Hydrothermal Liquefaction of Loblolly Pine: Effects of Various Wastes on Produced Biocrude

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Supporting Information

ABSTRACT: In this study, feedstock interaction of cow manure and digested sewage sludge on hydrothermal liquefaction (HTL) of loblolly pine (LP) was evaluated. Noncatalytic HTL experiments were performed at reaction temperatures of 250, 275, and 300 °C at a constant reaction time of 30 min. Cyclohexane and acetone were used for biocrude extraction separately. The study focuses on the characteristics of the produced biocrude, and thus, physiochemical properties of biocrudes were examined by gas chromatography–mass spectrometry, Fourier-transform infrared spectroscopy, density, and viscosity measurements, in addition to comparing mass and energy yields. On a LP basis, the biocrude yield reached as high as 30 and 17% for acetone and cyclohexane extraction, respectively, at the highest reaction temperature. Elemental carbon and energy contents increased with increasing HTL temperature for all cases. Alkalinity of the HTL process liquid (aqueous phase) increases from the HTL of sludge, and thus, it favored the formation of nonpolar compounds in biocrude. On the other hand, acidity of the reaction medium increases with the HTL of manure and pine, and thus, phenolic compounds in biocrude were increasing. Cyclohexane was more effective for sludge/LP biocrude extraction, whereas acetone was effective for manure/LP. Density of cyclohexane extracted sludge/LP biocrudes at 300 °C was less than 1000 kg m⁻³, whereas acetone-extracted biocrudes had densities greater than 1000 kg m⁻³. For all the biocrudes, viscosity was reduced considerably for the mixtures when compared to biocrudes from LP alone.

1. INTRODUCTION

In 2007, approximately 77.6 million animal units of cattle (dairy, beef, and other) produced 921 million metric tons of wet manure in the US. Although manure application to soil is a traditional and suitable method for manure management, it can contribute significantly to greenhouse gas emissions, particularly the release of methane. Furthermore, improper management of nutrients (nitrogen and phosphorous) can result in nutrient runoffs that can severely affect the water quality (eutrophication and harmful algal growth) and organisms of surrounding ecosystems. Similar to manure, hundreds of million tons of sewage sludge were produced from wastewater treatment facilities, which raise concerns regarding necessary handling and disposal. Like manure, sludge can be land-applied for beneficial use, but increasing urbanization and increasingly stringent environmental regulations are causing this to become a nonviable option. Alternative methods for sludge disposal require hauling and transportation, followed by land-filling or incineration, which leads to high costs and are considered unsustainable practices. Hydrothermal liquefaction (HTL) can utilize these abundant, wet feedstocks to produce biocrude which can then be used as liquid fuels or additional upgraded products.

HTL converts biomass, like sludge and manure, to biocrude in subcritical water, which can then be upgraded to liquid fuel. The reaction medium for the HTL process is water at high temperature, subcritical conditions (and water saturation pressures) ranging from 250 to 373 °C (4 to 22 bar). In addition to being an environmentally friendly solvent, water creates a favorable reaction medium because of its solvent properties at subcritical conditions. At the temperature range of interest, water’s dielectric constant decreases to values similar to organic solvents such as ethanol and n-butanol, thus making it suitable to dissolve nonpolar compounds. Additionally, acid- and base-catalyzed reactions that break down biomass polymers occur at HTL conditions due to 3 orders of magnitude
increase of ionic product of water compared to ambient conditions. Moisture contents of both cow manure and sewage sludge are often higher than 80%, which is ideal for HTL; however, there is a lack of high carbon content for higher throughput. In contrast, woody biomass (e.g., loblolly pine (LP)) has a higher carbon content but contains relatively low moisture and requires additional water for HTL.

Various studies have been reported on biocrude yield and quality affected by HTL reaction conditions for single feedstocks. Yin and Akhtar examined optimal reaction temperatures and times for HTL; it was reported that generally 300–310 °C and residence times of less than 15 min allow for maximum biocrude production before repolymerization and condensation reactions begin to dominate and start forming more solid char and gaseous products. Lignocellulosic feedstocks with high lignin content require higher reaction temperatures to reach the highest biomass-to-biocrude conversion because of lignin’s low reactivity.

HTL has been applied to various individual lignocellulosic feedstocks. The diversity of biomass feedstocks results in different biocrude conversions; the varying components that make-up biomass can have different reaction pathways that result in different conversion yields. Overall, biomass with higher make-ups of hemicellulose and cellulose allow for a larger biocrude conversion, whereas biomass with higher lignin content yields lower amounts of biocrude. HTL at 280 °C and 15 min of either sawdust or rice husks yielded approximately 8% biocrude, whereas the HTL of cattle manure at 310 °C and 15 min and that of swine manure at 300 °C and 30 min, which have 2–3 times less lignin content, reached yields of 48.8 and 30.2%, respectively.

Similar to feedstock compositions, the yield of produced biocrude also varies with different solvents used for biocrude extraction. The solvent can affect biocrude yield and composition as the solvent extracts certain compounds over others. For example, Valedez et al. showed how certain nonpolar solvents (hexadecane, decane, hexane, and cyclohexane) produced higher biocrude yields with lower carbon contents, while polar solvents (methoxycyclopentane, chloroform, and dichloromethane (DCM)) produced lower biocrude yield that had higher fatty acid composition. The solvent chosen for extraction should be taken into consideration for analysis and not just as a means of collecting and separating biocrude.

A review of the literature shows that less extensive research investigation has been reported on the effects of treating mixed biomass feedstocks under HTL conditions. Pedersen et al. recently examined the coliquefaction of crude glycerol and aspen wood at reaction temperatures of 380, 400, and 420 °C. The study found char formation was significantly reduced from 18.3% to as low as 3.42%, which suggested that the additional glycerol aided the suppression of lignin repolymerization, thus resulting in increased biocrude yields (at higher mass loadings). The varying reaction temperatures did not show a statistical significance in biocrude yield and the overall biocrude quality. Gai et al. applied HTL to a feedstock mix of microalgae (Chlorella pyrenoidosa) and rice husk in an attempt to examine synergistic effects to help promote higher rice husk conversions, as microalgae has been shown to be an excellent feedstock for HTL. Biocrude yields of feedstock mixtures (i.e., containing both microalgae and rice husk) were higher than that of the HTL of only rice husks. Additionally, 300 °C and 60 min were...
found to be the optimal reaction parameters for a 50:50 feedstock mixture which resulted in approximately 37.5% biocrude yield. Pedersen et al. and Gai et al. show the potential and positive effects that can be further studied and evaluated by treating different mixed biomass feedstocks under HTL conditions.

Therefore, the aim of this study was to evaluate the HTL of LP in the presence of sewage sludge or cow manure on the characteristics of biocrude that was produced. Manure and sludge are expected to provide an aqueous environment required for HTL, while LP will contribute additional carbon content. The effects of using a polar solvent versus a nonpolar solvent for extraction were also compared.

2. RESULTS AND DISCUSSION

2.1. Mass and Energy Yield of Biocrude. Biocrude yields from different reaction temperatures and extraction solvents are shown in Figure 1. Figure 1a,b shows biocrude yields calculated on a dry, mass-basis using acetone and cyclohexane as solvents, respectively. In general, biocrude yields from acetone extraction show higher yields for manure-containing runs than sludge-containing runs (as shown in Figure 1a). For instance, at 250 °C manure/LP has a yield of 12.0%; at the same reaction temperature, sludge/LP has a yield of 5.5%. Biocrude yields from cyclohexane extraction show higher yields for sludge-containing runs than manure-containing runs with increasing reaction temperature. Figure 1b shows that manure/LP and sludge/LP at 250 °C have yields 0.8 and 4.4%, respectively.

Manure-containing HTL runs have higher biocrude yields in acetone extraction than cyclohexane extraction, which suggests that the HTL of manure-containing slurries contain more polar compounds because acetone is a much more polar solvent than cyclohexane (a nonpolar solvent). Cow manure was also HTL-treated by Theegala and Midgett between temperatures of 250 and 300 °C for a reaction time of 15 min; yields of 16−18% were presented which corroborate manure-extracted biocrude favoring a more polar solvent. A shorter residence time of 15 min indicates the varying biocrude yields compared to 30 min residence time used in this study. Others have shown that a longer residence time can result in biocrude having more condensation reactions and yielding more char products, thus decreasing biocrude yield. HTL runs involving sludge, however, showed higher yields from cyclohexane extraction than acetone extraction, which indicates that the reacted biomass slurry contains more nonpolar compounds in its biocrude. Those nonpolar compounds have higher solubility in nonpolar solvents as shown from the higher yields.

Table 1. Ultimate Analysis and Energy Content of Produced Biocrudes

| solvent     | sample | T (°C) | C   | H   | O   | N   | HHV (MJ/kg) |
|-------------|--------|--------|-----|-----|-----|-----|-------------|
| acetone extract | LP     | 250    | 62.8 ± 0.2 | 5.7 ± 0.2 | 30.1 ± 0.9 | 0.1 ± 0.0 | 26.9 ± 0.3 |
|             |        | 275    | 66.4 ± 0.2 | 5.7 ± 0.2 | 24.7 ± 1.6 | 0.1 ± 0.0 | 28.8 ± 0.4 |
|             |        | 300    | 66.9 ± 0.5 | 5.6 ± 0.3 | 20.5 ± 1.8 | 0.1 ± 0.0 | 29.3 ± 0.2 |
| manure      | 250    | 61.5 ± 0.1 | 6.8 ± 0.1 | 20.1 ± 1.5 | 4.4 ± 0.0 | 29.4 ± 0.8 |
|             | 275    | 68.0 ± 0.6 | 6.7 ± 0.0 | 16.0 ± 0.1 | 3.9 ± 0.0 | 34.5 ± 3.2 |
|             | 300    | 68.5 ± 1.3 | 6.5 ± 0.1 | 15.5 ± 0.2 | 4.2 ± 0.1 | 32.2 ± 0.6 |
| sludge      | 250    | 72.6 ± 0.2 | 9.5 ± 0.2 | 11.1 ± 0.8 | 4.7 ± 0.0 | 38.3 ± 3.1 |
|             | 275    | 76.5 ± 0.5 | 9.0 ± 1.0 | 9.4 ± 0.6 | 3.1 ± 0.2 | 39.0 ± 0.7 |
|             | 300    | 82.1 ± 0.4 | 10.4 ± 0.1 | 4.1 ± 0.3 | 2.9 ± 0.1 | 38.2 ± 0.3 |
| manure/LP   | 250    | 54.7 ± 4.1 | 6.5 ± 0.5 | 23.1 ± 0.3 | 2.4 ± 0.2 | 26.5 ± 1.0 |
|             | 275    | 68.6 ± 0.5 | 6.6 ± 0.1 | 19.3 ± 0.3 | 2.7 ± 0.0 | 30.5 ± 1.4 |
|             | 300    | 63.0 ± 11.4 | 6.9 ± 0.1 | 16.6 ± 0.2 | 2.0 ± 0.4 | 33.3 ± 0.3 |
| cyclohexane extract | LP     | 250    | 60.7 ± 2.6 | 6.5 ± 0.8 | 13.5 ± 2.2 | 0.3 ± 0.0 | N/D |
|             | 275    | 66.9 ± 3.7 | 6.4 ± 0.2 | 19.7 ± 0.3 | 0.1 ± 0.1 | N/D |
|             | 300    | 70.0 ± 1.5 | 8.7 ± 0.5 | 10.2 ± 0.2 | 0.2 ± 0.0 | N/D |
| sludge      | 250    | 82.5 ± 1.6 | 9.3 ± 0.3 | 5.5 ± 1.1 | 2.5 ± 0.2 | 36.7 ± 4.4 |
|             | 275    | 81.0 ± 0.5 | 10.4 ± 0.1 | 4.8 ± 0.1 | 3.4 ± 0.1 | 43.3 ± 1.9 |
|             | 300    | 81.1 ± 2.8 | 10.8 ± 0.3 | 2.9 ± 0.1 | 2.6 ± 0.2 | 37.9 ± 1.8 |
| manure/LP   | 250    | 70.6 ± 1.0 | 9.3 ± 0.2 | 7.6 ± 0.3 | 0.7 ± 0.0 | N/D |
|             | 275    | 73.6 ± 5.0 | 9.6 ± 0.0 | 7.6 ± 0.2 | 0.8 ± 0.0 | N/D |
|             | 300    | 73.3 ± 0.4 | 9.0 ± 0.1 | 8.9 ± 0.5 | 1.2 ± 0.0 | N/D |
| sludge/LP   | 250    | 76.8 ± 5.8 | 10.1 ± 0.5 | 5.8 ± 0.3 | 2.2 ± 0.2 | 39.4 ± 0.5 |
|             | 275    | 78.1 ± 0.2 | 6.8 ± 0.1 | 17.9 ± 0.6 | 2.3 ± 0.2 | 41.0 ± 0.4 |
|             | 300    | 81.3 ± 0.1 | 9.7 ± 0.1 | 5.6 ± 0.2 | 3.1 ± 0.0 | 41.7 ± 1.0 |

*N/D: not determined due to insufficient sample.

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basis shows how much biocrude yield is affected with respect to LP (i.e., how much one constituent of the treated biomass slurry mix contributes to the overall yield of the biocrude). Yields on a LP basis were as high as 29.3% for manure/LP with acetone extraction and 17.0% for sludge/LP with cyclohexane extraction.

Overall, the highest biocrude yields were found at 300 °C. HTL of feedstocks with LP has yields that initially increase but show no substantial differences for the last two reaction temperatures. Conversely, they also stay leveled over the first two reaction temperatures but increase for the last two reaction temperatures. For example, manure/LP biocrude extracted with acetone remains relatively constant at approximately 12% for 250 and 275 °C but increases to 14.6% at 300 °C. The increase in the biocrude yield could be attributed to the increase in the breakdown of biomass constituents. Initial conversions of hemicellulose and cellulose into biocrude occurred at approximately 250 °C and continued to increase with increasing temperature.\(^{7,19}\) Although lignin also becomes reactive at 250 °C and has been found to decompose vigorously and react at 300–315 °C, it has also been shown to successively repolymerize, which can result in decreasing yield, thus having a conversion and yield that do not vary considerably.\(^{26}\)

Table 1 shows the elemental compositions, higher heating values (HHVs), and composition of biocrudes obtained from HTL of LP, manure, sludge, sludge/LP, and manure/LP from 250 to 300 °C. The lower yields produced from the sludge/LP acetone-extracted run and the manure cyclohexane-extracted run yielded insufficient samples for certain analyses (e.g., HHV requires approximately 0.5 g of sample), thus they were not shown in Table 1. Elemental carbon and oxygen contents of biocrude are considered, because the energy content of the fuel is a function of the composition.\(^{27}\) Carbon content increases with increasing HTL temperature for all samples except those produced from manure/LP with acetone and biocrudes from sludge with cyclohexane. The expected trend of increasing carbon content for these two cases falls within the experimental error determined. However, the carbon content of the mixture does not necessarily fall within the range of manure or LP alone. This difference can similarly be related to the organic acids produced by LP interacting with the manure.

Hydrogen content for samples produced with acetone changes insignificantly with increasing temperature. The hydrogen contents were also higher for biocrudes extracted with cyclohexane than for those extracted with acetone, except for sludge samples which exhibited similar compositions. Nitrogen content remains nearly constant for acetone-extracted biocrudes except for sludge which decreased from 4.7 to 2.9% from 250 to 300 °C. Increases in nitrogen for biocrudes extracted with cyclohexane were seen for the mixtures of manure/LP and sludge/LP. Oxygen content decreases with increased temperature for most samples, and the oxygen contents for biocrudes extracted with cyclohexane are lower than for those extracted with acetone. Under HTL conditions, oxygen is expected to be removed as CO\(_2\) during decarboxylation and as H\(_2\)O during dehydration reactions.\(^{28}\) Manure/LP extracted with cyclohexane increased in oxygen content from 7.6 to 8.9%. This suggests interaction between organic acids and manure forming a greater percentage of nonpolar oxygen containing molecules or more oxygenated compounds getting extracted from the mixture. The oxygen content of sludge and manure biocrude was lower than that for the digested sludge (18.9%) and swine manure (15.6%) biocrude reported in the literature.\(^{19}\) Nitrogen compositions of the manure/LP mixture in acetone were between the levels produced from the manure and LP individually. Nitrogen compositions of the sludge/LP mixture produced with cyclohexane were closer to the composition of sludge biocrude than LP alone, under similar conditions.

### 2.2. Chemical Characterization of Biocrude Using Gas Chromatography—Mass Spectrometry and Fourier-Transform Infrared Spectroscopy

Gas chromatography—mass spectrometry (GC–MS) was used to identify compounds making up the biocrude obtained at 300 °C (as carbon and energy contents were the highest at this temperature) and were categorized into organic acids, alcohols, hydrocarbons (HCs), phenols, or other compounds (Figure 2). A list of significant compounds identified in biocrude produced from 300 °C HTL reactions can be found in Table S1. The “others” category consists of identified compounds with small or nonreoccurring peak areas. Additionally, the maximum column temperature of gas chromatography (GC) reached to 260 °C, and thus, compounds with higher boiling points (e.g., long-chain HCs, etc.) were not identified. Physical observations of the biocrudes showed that sludge–cyclohexane-extracted HTL runs were less viscous than acetone-extracted HTL runs (discussed further in section 2.3.2). Thermal decomposition and hydrolysis of macromolecules produce monomer fragments. This is observed with the production of organic acids (acetic acid, fatty acids, etc.) from the degradation of fructose and glucose.\(^{30}\) In addition to producing organic acids, the hydrolysis of fatty acids produces alcohols.\(^{30}\) Figure 2 shows that phenols and HCs were the most produced compounds in all the biocrudes. The hydrolysis of lignin can be considered a main source of phenols, while the decarboxylation and hydrothermal decomposition of fatty acids have been shown to produce HCs.\(^{31,32}\) Following monomer fragmentation, reformation by dehydration and decarboxylation occurs (and polymerization for the formation of solid chars). Varying pH of the hydrothermal medium has been shown to result in different reaction pathways being favored for biocrude formation.\(^{33}\) It should be noted that hydrothermal treatment of LP and the hydrothermal treatment of dairy manure had produced acidic process liquids as result of produced organic acids, while the hydrothermal treatment of digested wastewater sludge had become more basic.\(^{34–36}\) This can further explain the more significant phenolic peak area present in the manure- or LP-containing runs, as furfural intermediates can degrade into phenols and furfural formation is more favored during acidic conditions.\(^{33}\) More HCs were
detected for sludge/LP HTL runs than manure/LP HTL runs. Watanabe et al. showed that increased alkalinity in hydrothermal media resulted in higher fatty acid decarboxylation, which yielded higher HC formation.38

Infrared spectroscopy was used to examine the different chemical bonds in the various biocrudes; wavelength identification for bonds is based on previous hydrothermal studies and HTL literature reviews.19,39,40 Figure S1 shows the chemical bands for the man-LP HTL runs extracted with acetone at all three reaction temperatures. In general, carbon and hydrogen bands can be observed at frequencies of 2840–3000, 1510 cm−1, and various bands less than 1000 cm−1, all of which correspond to aliphatic carbon groups, unsaturated aromatics and unsaturated aliphatic groups, and aromatic compounds, respectively. These bands are indicative of fatty acids and HCs, phenolic compounds detected by GC−MS. Additionally confirmed by GC−MS, alcohols and organic acids produced are also shown by bands at 1150, 1220, 1700, and 1350 cm−1. The increase in the reaction temperature results in higher band intensity at 1220, 1350, 1700 cm−1 and more distinct peak formations for bands between 700 and 800 cm−1; which suggests more alcohol, carboxylic acid, and aromatic formations as a result of further fragment degradation. Fourier-transform infrared spectroscopy (FTIR) plots for manure/LP runs extracted with cyclohexane at minimum and maximum reaction temperatures are presented in Figure S2. Aliphatic, aromatic, organic acid, and alcohol bands observed for manure/LP acetone were also observed for manure/LP cyclohexane extraction in addition to an alkane band at 1450 cm−1. However, the intensities for the aliphatic bands (2840–3000, 1510 cm−1) and the aromatic bands (bands less than 1000 cm−1) are of much higher suggesting cyclohexane as a better solvent for the extraction of nonpolar compounds as is also provided by the GC−MS. Figure S3 shows the FTIR plots of the sludge/LP runs at 275 °C using both solvents and the sludge/LP 300 °C run with acetone extraction. Although the sludge/LP HTL runs in Figure S3 share the same bands as the manure/LP runs, with respect to extraction solvent, band intensities could vary. Sludge/LP with cyclohexane extraction has high intensities for aliphatic groups and alkane groups. For cyclohexane extraction, the aromatic bands (<1000 cm−1) for manure/LP are of higher intensity than that of sludge/LP. To the author’s knowledge, FTIR plots of biocrude produced from the HTL of these mixed feedstocks have not been examined; however, the FTIR plots of the biocrude produced by individual feedstocks (LP, dairy manure, and digested sludge) share common bands for aromatics, alkanes, alcohols, and organic acids found throughout Figures S1–S3.19,24,41

### 2.3. Physical Properties of Biocrudes

#### 2.3.1. Density

The density of all sludge HTL biocrudes at 300 °C are presented in Figure 3. For cyclohexane extraction, sludge/LP 300 °C had a density of 972.4 ± 16.5 kg m−3, whereas sludge-only 300 °C had a density of 903.7 kg m−3. For acetone extraction, sludge/LP 300 °C and sludge-only 300 °C had densities of 1113.3 and 1052.5 kg m−3, respectively. Sludge/LP runs had higher bulk densities than the sludge-only run, with respect to the extraction solvent, which can be due to the extraction of additional compounds provided by the LP and the higher density of woody biomass biocrudes.52 Additionally, acetone-extracted biocrudes are shown to have higher viscosities than cyclohexane-extracted biocrudes. Aromatics have been shown to have higher densities than HCs like alkanes and alkenes.33 Thus, extraction of heavier molecular weight compounds by acetone, as shown in section GC−MS/FTIR by the increase in phenolic compounds, can result in higher density.

#### 2.3.2. Viscosity

The complex viscosities at 10 rad/s of the biocrude produced from 300 °C HTL are presented in Figure 4. Complex viscosity indicates the total resistance to dynamic shear, including both viscous resistance and elastic resistance. The behavior of these biocrudes was Newtonian or close to Newtonian. Complex viscosity is the same as Newtonian viscosity for the samples extracted with cyclohexane, which showed Newtonian behavior. The samples extracted with acetone showed some shear-thinning behavior, but each reached a Newtonian plateau by 10 rad/s.

Sludge/LP biocrudes extracted with acetone were quasi-Newtonian, with higher complex viscosity values seen at low frequency and a greater difference between measurements. This quasi-Newtonian behavior is probably due to higher molecular weight and polar compounds being extracted compared to cyclohexane, which extracts more nonpolar compounds. These higher molecular weight substances can be entangled causing some elastic component to the viscoelastic properties. More polar compounds tend to have attractive interactions that increase viscosity. The viscosity for the acetone-extracted sludge biocrude was several orders of magnitude higher than that of the sludge and sludge/LP biocrude extracted with cyclohexane. Even so, for sludge/LP biocrude extracted with acetone, a Newtonian plateau appears to be reached at a frequency of 10 rad/s.

Figure 4a shows sludge/LP biocrude viscosity values for cyclohexane extraction. Sludge/LP 300 °C had an average viscosity at 25 °C and 10 rad/s of 0.1285 ± 0.001 Pa·s, whereas sludge-only 300 °C had an average viscosity at 25 °C of 0.2638 ± 0.015 Pa·s. For cyclohexane extraction, sludge/LP 300 °C had an average viscosity at 50 °C and 10 rad/s of 0.03841 ± 0.002 Pa·s, whereas sludge-only 300 °C had an average viscosity at 50 °C of 0.07341 ± 0.006 Pa·s. Lower viscosity at higher temperatures is expected for any liquid, which suggests that handling of these kinds of biocrudes may be facilitated by increasing temperature. There was about 50% reduction in viscosity (at both temperatures) in biocrudes obtained from the mixed sludge/LP feedstock when compared to that for sludge-only, suggesting that mixing of biomass materials may be a valuable technique for improving viscosity. One underlying cause is probably the fact that the different biomass yields different molecular weight compounds. The lower weight chains can serve as lower viscosity lubricants for the higher molecular weight compounds. A wide molecular weight
distribution tends to lower viscosity. Another possible cause for lower viscosity for biocrude from mixtures is that the two compounds react during the HTL process to form lower molecular weight substances.

For acetone extraction (Figure 4b), sludge/LP 300 °C had an average viscosity of 298.95 ± 94 Pa·s at 25 °C and 10 rad/s. The viscosity of biocrude from sludge-only produced at 300 °C was highly viscous, hence the viscosity could not be measured at either temperature. For acetone extraction, LP-alone 300 °C biocrude had an average viscosity of 5908 ± 64 and 284 ± 124 Pa·s at 25 and 50 °C, respectively. For acetone extraction, sludge/LP 300 °C had an average viscosity of 170 ± 36 Pa·s at 50 °C and 10 rad/s. These viscosities suggest that extraction with acetone gives an essentially solid product. Higher handling temperatures than 50 °C would be required for handling this biocrude as a liquid. Nevertheless, the addition of sludge to the LP for acetone-extracted biocrude reduced viscosity to values lower than that for LP-alone biocrude.

The biocrudes from manure, LP, and their mixtures were all shear-thinning or pseudo-plastic with yield points. These biocrudes also appear to reach a Newtonian plateau at 10 rad/s. They were found to have very high viscosity and were essentially solid at 25 °C. For acetone extraction (Figure 4b), manure/LP 300 °C biocrude had an average viscosity at 25 °C and 10 rad/s of 1350 ± 70 Pa·s, whereas manure-only 300 °C biocrude was solid at 25 °C. As described above, LP-alone viscosity for these conditions was 5908 ± 64 Pa·s. At 50 °C and 10 rad/s, for acetone extraction, manure/LP 300 °C had an average viscosity of 152 ± 18 Pa·s, whereas manure-only 300 °C had an average viscosity at 50 °C of 4477 ± 175 Pa·s. As described above, LP-alone viscosity for these conditions was 284 ± 124 Pa·s. As found for the other mixtures, manure/LP 300 °C biocrude’s viscosity was lower than that of the single component biocrudes.

For cyclohexane extraction (Figure 4c), manure/LP 300 °C biocrude had an average viscosity at 25 °C and 10 rad/s of 3948 ± 248 Pa·s, whereas manure-only 300 °C biocrude was solid at 25 °C. As described above, LP-alone viscosity for these conditions was 5908 ± 64 Pa·s. At 50 °C and 10 rad/s, for cyclohexane extraction, manure/LP 300 °C had an average viscosity of 7.354 ± 0.61 Pa·s, whereas manure-only 300 °C had average viscosity at 50 °C of 27.37 ± 1.49 Pa·s. The change in viscosity was orders of magnitude lower with an increase in temperature of 25 °C. This unusual finding suggests that future work on the viscosity of these biocrudes and their microstructure should be pursued. The overall finding is clear: using a mixture of manure and LP to produce biocrude reduces viscosity considerably compared to using manure alone. Again,

![Figure 4. Complex viscosities at 10 rad/s of the biocrude produced from 300 °C HTL: (a) sludge-involved runs–cyclohexane extraction, (b*) manure- and sludge-involved runs–acetone extraction, (c) manure-involved runs–cyclohexane. (*) Manure-only biocrude at 25 °C was not measurable, so it was portrayed as the maximum value on the chart.](image)

![Table 2. Yield, Heating Value, and FTIR Area Peaks of the Sludge/LP 300 °C Cyclohexane Extracted Triplicate Runs](table)

| biocrude yield (%) | HHV (MJ/kg) | FTIR (%) |
|--------------------|-------------|----------|
|                    | 2920 | 2850 | 1700 | 1515 | 1455 | 1375 | 740 |
| run 1              | 8.2  | 41.7 | 1.60 | 3.22 | 2.19 | 1.00 | 3.18 | 2.26 | 1.82 |
| run 2              | 8.5  | 39.6 | 2.78 | 3.64 | 2.50 | 1.46 | 3.57 | 2.81 | 2.10 |
| run 3              | 6.3  | 38.9 | 2.52 | 3.53 | 2.44 | 1.46 | 3.45 | 2.74 | 2.04 |
| average            | 7.7  | 40.1 | 2.30 | 3.47 | 2.37 | 1.31 | 3.40 | 2.60 | 1.99 |
| SD                 | 1.2  | 1.2  | 0.62 | 0.22 | 0.16 | 0.27 | 0.27 | 0.20 | 0.30 |
| CV                 | 15.6%| 3.6% | 27.0%| 6.34%| 6.75%| 20.6%| 5.9% | 11.5%| 7.5% |
this effect may be due to a greater molecular weight distribution from the varied substances. The heterogeneous nature of these biocrudes likely caused the differences seen between samples. As biodiesel is expected to have a viscosity of 0.0017–0.0053 Pa·s, obviously these biocrudes will require further upgrading. Even so, using mixtures for HTL may be an important first step to reducing the extent of upgrading required to produce a low enough viscosity.

2.4. Experimental Reproducibility. Because of the long duration of the HTL experiments, all 30 runs were performed once. However, because of the quantitative nature of the data presented, insights into deviation and variance are important. Thus, an individual run, sludge/LP run at 300 °C extracted with cyclohexane, was performed in triplicate to examine reproducibility and deviation. Mass and energy yields for each trial are presented in Table 2 and averaged 7.7 ± 1.2% and 40.1 ± 1.2 MJ kg⁻¹, respectively. For chemical characteristics, FTIR plots of each sample produced are presented in Figure S4 and the peak areas of pertinent bands from those plots are presented in Table 2. The FTIR plots were not only shown to have additional interactions with LP on the biocrudes, but this commonality in the peak areas of pertinent bands from those plots are presented in Table 2. The FTIR plots were not only shown to share common peaks for each trial but also share similar peak intensities. The same aliphatic groups, aromatic bonds, and carboxyl groups were found in each plot. This commonality in peak consistency was further presented by quantifying peak areas, which had low standard deviations. Physical property consistency is shown by density in Figure 3, which averaged 972.4 ± 16.5 kg m⁻³. Overall, intrinsic physical and chemical properties were found to be consistent for the runs. The nonhomogeneity of waste feedstocks can result in the variable extraction yield. Because of the phase separation of cyclohexane and the process liquid, mass transfer consistency should be considered, which can be done with additional solvent usage and better mixing/stirring mechanisms.

3. CONCLUSIONS
Physical and chemical characteristics of biocrudes produced by the HTL of mixed feedstocks were compared to biocrudes produced by single-feedstock HTL. Specifically, when using mixed feedstocks, HTL of dairy manure and sewage sludge was shown to have additional interactions with LP on the biocrudes produced. This was shown by biocrude yields reaching as high as 30% for both acetone and cyclohexane extraction on a basis of LP. In terms of yield and HC extraction, cyclohexane is more effective for sludge/LP biocrude extraction. Carbon and oxygen content reached values greater than 75% and less than 5%, respectively, for cyclohexane-extracted sludge/LP. Carbon content reached values higher than 80% and oxygen content reached values lower than 5%, resulting in HHVs greater than 40 MJ kg⁻¹. For all the biocrudes, viscosity was reduced considerably for the mixtures, compared to biocrudes from a single biomass. For sludge-involved feedstocks treated at 300 °C, cyclohexane-extracted biocrudes had densities of less than 1000 kg m⁻³, whereas acetone-extracted biocrudes had densities greater than 1000 kg m⁻³ because of the fact that cyclohexane extracted lighter molecular weight compounds while acetone extracted heavier phenolic substances. More HCs were detected for the sludge/LP biocrude than manure/LP biocrude for both solvents.

4. MATERIALS AND METHOD

4.1. Feedstocks. Three different biomass samples were used in this study. The first was milled LP, acquired from Alabama. The second biomass used was digested sewage sludge, obtained from Truckee Meadows Water Reclamation Facility (Reno, NV). Lastly, cow manure was obtained from University of Nevada Reno’s Agricultural Experimental Station (Reno, NV) and used. Untreated feedstock characterization can be found in Table 3.

4.2. HTL. HTL was performed in a 1900 mL Parr benchtop reactor—model 4520 (Moline, IL). The temperature of the reactor was controlled using a model 4848 Parr proportional-integral-derivative controller, and the reactor pressure was not controlled but was monitored. Five different groups of experiments were each run at three different temperatures of 250, 275, and 300 °C. The first three groups of experiments consisted of base cases for the individual biomass (LP, manure, and sludge); for each run, 68 g of dried biomass sample was used with an additional 440 g of deionized water. The last two groups of experiments were blends of LP with manure or sludge (50:50 mass basis); for each run, 68 g of each dried sample was used with an additional 440 g of deionized water. Once the desired reactor temperature was reached, it was held for 30 min, followed by reactor cooling. After reactor cooling, the gases produced were vent-out through the gas valves. The heating time and cooling time was approximately 30 and 20 min, respectively. Depending on which solvent was used, the contents were filtered as described below; the solid was dried and stored. This procedure was followed for two different solvent extractions, so there was a total of 30 runs, 15 for each solvent.

4.3. Solvent Extraction. Each set of experiments were performed twice: one set using acetone as the solvent for biocrude extraction and the other using cyclohexane, to evaluate extracted biocrude with respect to the choice of solvent.

4.3.1. Cyclohexane Extraction. For all the cyclohexane experiments, the contents of the reactor were mixed with 300 mL of high-performance liquid chromatography (HPLC) grade cyclohexane (Macron Fine Chemicals) for 45 min. The solid was then separated from the liquid using a vacuum flask with a size one Whatman filter paper, and the liquid (cyclohexane–biocrude and water mixture) was transferred to a separatory funnel and held for 30 min to allow for phase separation between the cyclohexane–biocrude and the water phase. The separated cyclohexane–biocrude nonpolar phase was then placed in a BUCHI RotoVap (model R-205) to distill cyclohexane at 65 °C. The recovered biocrude was transferred to a 20 mL glass vial with a screw cap, weighed, and stored in a cool desiccator until further analysis.

| sample  | moisture content (wt %) | C (wt %) | H (wt %) | O (wt %) | N (wt %) | hemicellulose | cellulose | lignin | aqueous solubles | ash (wt %) |
|---------|-------------------------|---------|---------|---------|---------|-------------|----------|-------|----------------|-----------|
| LP      | 3.6                     | 49.5 ± 1.0 | 5.9 ± 0.1 | 41.2 ± 1.2 | 0.1 ± 0.0 | 11.9         | 54       | 25    | 8.7            | 0.4       |
| manure  | 84                      | 44.8 ± 0.1 | 5.2 ± 0.3 | 34.4 ± 0.9 | 9.4 ± 1.0 | 12.8         | 22.2     | 2.3   | 47             | 15.7      |
| sludge  | 86                      | 36.0 ± 3.0 | 5.8 ± 0.4 | 29.6 ± 3.0 | 3.7 ± 2.1 |             |          |       |                |           |

Table 3. Characterization of Untreated Feedstocks
4.3.2. Acetone Extraction. After HTL reaction, the solid products were separated from the liquid products in a vacuum flask using a size 1 Whatman filter. The biocrude was then extracted from the solid by mixing the solid with 300 mL of HPLC grade acetone (Macron Fine Chemicals) for 45 min. Then, the solid and acetone slurry was transferred to a vacuum flask to separate the liquid (acetone and acetone-extracted biocrude) from the solid. Acetone was separated from the acetone—biocrude mixture with a BüCHI RotoVap at 60 °C. The recovered biocrude was transferred to a 20 mL glass vial with a screw cap, weighed, and stored in a desiccator until further analysis.

4.4. Analytical Methods. Biocrudes produced by the HTL of manure/LP mixture and the HTL of sludge/LP mixture were physically and chemically characterized to evaluate the effects of treating the mixed feedstocks.

4.4.1. Chemical Characterization. The biocrudes were characterized by an Agilent 6890 series GC–MS equipped with an Agilent DB-5-MS column (30 m × 0.25 mm i.d., 0.25 μm film thickness) and an Agilent 5973 mass spectrum detector. Samples for GC analysis were prepared by dissolving 10–50 mg of sample in a 1.5 mL GC vial filled with 10% acetone in n-hexane solution. Further details of the GC–MS method are provided elsewhere.44 A Nicolet 6700 FTIR-ATR with a SmartiTR diamond ATR (Thermo Scientific, Waltham, MA USA) was also used for spectral analysis to examine the chemical bonds in the biocrude. Finally, elemental analysis was performed to determine the carbon, hydrogen, nitrogen, and oxygen compositions of the biocrude by using a Euro EA3000 CHNS-O analyzer (Eurovector). The latter two characterizations are similar to the methods used in previous literature.35 Fiber analysis was performed for untreated lignocellulosic biomass and was performed using a method previously used in the literature.39

4.4.2. HHV. The HHV of the biocrude samples produced were measured in a Parr 1241 adiabatic oxygen bomb calorimeter (Moline, IL) connected to a resistance temperature detector temperature-recording probe following the ASTM D4809 method. All HHVs were reported on a dry, ash-free basis.

4.4.3. Density Measurement. Densities of five biocrude samples were measured in a 2 mL Corning PYREX borosilicate glass Gay-Lussac specific gravity vial, also known as a pycnometer. The entire vial was filled with the sample and then capped with a capillary infused glass cork. Any sample overflowing from the capillary was wiped off. Because of the highly viscous nature of the biocrude samples, the vial was first filled with the sample and then placed in an oven (at 45 °C) for 5 min to allow the sample to settle in the bottom of the vial. Once the warm biocrude settled, the vial would be taken out of the oven and cooled to room temperature. Additional sample would be added, and the warming process would be repeated until the vial and capillary were completely filled.

4.4.4. Viscosity Measurement. Viscosity of biocrude samples was measured using a rotational/shear AR 1500ex rheometer (TA Instruments) using a cone and plate configuration. The rheometer was equipped with a Peltier plate for heating and a TC-202 water bath for cooling. Viscoelastic properties were studied at 25 and 50 °C in a range of 0.1–10 rad/s. Two measurements were taken for each sample at each temperature.

4.5. Experimental Reproducibility. A reproducibility study used by Theegala et al. was similarly conducted for the data in the present study; sludge/LP at 300 °C extracted with cyclohexane was performed in triplicate to examine reproducibility of certain properties of the biocrude production.24 This specific run was chosen as it was one of the biocrudes produced from mixed feedstocks and also provided enough sample (due to its higher yield) for various analytical testing and characterizations. HHV, FTIR, and density were measured and compared for each repeated run and were performed using the same methods mentioned above.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomea.8b00045.

GC–MS, GC–MS list of identified compounds in HTL reactions, FTIR, FTIR of HTL runs, and FTIR of triplicate run (PDF)

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Notes

The authors declare no competing financial interest.

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