond to aliphatic compounds, with the main representatives being linear, paraffinic hydrocarbons in the C_{10}−C_{18} range. In comparison to the stabilized oil, there is a clear reduction in the carbon atom number, confirming the occurrence of hydrocracking reactions that increase the gasoline- and

diesel-range fractions in the product, but also reduce the oil yield and generate light hydrocarbon gases. There is also substantial formation of aromatic hydrocarbons, mainly monoaromatics (benzene, toluene, and xylene (BTX) and alkylbenzenes). Monoaromatics can form from fatty acid fractions through intermediate *n*-alkanes via cyclization and aromatization reactions[21] and through selective ring-opening and dehydrogenation reactions of the sterols in the HTL biocrude, which has been reported on commercial hydro-treating catalysts at these temperatures.[22] Increasing the severity of the hydrotreatment to 400 °C substantially enhances these reactions, as the monoaromatics become dominant (at the expense of aliphatics, which also lose carbon atoms), in addition to the formation of a significant portion of
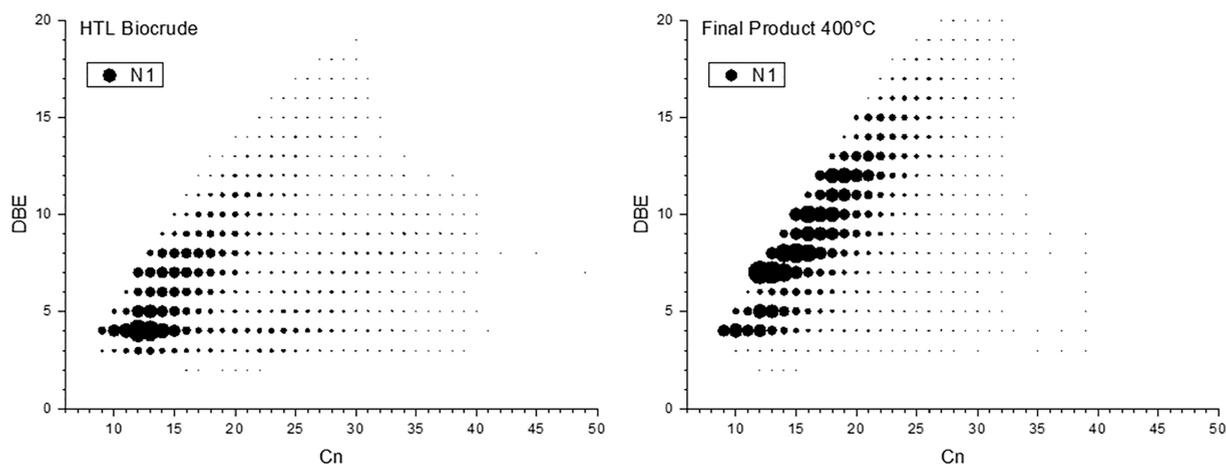
Figure 6. DBE versus carbon number of N1 compounds determined by FTICR−MS in the HTL feedstock and final product at 400 °C.
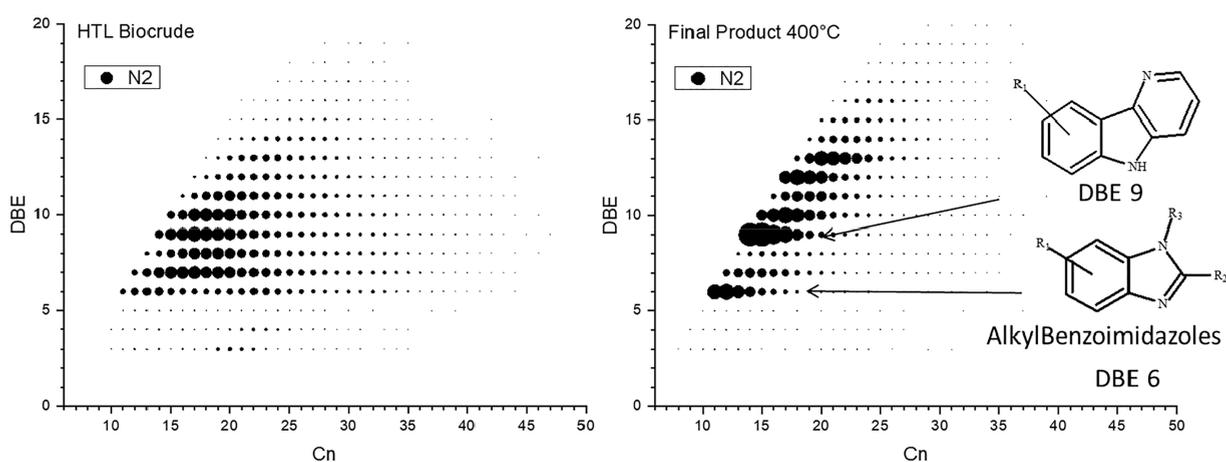

Figure 7. DBE versus carbon number of N2 compounds determined by FTICR−MS in the HTL feedstock and final product at 400 °C.

polyaromatic hydrocarbons, mainly alkylated naphthalenes, phenanthrenes, pyrenes, and chrysenes. It should be noted that at all conditions, the concentration of nitrogenated compounds remains largely invariable, consistent with the low HDN degree, confirming the resilience of these compounds.

3.3.2. FTICR−MS Analysis. In-depth chemical character-ization of the HTL oils was further conducted with FTICR−MS analysis, which can characterize the entire oil sample with high accuracy and resolution, as opposed to GC−MS, which concerns the volatile part of the oil (boiling point < 500 °C). APCI in the positive ion mode was selected as the most suitable ionization technique to thoroughly characterize the complex biocrude and upgraded oil samples, because it allows for effective ionization of the N- and O-containing compounds and is less affected by ion suppression.[23] It should be noted that APCI does not allow for ionization of low proton affinity species (low-polarity compounds), such as saturated and monounsaturated hydrocarbons. Fatty acids are also ionized with low efficiency in the positive ion mode.

The full-range positive-ion APCI−FTICR mass spectra of the HTL biocrude and the three upgraded oil samples are presented in Figure 4. The spectra contain around 12 000 different mass peaks, confirming the high complexity of the HTL oils. Most of the peaks were assigned specific molecular formulas, considering a certain range of C, H, O, N, and S. The element range was selected on the basis of the elemental

analysis results in Table 3. The identified compounds were then grouped into classes according to the heteroatom content and were quantified on the basis of the peak abundances in the mass spectra. The spectra in Figure 4 are shown as fingerprint spectra, with the main classes of compounds represented by different colors. The normalized distribution of classes in the samples is reported in Figure 5. In all samples, most of the compound families contain nitrogen and oxygen.

The molecular weight distribution of the detected ions in the HTL biocrude feedstock (Figure 4a) is in the mass range of m/z 130−650, with most abundant species in the range 150−400. The classes N2, O1N2, O1N1, N1, and N3 show the most intense ions, confirming the high concentration of fatty acid amides and nitrogenated compounds in the oil. The stabilization step at 250 °C interestingly leads to the formation of heavier molecules than those in the feed, in the mass range of 650−850. These heavy compounds belong to the O1N2 and O2N2 classes, pointing out to dimerization reactions of the original amides to amide dimers. This concurs with the findings of the high-temperature simulated distillation (Figure 2) that showed that the hydrotreated oil at 250 °C is slightly heavier than the original feedstock. These dimers disappear in the final upgraded products, after hydrotreatment at 350 and 400 °C, with a concurrent decrease of the OxNy class compounds and a significant increase of the N1 and N2 compound classes. It is established that amides are reduced
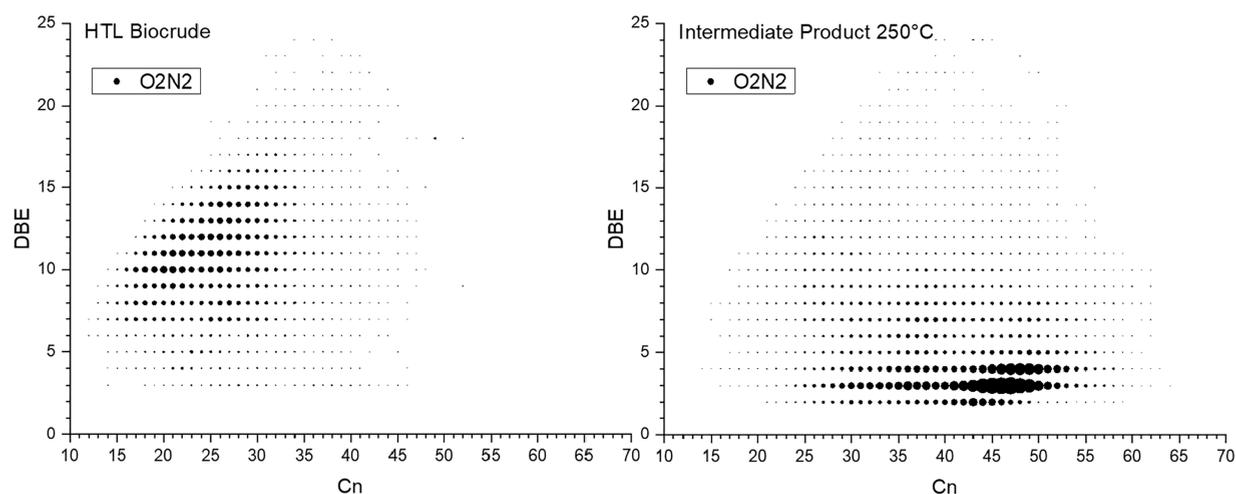
Figure 8. DBE versus carbon number of N2 compounds determined by FTICR−MS in the HTL feedstock and intermediate product at 250 °C.

more easily than amines, nitriles, or heterocyclic nitrogen compounds that require more severe conditions.[24] The GC−MS results (see Figure 3) suggest that the amides are readily converted into saturated hydrocarbons, and the OxNy heteroaromatic species are efficiently deoxygenated into Nx compounds. The FTICR−MS analysis also confirms that upgrading at 400 °C leads to a much lighter oil, as the detected ion molecular weight distribution shifts to a lower mass range compared to 350 °C, thus confirming the Simdist results. In a recent work, Cronin et al.[25] investigated the distribution of nitrogenates present in upgraded and non-upgraded HTL oil from food waste, sewage sludge, and fats, oils, and grease, by two-dimensional (2D) GC−MS. They also highlighted that pyrazines and amides are more efficiently removed via upgrading, while pyrroles, pyrrolidines, indoles, pyrimidines, pyridines, and imidazoles are more recalcitrant toward HDN, in agreement with our results.

Enhanced spectra analysis allows for the further description of the molecular compounds in each specific class and determination of the DBE, which is defined as the number of rings plus double bonds in a neutral molecule. Figures 6 and 7 show the degree of unsaturation (DBE) versus the number of carbon atoms in compounds with one and two nitrogen atoms (N1 and N2 classes) in the HTL biocrude and the final upgraded liquid product (400 °C), as determined by FTICR−MS. In Figure S1 of the Supporting Information, other class (OxNy) plots related to the HTL biocrude and the final product are shown. It is evident that the oxygen-containing classes are drastically reduced in the final upgraded oil. With regard to the N1 species (Figure 6), the HTL biocrude contains alkylpyridines (DBE of 4) as main compounds, together with other species spread in the Cn of 9−35 and DBE of 3−15 range. The final upgraded product (400 °C) shows intense compounds with DBE from 4 to 15 and with a lower number of carbon atoms (9−25). Considering a constant value of DBE, the length of the homologous series, at an increasing number of carbons, is related to the degree of alkylation. Thus, the final product shows a lower degree of alkylation of these N-containing compounds. Figure S2 of the Supporting Information shows the Cn versus DBE plots related to the N1 class for the four oil samples analyzed by FTICR−MS. The transformation from high alkylated compounds in the HTL biocrude to more condensed structures in the upgraded

products is clearly visible from the distribution of the main compounds (at a constant value of DBE and narrower series at increased Cn values).

With regard to the N2 class (Figure 7), the HTL biocrude has high concentration of molecules with 10−25 carbon atoms and 5−12 DBE. The remaining N2 molecules in the upgraded product are smaller (10−15 carbon atoms) with DBE of 6 (such as alkyl benzimidazoles) and DBE of 9, 10, and 12, likely related to condensed N-containing aromatic polycyclic structures. Both of these N1 and N2 compounds are produced by deoxygenation, partial denitrogenation, and cracking of more complex structures present in the HTL biocrude as classes Nx and NxOy, resulting in more condensed heteroaromatic structures with short linked alkyl chains. Indeed, these compounds appear to be more resilient to the hydrotreating upgrading process.

Finally, the plots in Figure 8 show the class O2N2 in the HTL biocrude compared to O2N2 found in the intermediate product (250 °C). In the plot on the right, species with a high number of carbon atoms (35−55) and with DBE of 1−3 appear. This result confirms the formation of heavy aliphatic products (as shown in Figure 4b), consistent with the dimerization of unsaturated aliphatic amides (DBE of 2 and Cn of 42−55) detected in the HTL biocrude.

3.4. Co-processing Compatibility of Upgraded HTL Oil. The hydrotreatment of sewage sludge-derived HTL biocrude achieves dramatic improvement in the quality of the oil. Still, the properties of the upgraded products do not meet the current specifications of road transport fuels. An alternative approach to the stand-alone upgrading of renewable feedstocks to drop-in biofuels is the incorporation and co-processing of these oils in conventional fuel production processes at existing refineries. In a recent detailed investigation of the compatibility of HTL oil with fossil feedstocks for co-refining,[26] HTL oil from pinewood was shown to be immiscible with straight-run gas oil as a result of the dissimilarities in the containing compound structures and the different polarities of the two feeds. Deoxygenated upgraded bio-oil was, however, completely miscible at any blending ratio, because it had a significantly lower oxygen content and, therefore, lower polarity. Chiaberge et al.[27] also demonstrated the successful blending of 20% partially upgraded sewage sludge-derived HTL oil with low-sulfur fossil

crude and its co-distillation to gasoline, kerosene, diesel, and residue fuel cuts.

To assess the co-processing compatibility of the upgraded sewage sludge-derived HTL oil in this work, we prepared and fully characterized a 10 wt % blend of upgraded HTL oil from the two-stage hydrotreating test at 350 °C with a low-sulfur, low-nitrogen VGO, typically used as feedstock in cracking units. The renewable fuel demonstrated high affinity and compatibility with the fossil-based refinery stream, achieving full miscibility with the VGO and obtaining a stable blend. The physicochemical properties and elemental composition of the upgraded HTL oil, VGO feedstock, and 10 wt % blend are presented in Table 4. As expected, the properties of the blend

Table 4. Physicochemical Properties and Elemental Composition of the 10 wt % Upgraded HTL/VGO Blend and Individual Blend Components

property	VGO	upgraded HTL[a]	10 wt % upgraded HTL/VGO blend
density at 60 °C (g/cm^3)	0.85	0.88	0.85
heating value (MJ/kg)	44.7	41.6	44.7
MCRT (wt %)	0.02	9.4	0.4
TAN (mg of KOH/g)	0.1	3.7	0.4
viscosity at 50 °C (cP)	21.2	N/A	14.0
H_2O content (wt %)		1.1	
Elemental Analysis (wt %, db)			
carbon	86.7	83.7	86.6
hydrogen	13.2	11.3	13.0
nitrogen	0.01	2.20	0.22
sulfur	0.02	0.20	0.03
oxygen (by difference)	0.07	2.60	0.16

[a]Upgraded HTL refers to the upgraded HTL oil from the two-stage hydrotreating test at 250 and 350 °C.

fall in between those of the VGO and the upgraded HTL oil. The main contribution of the renewable fuel is apparent mainly in the nitrogen content, which is higher in the blend compared to the fossil VGO stream, as a result of the N-containing molecules in the sewage sludge-derived upgraded product. The TAN value of the blend is 0.4 mg of KOH/g, which is acceptable for treatment in conventional refineries (typical values of commonly refined crude oil are <0.5 mg of KOH/g[27]).
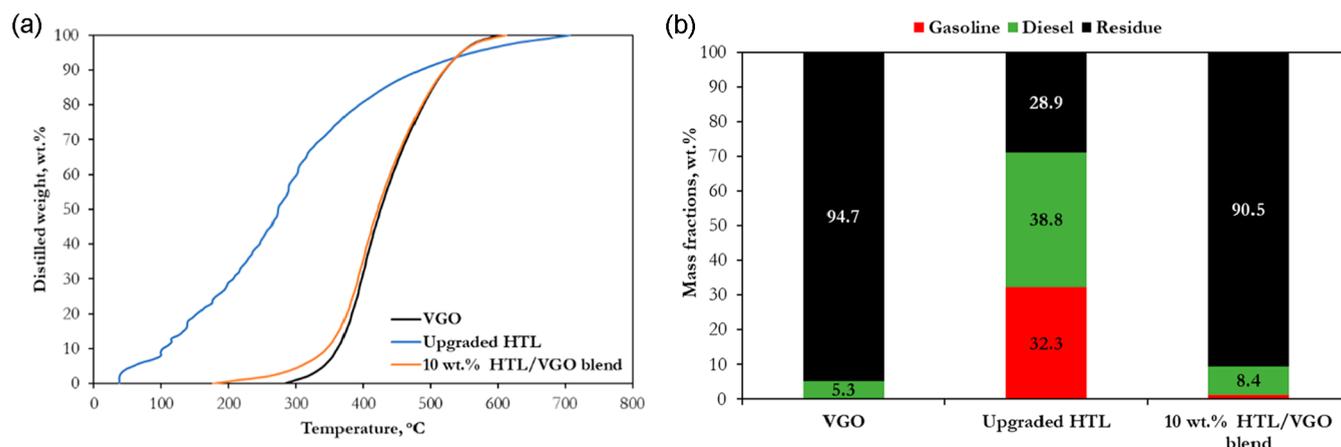
The simulated distillation curves of the samples are presented in Figure 9a, together with the simulated weight fractions in the gasoline, diesel, and residue range (Figure 9b). The VGO feedstock is much heavier than the upgraded HTL product and consists of ~95% of heavy boiling components. The boiling curve and the distillation fractions of the blend are similar to those of the VGO. Overall, the properties of the blend highlight its suitability for further processing in conventional refinery processes, offering an attractive, alternative pathway for introducing renewable carbon in transportation fuels.

4. CONCLUSION

This work shows that the two-stage hydrotreating of sewage sludge-derived HTL oil at mild reaction conditions can significantly improve its quality with potential use in fuel applications. Advanced characterization with GC−MS and FTICR−MS reveals that the HTL biocrude has high complexity, mainly consisting of long-chain saturated fatty acids and amides, long-chain aliphatics, carbonyls (ketones), and alkyl-substituted heterocyclic nitrogenated compounds. This composition is reflected in its high acidity and high nitrogen and oxygen content (2.3 and 10 wt % db, respectively).

The first hydrotreating step at 250 °C and 80 bar H_2 causes a significant decrease in the acidity and oxygen content of the oil as a result of the HDO of the long-chain fatty acids to the respective paraffins. There is also drastic elimination of the carbonyl compounds, mainly responsible for the instability of bio-oils, underlying the importance of the mild stabilization step in reducing extensive coking in the subsequent hydrogenation under more severe conditions. However, this intermediate oil is slightly heavier than the original feedstock as a result of dimerization of the original amides to amide dimers.

The second hydrotreating step at a higher temperature drastically changes the properties and composition of the oil. In comparison to the stabilized oil, there is a clear reduction in the carbon atom number, confirming the occurrence of hydrocracking reactions that increase the gasoline- and diesel-range fractions in the product, but also reduce the

Figure 9. (a) Simulated distillation curves and (b) gasoline-range (cut-off point 216 °C), diesel-range (cut-off point 343 °C), and residue fractions of the 10 wt % upgraded HTL/VGO blend and individual blend components.

liquid yield and generate light hydrocarbon gases. At 350 °C, the oil mainly consists of C_{10}–C_{18} alkanes and monoaromatics (BTX and alkylbenzenes). Increasing the severity of the hydrotreatment to 400 °C substantially enhances the monoaromatic content at the expense of aliphatics, in addition to the formation of a significant amount of polyaromatic hydrocarbons, mainly alkylated naphthalenes, phenanthrenes, pyrenes, and chrysenes. With regard to the heteroatom content, the results obtained at 350 and 400 °C are very similar, with oxygen and sulfur removal in the order of 73–74%. The nitrogen-containing compounds appear on the other hand extremely resilient, and only negligible nitrogen removal is achieved at all investigated conditions. FTICR–MS shows that hydrotreatment at 350 and 400 °C decreases the compounds in the OxNy classes, but significantly increases the N1 and N2 molecules. Therefore, the amides are readily converted into saturated hydrocarbons, and the OxNy heteroaromatic species are efficiently deoxygenated into Nx compounds. However, heterocyclic nitrogen compounds require further optimization of the catalyst and process conditions to be removed.

The above highlight that the development of an efficient upgrading process for complex feedstocks, such as sewage sludge-derived HTL oil, necessitates detailed knowledge of the molecular composition and specific heteroatom-containing compounds to understand and optimize the hydrotreating reactions. The advanced chemical characterization of the feedstock and hydrotreated products constitutes a valuable tool for the optimization of the hydrotreating catalysts and process. An attractive alternative to a stand-alone hydrotreating process is the co-processing of these renewable streams in a conventional refinery. To that end, we demonstrated that the upgraded HTL oil is fully miscible in fossil-based VGO in a 10 wt % blend, with properties that fulfill the requirements for further processing in conventional refinery processes.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c01746.

Degree of unsaturation (DBE) versus the number of carbon atoms for the O1N1, O1N2, and O2N1 classes in the HTL biocrude (top) and upgraded final product at 400 °C (bottom), obtained by APCI(+) FTICR–MS elaboration (Figure S1) and degree of unsaturation (DBE) versus the number of carbon atoms for the N1 class in the HTL biocrude, the intermediate product at 250 °C, the final product at 350 °C, and the final product at 400 °C, obtained by APCI(+) FTICR–MS elaboration (Figure S2) (PDF)

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Notes

The authors declare no competing financial interest.

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