

# **Impact of Storage and Blending of Algae and Forest Product Residue on Fuel Blendstock Production**

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## **Abstract**

Seasonal impacts on the production of algae biomass require blending with other feedstocks such as wood to maintain consistent annual conversion capacity. Idaho National Laboratory (INL) has developed a long-term storage strategy for algae biomass using ensiling, or anaerobic wet storage, that was tested for blends of algae and wood to stabilize the feedstock supply for processing to fuels. Additionally, blending biomass (algae and wood) leverages existing biomass storage approaches commonly used by the feed and forage industry. Earlier research also has demonstrated positive results that indicate ensiling is more effective and economical in normalizing biomass feedstock supply prior to conversions such as HTL (hydrothermal liquefaction) than preserving biomass by drying.

By assessing impacts beginning with upstream logistic operations and proceeding through each conversion step, this work focuses on conversion of ensiled and blended biomass to fungible liquid transportation fuel blendstocks. This is accomplished by conversion of the blended biomass (62% *Chlorella* sp. blended with 38% loblolly pine forest product residues [FPR]) to bio-crude through HTL and subsequent upgrading through HT (hydrotreating) with a commercial refinery catalyst analogous to a refinery process to produce hydrocarbon fuel. Results indicate that carbon retention and quality are preserved in both the bio-crude and upgraded fuel from the ensiled blend, indicating the potential of this approach for managing seasonal variations in algae biomass productivity.

## **1. Introduction**

Renewable feedstocks face supply and logistic hurdles that must be overcome if their use is to achieve market penetration. Currently, government tax credits must be provided to enable successful entry. Energy crops and crop residues are seasonally available and require preservation

to be available year-round for bioenergy production. Such challenges lead to introduce significant uncertainties that affect the final conversion cost; these uncertainties need to be addressed to achieve market viability [1, 2]. However, despite the logistical and supply challenges presented by adopting renewable feedstocks, some refineries have decided to retrofit their equipment so renewable feedstocks can be used and have shifted to feedstocks that are reliable and regionally available (e.g., fat, oils, and grease) [3]. In addition to being cost competitive, this approach provides an immediate return in the form of incentives and credits as it enables refineries to achieve significant greenhouse gas reductions planned by 2024 by transitioning away from the use of fossil fuels. The oil industry exemplifies this approach in their shift to focus on renewables to lower their carbon footprint tenfold by 2030 [4]. The financial and environmental benefits accrued by adopting renewable feedstocks are incentives for developing unconventional feedstocks such as HTL (Hydrothermal liquefaction) biocrude oils as a possible source of reliable and cost-effective feedstock for refineries.

However, to be competitive from both an economically viable and environmentally sustainable perspective, any refinery, especially biorefineries, must balance the often-competing factors of feedstock cost, quality, and availability. Maintaining consistent feedstock supply is paramount to enabling these refineries to operate at their design capacities. Multiple approaches have been suggested to achieve this goal, including blending feedstocks to meet quality specifications, seasonal campaigns based on crop availability and time of harvest, and long-term storage to manage seasonal variations [2, 5-10]. Understanding how different conversion approaches will respond to these feedstock supply chain challenges can reveal strategies that help define the likely conversion choice suitable for a range of feedstocks.

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## 1.1 Rationale for algae and forest residue

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Two feedstocks that have been investigated thoroughly for conversion through HTL are microalgae and woody biomass. Microalgae feedstock is promising for HTL conversion because of its high-lipid content so C16–C18 fatty acids can be converted into drop-in fuels for diesel and jet fuel. Under HT conditions, fatty acids undergo complex hydrogenation steps to remove oxygen heteroatoms and transform them to pure alkanes, and because of its boiling point, they concentrate in the diesel fuel blendstock. To further understand the potential of microalgae feedstock, an estimated 78 million tons of microalgae grown in saline water could be available annually by 2030 according to the *2016 Billion Ton Report* [1]. In contrast, 113 million tons of forest residues and thinnings currently are available annually for bioenergy conversion with similar tonnages likely available in 2040 [1]. Conversion systems that are flexible with regard to feedstock will be important to accommodate supplies that vary seasonally and annually for near-, mid-, and long-term use strategies. Additionally, understanding seasonal availability of feedstock resources, such as woody or algae biomass, will inform feedstock logistics supply operations and associated conversion strategies.

Algae biomass cultivation productivity is based on geographical location with solar irradiance having the largest impact on productivity levels [11], with temperature, humidity, and other environmental factors playing important but lesser roles in productivity. Winter productivity levels can be three to five times less than summer productivity, requiring a biorefinery to use either long-term storage to maintain consistent feed rate of a single feedstock type or alternative feedstocks during low biomass productivity months [12]. In the United States, southern states most likely will experience a significant increase in algae cultivation as the industry develops. The high moisture

content of microalgae aligns it well with moisture-tolerant thermochemical processing options such as HTL [13].

Woody biomass is abundant in the southeastern United States, and it generally contains a high lignin content that is often ideal for thermochemical conversion approaches. Whitewood is used in the pulp and paper industry and accordingly demands a higher feedstock price compared to its forest residue component. Despite its cost advantage, FPRs fail to meet the quality requirements that are used for the pulp and paper industry. Therefore, FPRs, which generally are taken from the tops of trees and consist of needles, small branches and twigs, and bark, are available for a lower cost than their whitewood counterpart. Each of these anatomical fractions has a unique chemical property based on their physiological function, but in general, FPRs are characterized by higher levels of inorganics because they are actively growing tissues. For example, Yoshida et al. [14] showed how inorganics, such as calcium, magnesium, potassium, and phosphate are elevated in actively growing tissues such as cambium tissue and bark. These inorganics can deleteriously affect conversion processes that require catalysts, such as catalytic fast pyrolysis. A thorough review of these impacts has been documented by Li et al [15]. HTL is more tolerant to these ash species because it does not require a catalyst and has shown that calcium and potassium in bark can positively impact biocrude yield [16]. Therefore, forest residue is a feedstock type that is well suited for HTL.

### *1.2 Rationale for blending and ensiling*

Blending biomass has multiple benefits for a biorefinery including increasing feedstock flexibility, reducing transportation draw radius, and managing feedstock variability. Blending also can be used to meet critical material and quality specifications for the conversion process. For example, algae biomass has a high nitrogen content, and nitrogen reduces the quality of the oil

produced [17]. Blending algae with a low nitrogen resource, such as an agricultural or forest residue, is an option for managing nitrogen content in bio-oil. Blending algae into a feedstock also positively influences the buffering required in HTL, as lignocellulosic biomass contains acetyl groups in hemicellulose that result in the lowering the pH when they are hydrolyzed during conversion. Using a blend of algae and woody biomass in HTL has been demonstrated to result in reaction products that were not formed when the two feedstocks were converted separately [18]. Furthermore, from an economic feasibility standpoint, a recent techno-economic analysis at Pacific Northwest National Laboratory (PNNL) also demonstrated that blending algae and woody biomass together can yield a cost-competitive feedstock in the HTL and HT pathway to produce fuel blendstock, resulting in a decrease of the minimum fuel selling price to produce naphtha and diesel blendstock by 21%. The conversion-only cost (excluding cost of the feedstock) was reduced by 13% compared to the algae-only case [2].

Blending has been demonstrated as an approach for changing the feeding and handling attributes of algae as well as encouraging conditions for long-term stability in anaerobic storage[5, 9]. Long-term wet storage, commonly referred to as ensiling, of microalgae has been demonstrated to preserve algae biomass under high-moisture, anaerobic conditions when blended with corn stover [5] and the yard waste fraction of municipal solid waste [9]. These blends consisted of up to 40 wt% microalgae and recently have been reported to contain 100% microalgae [8], and stability has been demonstrated over a 6-month period. The principles of ensiling are the foundation of this approach, where oxygen exclusion followed by fermentation of soluble sugars by lactic acid bacteria results in a low-pH environment that is protected from further degradation as long as anaerobic conditions are maintained. Ensiling has been extensively reviewed elsewhere for its use in the forage industry and in bioenergy feedstock logistics systems [7]. Moreover,

ensiling microalgae is compatible with the HTL pathway since the need for drying to maintain stability is eliminated. Blending microalgae (typically harvested at 80% moisture (wet basis) with lignocellulosic biomass has the added benefit of meeting the desired ensiling moisture content range of 40-70% moisture (wet basis), which allows this pathway to utilize the existing infrastructure and storage approaches of the forage industry, such as drive over piles or silage tubes. Techno-economic analysis based on compositional changes observed in storage has shown that this approach can be a cost-effective means for managing the seasonal variation of algae biomass for thermochemical conversion using HTL [5] and for biochemical conversion based on fermentation [8]. Recent biochemical conversion studies have shown no observable difference in conversion of stored vs. unstored algae biomass [7].

However, no studies have been reported that examine the impact of storage on HTL/HT conversion by evaluating the result of direct conversion of ensiled microalgae blends through the entire conversion process. Thus, the goal of this work is to assess the feasibility of ensiling microalgae with low-cost forest residues and assessing the conversion potential in HTL and subsequent HT upgrading to fuels. A blend of algae and wood in this study was to reflect the optimal composition that will be used throughout the year in an HTL biorefinery based on the availability of algae and wood. The primary objective is to report on the storage stability of the microalgae and forest residue blend over a 3-month period to understand long-term preservation and any compositional changes that may occur. HTL performance was assessed including analysis of gaseous, aqueous, and bio-crude phases. Finally, the quality of resulting fuel was assessed after HT.

### 1.3 *Hydrothermal liquefaction and hydrotreating pathways*

HTL is a promising conversion technology that can accept biomass feedstocks that possess a wide range of chemical and physical quality attributes. Most importantly, HTL technology can accept wet biomass or feedstock with high moisture content—typically above 20%—where other technologies require drying processes to reduce moisture content to acceptable levels. For instance, pyrolysis requires low-moisture biomass—typically below 10 wt%—to enable rapid heating rates to high temperatures (500°C) to decompose biomass to pyrolysis liquids [19]. These processing conditions limit pyrolysis to conversion of feedstocks that are either dry initially or that can be dried economically. HTL has the advantage of accepting lower value, under-utilized carbon from wet waste and forest residues such as the ones used in this study. HTL treatment can concentrate these wastes through conversion to a transportable, energy-dense liquid called biocrude.

However, the current state-of-art HTL process produces bio-crude with high amounts of heteroatoms (i.e., oxygen, nitrogen, and sulfur) and inorganic elements, thus limiting its use for fuel applications. Catalytic HT is an effective and proven way to upgrade low-quality liquid biocrude by transforming it to a higher-value hydrocarbon stream compatible with the current fuel infrastructure and is widely practiced in petroleum refineries [20] [21] [22]. Catalytic HT of biocrude can help introduce market-ready hydrocarbons by converting biocrude heteroatoms (oxygen, nitrogen, and sulfur) and removing them from the desired liquid fuel products, such as diesel and jet fuels.

Hydrotreating technology consists of complex parallel reactions that use high-pressure hydrogen and moderate temperature with an active metal catalyst such as cobalt or nickel. The catalyst enables effective hydrogenation that is selective to heteroatoms present in biocrude and eliminate and separate them to low levels comparable to those fuels blendstock produced from

fossil sources by refineries. In addition, they minimize deposition of carbonaceous deposits [23, 24], thereby enabling increased catalyst lifetime. HT is a proven technology that has been applied to refinery feedstocks to produce high-quality fuels such as ultra-low sulfur diesel from light gas oils and other many applications to produce fuels and chemicals for use in various industry processes.[25]

## 2. Methods and Materials

### 2.1 Biomass sources

*Chlorella* sp. biomass was provided by Global Algae Innovations (<http://www.globalgae.com>). Biomass for the storage experiment was sourced from Halifax County, Virginia, from a Loblolly Pine plantation with a minor component of Virginia Pine and consisted primarily of tops and branches. Southern Loblolly Pine FPR was obtained from Iowa State University for use in the non-stored HTL tests. Initial size reduction of the FPR biomass was performed in INL's Biomass Feedstock National User Facility with a hammermill (Schutte-Buffalo, Buffalo, NY) equipped with a 2-mm screen. Subsequent size reduction was performed using two passes through a knife mill (Wiley-Thomas 4, Thomas Scientific, Swedesboro, NJ) with a 1-mm screen followed by a 0.5-mm screen. Blends of dried *Chlorella* sp. and FPR biomass were formulated to replicate blends that had been previously tested for HTL conversion by PNNL (38.2% *Chlorella* sp. and 61.8% FPR, ash-free dry weight basis) and were rehydrated to 69% moisture (wet basis).

## 2.2 Long-term storage

*Lactobacillus plantarum* was added to the biomass at a rate of  $3.5 \times 10^5$  cfu g<sup>-1</sup> of blend (wet basis) to promote lactic acid fermentation. The blends were stored anaerobically at two different scales to enable stability characterization at bench scale (100 mL in triplicate) without disturbing the larger samples (20 L in triplicate, 200 times bench-scale) intended for conversion studies at PNNL. The 100-mL reactors consisted of glass jars (Ball, Broomfield, CO) with airtight lids fitted with a through-lid bulkhead tube adapter (P/N SS-400-R1-4, Swagelok, Solon, OH) and a ball valve (P/N B-43S4, Swagelok, Solon, OH) with an aluminized gas collection bag (SKC, Eighty Four, PA) attached with a short (1 inch) length of silicone peristaltic pump tubing (Cole Parmer, Vernon Hills, IL). The 20-L reactors consisted of plastic buckets fitted with a screw-top lid (M & M Industries, Chattanooga, TN) and a through-lid bulkhead fitting and valve as described for the bench-scale reactors. Bench-scale reactors were sampled after 103 days in storage, and biomass was provided to PNNL for preliminary material characterization. The larger reactors were sampled after 123 days, homogenized into one composite sample, and shipped to PNNL frozen. Drying and freezing of the biomass was performed to facilitate experimentation at two different locations, and this approach is not anticipated to positively or negatively influence the HTL results.

Moisture content and dry matter loss were determined as described previously [6]. The composition of produced gases, specifically oxygen, carbon dioxide, carbon monoxide, methane, and hydrogen, was determined using gas chromatography as described previously [6]. Assessment for nitrous gases was performed using Nitrous Gases 100/c and Nitrogen Dioxide 0.5/c Draeger tubes (Draeger Safety Inc., Pittsburgh, PA). Organic acids were extracted from samples using a

1:10 ratio of wet biomass to 18 M $\Omega$  nano-pure water and analyzed via high-performance liquid chromatography according to a method described previously [6].

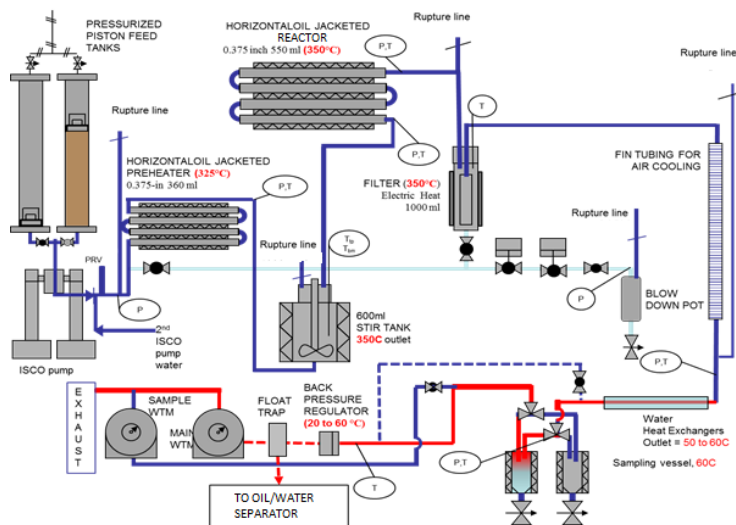
### 2.3 Hydrothermal liquefaction

Blends of dried *Chlorella* sp. and FPR biomass were formulated to create pumpable slurries (typically 10–20% solids) with a volume mean particle size of 20–100  $\mu\text{m}$  using Hockmeyer Model HCPS-2.5 Counter Peg Immersion. The reduction was achieved in a rotating basket containing 3-mm diameter spherical grinding media. The maximum rotation of the pegs in the basket was 1800 rpm. There also was a sweep blade powered by a 1.5 horsepower electric motor used to continually move slurry to ensure consistency. The basket was raised from and lowered into the slurry through a 36 inch rise hydraulic lift. To dissipate heat, cooling water from a dedicated chiller was recirculated through the jacketed processing vessel.

HTL tests were performed in a bench-scale continuous process unit described previously [22]. Conditions for the HTL process are presented in Table 1, and a flow diagram of the process used to convert the slurry biomass to biocrude is shown in Figure 1.

**Table 1. Condition of HTL process for conversion to biocrude**

| Parameter                           | Units              | Non-Ensilid | Ensilid |
|-------------------------------------|--------------------|-------------|---------|
| Temperature                         | $^{\circ}\text{C}$ | 340         | 348     |
| Pressure                            | psig               | 2900        | 2900    |
| Reactor volume                      | L                  | 0.50        | 1.15    |
| Feed rate                           | L/h                | 3.95        | 3.98    |
| Liquid hourly space velocity (LHSV) | L/L/h              | 7.9         | 3.5     |

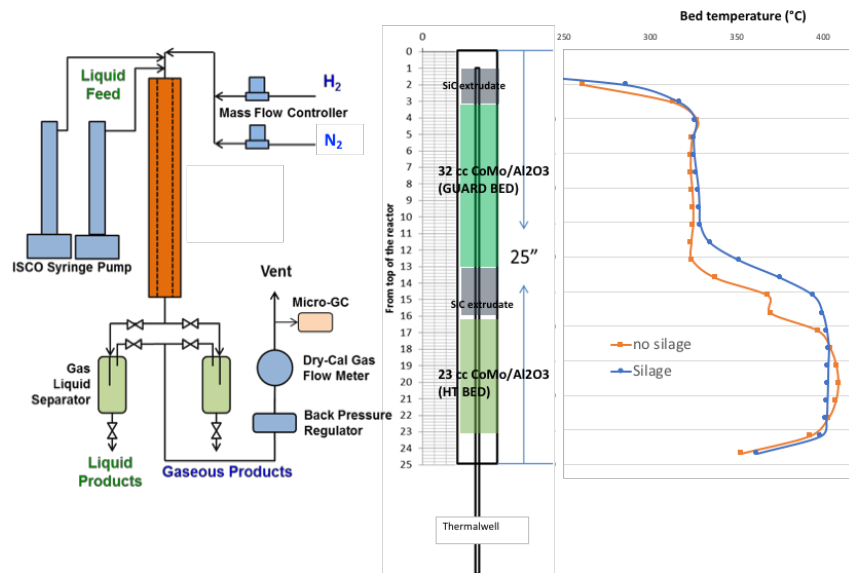


**Figure 1. Process flow diagram for HTL process of slurry biomass to biocrude.**

Data reported reflects sample of a continuous process, and representative sample ( $n = 1$ ). Mass and carbon balances were calculated to determine yields in the biocrude, aqueous, solid, and gas phases. Carbon, hydrogen, nitrogen, oxygen, sulfur, higher heating value (HHV), total acid number (TAN), density, and viscosity measurements were performed, as described previously by work of Elliott et al [22].

#### 2.4 Hydrotreating of the Biocrude

To improve the quality of the biocrude, a 60-cc fixed bed hydrotreater system was used to study removal of heteroatoms such as oxygen, nitrogen, and sulfur from the biocrude. Two identical reactor systems were used to study biocrudes derived from ensiled and non-ensiled biomass. Each system is equipped with a total of 55-cc catalyst volume and dual-heating zones to allow testing at two different temperatures. The hydrotreater configuration is shown in Figure 2.



**Figure 2. Hydrotreater configuration and temperature profile of the reactor**

The tests, equipment configuration, and product analysis are similar to those used in earlier work that use HTL biocrude as a feedstock [18, 26]. The approach also has been used for upgrading fast pyrolysis and catalytic fast pyrolysis oils by PNNL [27, 28]. The catalyst tested was a commercially available HT catalyst sold as CoMo/Al<sub>2</sub>O<sub>3</sub> (Alfa Aesar Co). It contains cobalt oxide (3.4–4.5 wt%) and molybdenum oxide (11.5–14.5%) on an aluminum oxide support. This catalyst is available commercially [29]. For use in this study, this catalyst was size reduced to a size between -20 and +40 mesh to help improve catalyst wetting in the reactor (i.e., by maximizing the ratio between reactor to catalyst particle diameter). Once loaded, the catalyst was then sulfided in situ to form the activated CoMoS that targets heteroatom removal and hydrogenates aromatics and heteroatoms (i.e., nitrogen, oxygen, etc.). The in situ sulfiding procedure is described here. Reactor pressure was set at 1500 psig and hydrogen was set to flow at a ratio of 2000 L-hydrogen/L-sulfiding solution. For the sulfiding solution, 35 wt% di-tert-

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butyldisulfide (DTBDS)/decane was used and pumped into the reactor as the temperature reached 150°C. At a sulfiding temperature of 400°C, the DTBDS thermally decomposed to H<sub>2</sub>S and bound with the catalyst surface to form the active sulfide form. The sulfiding temperature profile consisted of increasing the temperature to 150°C in 1 h (a rate of 2.1°C/h), followed by ramping to 400°C in 3 h and soaking at that temperature for another 4 h. Once the catalyst was activated in the sulfide MoS form, evidenced by H<sub>2</sub>S breakthrough at the reactor effluent, the rest of the sulfiding solution was removed from the bed, and the reaction then was continued by introducing filtered biocrude-oil (using a 1 µm screen), which was injected through the top of the reactor towards a continuous, down-flow packed bed reactor loaded with a commercial Co-Mo sulfide-based HT catalyst. The hydrotreater operating parameters are listed in Table 2.

**Table 2. Hydrotreater operating parameters**

| HT Parameter                                     | Blend Non-Ensiled | Blend-Ensiled |
|--|-------------------|---------------|
| Top guard bed temperature (°C) – (3–13 in.)      | 325               | 325           |
| Polishing bed temperature (°C) – (16–23 in.)     | 409               | 402           |
| Pressure (psig)                                  | 1551              | 1595          |
| Guard bed reactor volume at temperature (mL)     | 32                | 32            |
| Polishing bed reactor volume at temperature (mL) | 22.5              | 22.5          |
| Feed Rate (mL/h)                                 | 8                 | 8             |
| Guard bed LHSV (L/L/h)                           | 0.25              | 0.25          |
| Polishing bed LHSV (L/L/h)                       | 0.36              | 0.36          |
| Hydrogen/feed ratio (L/L/h)                      | 1256              | 1245          |

For this specific test, a bio-oil LHSV 0.25 L/L/h was chosen for the guard bed, and 0.36 L/L/h was chosen for the subsequent HT of HTL biocrude as it performed with consistent HDO performance across different feedstocks in the past.

### 2.5 Bio-crude and fuel blendstock characterization

The filtered bio-crude was then characterized for elemental composition including carbon, hydrogen, nitrogen (ASTM D5291/D5373), oxygen (ASTM D5373mod), sulfur (ASTM D1552/D4239) and water content (Karl Fischer titration, ASTM D6869). Elemental composition

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(carbon, hydrogen, oxygen, nitrogen, and sulfur) was reported on a dry basis and normalized to 100 wt%. Viscosity and density measurements were conducted on a Stabinger® viscometer (Anton Paar SVM 3000) at 20°C. The carbonyl contents of the bio-oil samples were determined using a modified titration method (i.e., the modified Faix method). A modified ASTM Standard Method D664 for determining the acid content of petroleum products was used to determine both carboxylic acid numbers and TANs of bio-oils. The TAN includes carboxylic acids as well as weaker acidic compounds such as phenolics. Therefore, the phenolic number (PhAN) was calculated by the difference between the TAN and the carboxylic acid number. ASTM Standard Method D2887 (Simulated Distillation Method) also was used to analyze the hydrocarbon blend. The produced aqueous products also were analyzed. EPA Method 9060A was used to measure the total organic carbon.

### 3. Result and Discussion

#### 3.1 Storage performance

A *Chlorella* sp./FPR blend (38/62) with 68.7% moisture content was inoculated with *Lactobacillus plantarum*  $3.5 \times 10^5$  cfu g<sup>-1</sup> of blend (wet basis) and stored for 103 days (100 mL) or 123 days (20 L) in anaerobic conditions. The bench-scale and larger reactors performed similarly during the storage period. Dry matter losses were low at 3.8% and 2.6% for 100 mL and 20 L reactors, respectively Table 3

**Table 3. Storage stability of a blend of *Chlorella* sp. lgaе biomass and FPR at bench scale and 200 times bench scale after 103 and 123 days of anaerobic storage**

| Treatment       | Dry Matter Loss<br>(%, dry basis) | pH         | Organic acid<br>(%, dry basis) | CO <sub>2</sub><br>(g/kg, dry basis) | Hydrogen<br>(mg/kg, dry basis) |
|-----------------|-----------------------------------|------------|--------------------------------|--------------------------------------|--------------------------------|
| 100 mL reactors | 3.8 ±0.6                          | 5.81 ±0.12 | 4.8 ± 0.1                      | 0.00 ±0.00                           | 21.29 ±36.87                   |
| 20 L reactors   | 2.6 ±1.3                          | 5.56 ±0.02 | 5.4 ± 0.1                      | 4.79 ±2.14                           | 0.11 ±0.04                     |

Previous storage experiments of algae/herbaceous biomass blends experienced losses that typically ranged from 5–10% (results from unpublished work). The organic acid composition did not vary substantially from one experimental scale to another. Acetic acid was the most prominent organic acid at either scale with  $2.7 \pm 0.1\%$  at 100 mL scale and  $3.1 \pm 0.1\%$  at 20 L scale. Butyric acid was next most abundant with 1.3% in 100 mL storage reactors and 1.5% at the larger scale. Lactic acid, which is typically present in well-preserved algae blends, was not detected in the stored biomass at either scale. Instead, there was a significant amount of acetate, which also is an effective preservative for ensiled biomass. Butyric acid was observed in quantities greater than 1%. Butyric acid is usually absent in well-ensiled biomass and its presence (pKa 4.82) and the lack of lactic acid (pKa 3.86) is likely responsible for the higher than usual pH observed for ensiled material (5.5 and 5.8 compared to typical levels ranging from 3.8–4.2).

Gas production was observed over the storage duration with most of the gas produced during the first week of storage. Carbon dioxide was the primary gas constituent and averaged 4.79 g CO<sub>2</sub>/kg biomass (0.11 moles CO<sub>2</sub>/kg biomass) in the 20-L reactors. Carbon dioxide production is consistent with the degradation of carbohydrates as described previously [30, 31]. Hydrogen was also present in the 20-L reactors at 0.11 g hydrogen/kg biomass (0.05 moles hydrogen/kg biomass). Gas production observed in the 100-mL reactors was much more variable with some reactors having significant amount of gas collected and others much less. A good example of this variation is one of the three 100-mL reactors produced significant levels of hydrogen while no hydrogen was observed in either of the other two replicate reactors. No other greenhouse gases were detected over the storage duration including carbon monoxide, methane, and nitrogen containing gases (e.g., nitrogen dioxide, nitric oxide, etc.). These results are promising from a life cycle assessment perspective. As described in Wendt et al. [5], the wet storage approach for algal biomass

stabilization significantly reduces greenhouse gas releases compared to an approach that uses natural-gas based drying for biomass stabilization. In those scenarios, approximately 40 kg CO<sub>2</sub> equivalent/metric tonnes of biomass for wet storage were released compared to 993 kg CO<sub>2</sub> equivalent/metric tonnes for drying algal biomass. The biologically produced gases in this study would add an additional 4.79 kg CO<sub>2</sub> equivalent/metric tonne biomass, which is much lower than release of carbon dioxide associated with natural gas fed dryers.

### 3.2 HTL performance

HTL was performed at PNNL on the ensiled loblolly pine FPR/*Chlorella* sp. blend, and results were compared to a non-stored blend of similar blend ratio and composition. Overall biocrude yields from HTL are shown in Table 4, which describes the mass and carbon balance in the biocrude, aqueous, solid, and gas phases. While there are small differences in product distribution, the overall HTL system performance and biocrude yields were the same within the limitations of the experiment.

**Table 4. Normalized HTL yields for the FPR/*Chlorella* sp. blends**

|                            | Unit  | Non-ensiled | Ensiled |
|----------------------------|---|-------------|---------|
| Mass Balance               | %   | 99.3        | 100     |
| Biocrude Yield, Mass (N)   | $\text{g}_{\text{oil}}/\text{g}_{\text{fd}}$ (g feed) | 0.411       | 0.394   |
| Solid Yield, Mass (N)      | $\text{g}_{\text{solid}}/\text{g}_{\text{fd}}$        | 0.020       | 0.036   |
| Gas Yield, Mass (N)        | $\text{g}_{\text{gas}}/\text{g}_{\text{fd}}$          | 0.208       | 0.164   |
| Aqueous Yield, Mass (N)    | $\text{g}_{\text{aq}}/\text{g}_{\text{fd}}$           | 0.361       | 0.406   |
| Biocrude Yield, Carbon (N) | $\text{g}_{\text{oil}}/\text{g}_{\text{fd}}$          | 0.608       | 0.617   |
| Solid Yield, Carbon(N)     | $\text{g}_{\text{solid}}/\text{g}_{\text{fd}}$        | 0.0367      | 0.057   |
| Gas Yield, Carbon (N)      | $\text{g}_{\text{gas}}/\text{g}_{\text{fd}}$          | 0.116       | 0.096   |
| Aqueous Yield, Carbon (N)  | $\text{g}_{\text{aq}}/\text{g}_{\text{fd}}$           | 0.239       | 0.23    |

Biocrude qualities for the two conditions were equivalent for the two feedstocks in terms of heating value, nitrogen, sulfur, moisture, TAN, density, and viscosity. Minor compositional

changes in carbon, hydrogen, and oxygen content were observed in the biocrude, resulting in slightly lower oxygen:carbon and hydrogen:carbon ratios as a result of storage. This is consistent with lower oxygen:carbon and hydrogen:carbon ratios in the raw feedstock as a result of storage. Lower oxygen:carbon ratios are generally favorable in biocrude because oxygen must be removed in the final fuel product [32]. Catalytic upgrading of the biocrude was performed at PNNL to assess the impact of these compositional changes on final biofuel quality.

An additional key finding observed in the preparation of feedstock for HTL conversion was that long-term storage improved performance in the immersion mill compared to the non-stored blend that was processed in the mill. This allowed for a higher solids content and lower overall ash to be used in the HTL process—19% vs. 16% for the non-stored blend (Table 5). Based on qualitative observations, it also appeared to result in reduced energy consumption during milling, however, energy consumption during immersion milling was not measured as a part of this effort. Quantification and valorization of this benefit associated with long-term storage will be assessed in future studies.

**Table 5 HTL feed characterization**

| <b>Parameter</b>         | <b>Units</b> | <b>Non-Ensiled</b> | <b>Ensiled</b> |
|--------------------------|--------------|--------------------|----------------|
| Total solids in feed     | wt%          | 16.1%              | 19.2%          |
| Ash in dry feed          | wt%          | 8.5%               | 5.6%           |
| Average feed density     | g/mL, 20°C   | 1.047              | 1.058          |
| Feed rate                | g (*AFDB)/h  | 608                | 764            |
| Biomass feed composition |              |                    |                |
| C                        | wt%          | 46.2%              | 47.1%          |
| H                        | wt%          | 6.5%               | 6.6%           |
| N                        | wt%          | 2.8%               | 2.4%           |
| O                        | wt%          | 31.6%              | 34.4%          |
| S                        | wt%          | 0.26%              | 0.26%          |
| Chemical oxygen demand   | mg O/L       | 207,900            | 258,900        |
| pH                       | pH unit      | 6.19               | 5.46           |

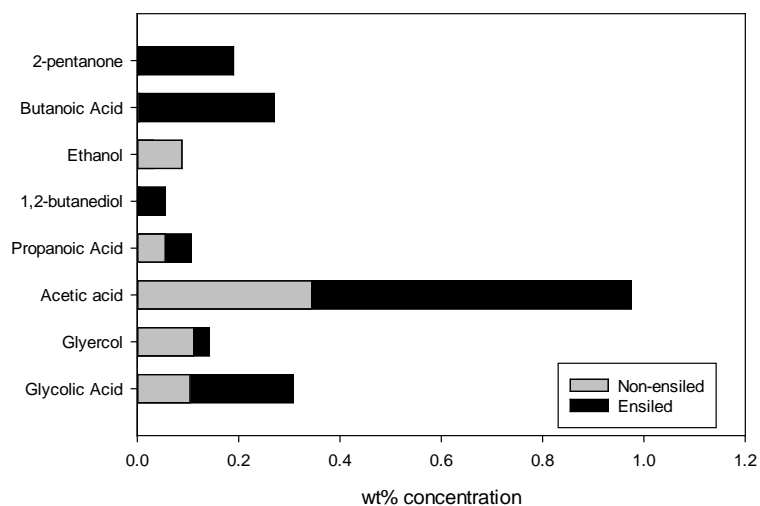
\*Ash-free and dry basis

### 3.3 Fate of light acids

The aqueous fraction of the biocrude from the HTL process was relatively clean and colorless. This fraction provides an opportunity for recovery of valuable side products in the form of carboxylic acids. The aqueous fraction from HTL conversion of ensiled biomass (Table 6) also had a lower pH, higher carbon content (2.2%) and higher chemical oxygen demand (65,200 mg-oxygen/L) than from non-ensiled biomass due to the presence of higher amounts of light acids such as acetic acid, glycolic acids, butanoic acids and propanoic acids that partitioned toward the aqueous fraction (Figure 3) and the presence of 2-pentanone, which is unique to ensiled biomass.

**Table 6. Aqueous HTL product characterization**

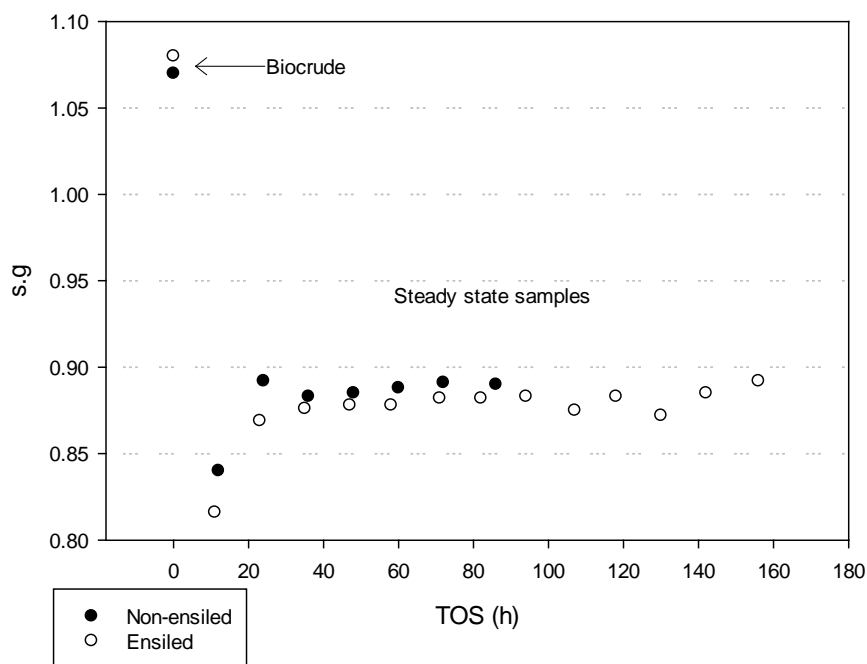
|                        |             | <b>Non-Ensiled</b> | <b>Ensiled</b> |
|------------------------|-------------|--------------------|----------------|
| Nitrogen               | wt%         | 0.21%              | 0.15%          |
| Ammonia                | wt%         | 0.13%              | 0.08%          |
| Total carbon           | wt%         | 1.98%              | 2.20%          |
| Total organic carbon   | wt%         | 2.30%              | 1.90%          |
| Chemical oxygen demand | Mg-oxygen/L | 57,000             | 65,200         |
| pH                     |             | 6.3                | 4.7            |



**Figure 3. Speciation of light acids in aqueous HTL product (determined using high-performance liquid chromatography)**

### 3.4 Hydrotreating performance

HT testing for both biocrudes was performed as planned, and both tests reached a steady-state density after times on stream (TOS) of 70 h (Figure 4), and from the set time window, for non-ensiled biomass (TOS 72–86 h) and ensiled biomass (TOS 71–82 h), liquid samples and gas samples were collected and analyzed for final yields calculation and reporting. HT test for the non-ensiled biomass ended at TOS 82h, but the ensiled biomass continued on until TOS of 155h to allow testing for extended catalyst lifetime. However, as density arises, guard bed temperature were raised to overcome deactivation of the catalyst, from the original temperature of 325 °C, then to 350°C and lastly to 375°C before finally shut-down due to high pressure drop which will be discussed in depth in the following discussion section.



**Figure 4. Plot of density vs. TOS of blendstock from ensiled and non-ensiled biomass**

In terms of overall yields, the hydrotreating process shows very similar result in terms of final yield of the fuel blendstock on both a dry-weight and %-carbon basis, at 92.3 wt% C for non-ensiled biomass and 92.8 wt% C for ensiled biomass seen in Table 7. The difference in terms of mass yields is within experimental error. Largest difference is noted on the aqueous and gas yields.

The produced fuel blendstock was then combined and analyzed in detail (the results are presented in Table 8. Biocrude upgrading resulted in immediate improvement of fuel quality, marked by decrease of heteroatoms across biocrudes, with oxygen as low as 1 wt% and nitrogen and sulfur also shown significant decrease.

**Table 7.** Summary of normalized yields of hydrotreating products from ensiled and non-ensiled biomass.

| Mass and carbon yields (dry, ash free, normalized) N = normalized | Units                               | Non-Ensiled | Ensiled |
|---|-------------------------------------|-------------|---------|
| Mass balance  | %                                   | 103         | 102     |
| Fuel blendstock yield, mass (N)                                   | $\frac{g_{oil}}{g_{biocrude}}$      | 0.899       | 0.883   |
| Gas yield, mass (N)   | $\frac{g_{gas}}{g_{biocrude}}$      | 0.082       | 0.073   |
| Aqueous yield, mass (N)   | $\frac{g_{aqueous}}{g_{biocrude}}$  | 0.079       | 0.099   |
| Hydrogen consumption  | $\frac{g_{hydrogen}}{g_{biocrude}}$ | 0.061       | 0.056   |
| Fuel blendstock yield, carbon (N)                                 | $\frac{g_{oil}}{g_{biocrude}}$      | 0.923       | 0.928   |
| Gas yield, carbon (N)   | $\frac{g_{gas}}{g_{biocrude}}$      | 0.077       | 0.072   |

The final density of the fuel blendstock obtained from hydrotreating ensiled and non-ensiled biocrudes decreased and were not significantly different from each another. Also, the TAN values decreased to below the level of detection, which is an indication of improved fuel quality. Improvement in heating value due to HT upgrades the energy density of the biocrude to be on par with fossil-derived fuels, reaching energy densities of 45.1–45.8 MJ/kg, comparable to diesel fuel (45.6 MJ/kg), kerosene (46.2 MJ/kg), or gasoline (46.4 MJ/kg) and significantly higher than heavy fuel oil (41.8 MJ/kg).

**Table 8.** Quality summary of the biocrude and upgraded blendstock from ensiled and non-ensiled biomass

|                    | Units                        | Biocrude                   |         | Blendstock  |         |         |
|--------------------|------------------------------|----------------------------|---------|-------------|---------|---------|
|                    |                              | Non-Ensiled                | Ensiled | Non-Ensiled | Ensiled |         |
| Elemental Analysis | Carbon                       | wt% (dry)                  | 72      | 81          | 85      | 85      |
|                    | Hydrogen                     | wt% (dry)                  | 8.40    | 8.60        | 12      | 1       |
|                    | Oxygen                       | wt% (dry)                  | 14.70   | 6.20        | 1.01    | 0.96    |
|                    | Nitrogen                     | wt% (dry)                  | 3.60    | 3.60        | 1.89    | 1.50    |
|                    | Sulfur                       | wt% (dry)                  | 0.30    | 0.20        | <0.05   | 0.06    |
|                    | Hydrogen:Carbon, molar ratio |                            | 1.39    | 1.25        | 1.71    | 1.76    |
|                    | Proximate analysis           | HHV                        | MJ/kg   | 33.6        | 37.8    | 45.1*   |
| TAN                |                              | $\frac{mg_{KOH}}{g_{oil}}$ | 49      | 56          | BDL     | BDL     |
| Density            |                              | $\frac{g}{cc}$ @40°C       | 1.07    | 1.08        | 0.89**  | 0.882** |
| Viscosity          |                              | cSt@40°C                   | 12,813  | 14,746      | 12.81** | 9.77**  |
| Water (KF)         |                              | wt%                        | 12.50   | 10.80       | 0.20    | 0.06    |
| Ash                |                              | wt%                        | 0.48    | n.d.        | n.d.    | n.d.    |
| Filterable solids  |                              | wt%                        | 0.58    | 0.21        | n.d.    | n.d.    |

|                               |                        |     |      |      |      |      |
|-------------------------------|------------------------|-----|------|------|------|------|
| Boiling point from ASTM D2887 | IBP – 184°C (gasoline) | wt% | n.d  | n.d  | 17.1 | 18.8 |
|                               | 184–344°C (diesel)     | wt% | n.d  | n.d  | 44.1 | 45.1 |
|                               | >344°C heavies         | wt% | n.d  | n.d  | 38.8 | 36.1 |
|                               | 153–256°C jet          | wt% | n.d  | n.d  | 18.3 | 19.7 |
| Product Gas composition       | Methane                | wt% | 0.26 | 0.26 | 30.2 | 24.4 |
|                               | Ethane                 | wt% | 0.12 | 0.12 | 25.9 | 30.5 |
|                               | Propane                | wt% | BDL  | BDL  | 19.5 | 22.2 |
|                               | Butane                 | wt% | 0.04 | 0.04 | 14   | 16.5 |
|                               | Pentane                | wt% | 0.06 | 0.06 | 8.5  | 6.4  |
|                               | Carbon monoxide        | wt% | BDL  | BDL  | 1.9  | 0    |
|                               | Carbon dioxide         | Wt% | bal  | bal  | BDL  | BDL  |
| Degree of heteroatom removal  | Degree of HDO          | %   | n.d  | n.d  | 93   | 84   |
|                               | Degree of HDS          | %   | n.d  | n.d  | n.d  | 70   |
|                               | Degree of HDN          | %   | n.d  | n.d  | 48   | 58   |

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\* Calculated (HHV (MJ/kg) = 33.5 (carbon) + 142.3 (hydrogen) – 15.4 (oxygen) – 24.5 nitrogen Reference [33]

\*\* Measured at 20°C

IBP. Initial boiling point

n.d. Not determined

BDL. Below detection limit

The final density of the fuel blendstock obtained from hydrotreating ensiled and non-ensiled biocrudes decreased and were not significantly different from one another. Also, TAN, ash and moisture values decreased to below the level of detection, signifying increased fuel quality. Improvement in heating value, due to hydrotreating, upgrades the energy density of the biocrude to be on par with fossil-derived fuels, reaching energy densities of 45.1-45.8 MJ/kg, comparable to diesel fuel (45.6 MJ/kg) or kerosene (46.2 MJ/kg) or gasoline (46.4 MJ/kg) and significantly higher than heavy fuel oil (41.8 MJ/kg).

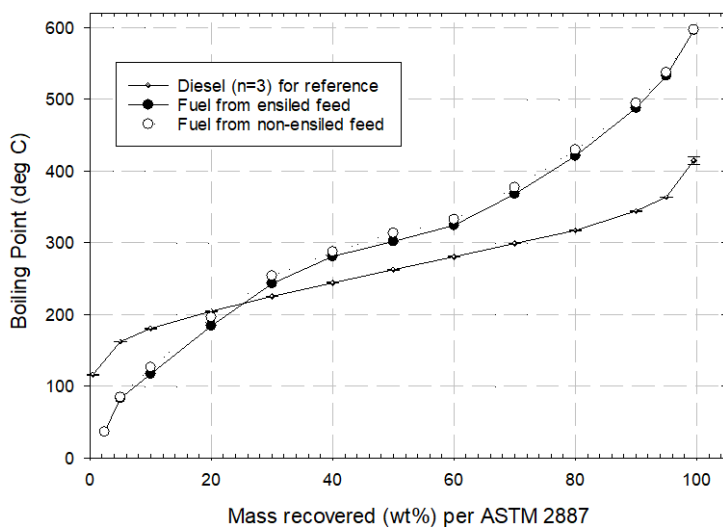
The reason for the improved quality from ensiling may result from carbohydrate degradation that occurs during storage and organic acids formed in this process. Fermentation during ensiling produces organic acids such as acetate, and degradation of hemicellulose can lead to deacetylation of this polymer, resulting in increased organic acid (e.g., acetic acid) content in the stored material. Hemicellulose in unscored material would still be acetylated at the time of conversion and could lead to acetylated compounds in the biocrude. Subsequent HTL conversion of the stored material causes the acetic acid to concentrate in the aqueous phase (Figure 3) and not in the biocrude. Thus, carboxylic acids such as acetic acid and other low molecular weight organic acids could result in inefficient consumption of hydrogen by their conversion to low-value products such as light gases.

The impact of deacetylation and subsequent removal of acetate to the aqueous phase on quality is supported by notable differences in gas composition from hydrotreating of the biocrude derived from ensiled vs. non-ensiled biomass. As seen in Table 8. Quality summary of the biocrude and upgraded blendstock from ensiled and non-ensiled biomass Table 8, the ensiled biomass shows decreased methane production and increased C2–C5 hydrocarbon gases. The degree of hydrogenation was also lower due decreased amount of acetate in the biocrude from the ensiled feed, which finally leads to less hydrogen consumption (0.056 vs. 0.061 g/g) and may lead to

improved processing efficiency. In contrast, the degree of cracking is increased because of the presence of additional acetate in the non-ensiled biomass as evidenced by the higher methane:ethane ratio in the HT gas composition.

### 3.5 Fuel cut yield

The hydrocarbon blendstock was analyzed by using ASTM Standard Method D2887 (Simulated Distillation). The results from the use of this method, which is standardized for the analysis of diesel fuels and kerosene, show the final product is closely comparable to sweet crude oil and also shows differences in the low-temperature distillate range when compared to diesel fuels. The results are shown in the simulated distillation curve Figure 5 and in Table 8 for the calculated distribution for each fraction.

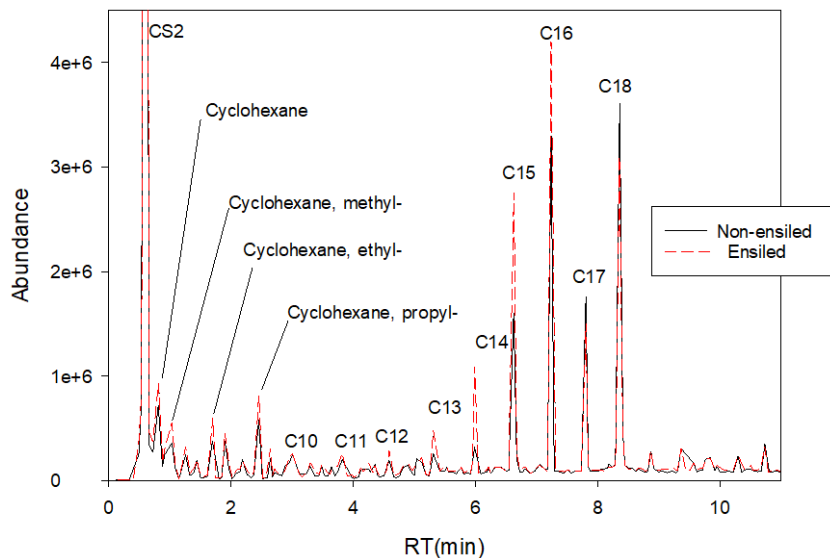


**Figure 5. Simulated distillation curve of the hydrotreated fuel from the HTL biocrude**

First, there was a higher concentration of gasoline range fuels from the ensiled biomass (18.8 wt%) vs. non-ensiled biomass (17.1wt%). Furthermore, there was a significant portion of the hydrotreated fuel that fell in the diesel distillate range (44 wt% for non-ensiled and 45.1 wt% for ensiled biomass) and a small tail end that fell into the distillation range of heavy residual oil (36.1 for non-ensiled and 38.8wt% for ensiled biomass). Overall, there were more than 87 wt% of the products that were in the diesel and heavies boiling point range. In terms of blendstock yields, both processes (ensiled and non-ensiled) had minor differences; however, in terms of fuel quality, the ensiled feed resulted in increased lighter fractions such as gasoline and diesel but less heavies. The limited degradation experienced during ensiling could have reduced the molecular weight of large biomacromolecules, lignin, cellulose, and hemicellulose, resulting in smaller molecules in the final fuel. Subsequently, this resulted in deeper hydrogenation activity through hydrodearomatization on aromatic compounds originally present in the biocrude, and this will be subject of discussion in the next section of this paper.

### *3.6 Speciation of hydrocarbons in the fuel blendstock*

The hydrocarbons present in the hydrotreated blendstock consisted of both cyclic hydrocarbons and linear long-chain alkanes, as shown in Figure 6.



**Figure 6. Chromatogram of hydrocarbon product from ensiled vs non-ensiled process**

Interestingly, there is an apparent increase in the amount of saturated linear and cyclic alkanes in the ensiled biomass. The increased recovery of long-chain alkanes from ensiled biomass is consistent with fatty acid extractions conducted on both ensiled and non-ensiled microalgae biomass in which fatty acid recovery from ensiled biomass exceeded that of the non-ensiled material by 12% [7]. The mechanism responsible for increased fatty acid extraction from ensiled biomass also could be the cause of the observed increase in linear hydrocarbon content in upgraded HTL oils from ensiled algae/pine blends.

As seen in Figure 6, the presence of cyclic alkanes, such as cyclohexanes and substituted cyclohexanes (methyl-, ethyl-, and propyl-), are primarily compounds with boiling points within the gasoline range (<184°C), while the linear alkanes, C12–C16, are characteristic of diesel range molecules (boiling points from 184–344°C). The ensiled blended material yielded a greater

concentration of both cyclic alkanes and linear alkanes than the non-ensiled blend. This can be explained by the fact that ensiling allows improved hydrogenation of aromatic hydrocarbons via hydrodearomatization, which resulted in higher saturation of the ensiled product (hydrogen:carbon ratio of 1.76), despite starting out at much lower saturation (hydrogen:carbon ratio of 1.25) in the feed. This can be further attributed to the earlier removal of light oxygenated molecules during HTL which would otherwise provide competitive adsorption to the HT catalyst site. Hence, ensiling led to improved content of both gasoline and diesel fuel in the hydrocarbon product.

Moreover, identification of components in the heavy fuel fraction ( $>344^{\circ}\text{C}$ ) is beyond the scope of the current work and is not possible with the current gas-chromatography–mass spectroscopy analytical method employed within our laboratory. Analysis of the heavy fractions may require approaches more suitable for cross-examining the heavy fraction from petroleum products, such as IP 469 that can resolve the heavy fraction into its individual classes of saturated, asphaltenes, resins, and aromatics. This approach may be addressed in future research.

### 3.7 *Heteroatom removal*

During ensiling, fermentation caused the easily accessible carbohydrates (i.e., compounds with high oxygen contents) to be consumed to produce fermentation products such as acetic acid, while proteins (compounds with high nitrogen contents) are unaffected by storage. The ensiling process therefore results in a feedstock with relatively less oxygen and relatively more nitrogen. This change in composition manifests itself in the final hydrotreated product after subsequent HTL and HT, resulting in increased HDN (Hydrodenitrogenation) activity of the present nitrogenated molecules whereas lighter oxygenated molecules have been eliminated via ensiling and subsequent separation in the HTL aqueous fraction.

In this study, the final nitrogen content was observed to be high on both blendstocks (1.89% for non-ensiled, and 1.50% for ensiled), and this has adverse consequence for final fuel quality. In terms of N-removal performance, both biocrude had identical N-content of 3.60wt%. However, the ensiled-biomass had higher HDN performance at 58% removal rate, versus 48% for the non-ensiled biomass. The data suggest that removal of acetates may lead to improved accessibility of nitrogenated compounds towards the active catalytic sites due to less competitive adsorption with lower molecular weight organic molecules which reacts at much faster rate. Removal of acetates also means that the HDO rate also would decrease consistent with the higher HDN activity, which was observed in this study, down from a 93% to a 84% removal rate for ensiled biomass and for non-ensiled biomass, respectively. As seen in Table 6, the final densities of the fuel blendstock obtained from hydrotreating ensiled and non-ensiled biocrudes decreased and were not significantly different from each other. Also, the TAN, ash, and moisture values decreased to below the levels of detection, which is an indication of improved fuel quality. The improvement in heating value due to HT upgrades the energy density of the biocrude to be on par with fossil-derived fuels, reaching energy densities of 45.1–45.8 MJ/kg, comparable to diesel fuel (45.6 MJ/kg), kerosene (46.2 MJ/kg), or gasoline (46.4 MJ/kg) and significantly higher than heavy fuel oil (41.8 MJ/kg).

To further eliminate the heteroatom content, two main strategies are considered: 1) using a different type of catalyst, such as one tuned for HDN and 2) using a more severe conditions, especially for complete nitrogenated molecules within biocrude [34] [22]. In addition, employing a bifunctional catalyst containing hydrogenation promoters, such as nickel and tungsten or molybdenum sulfide (MoS<sub>2</sub>), and with additional promoters, such as phosphorus or boron to increase acidity, supported on an acid support, such as silica or alumina, can accelerate nitrogen

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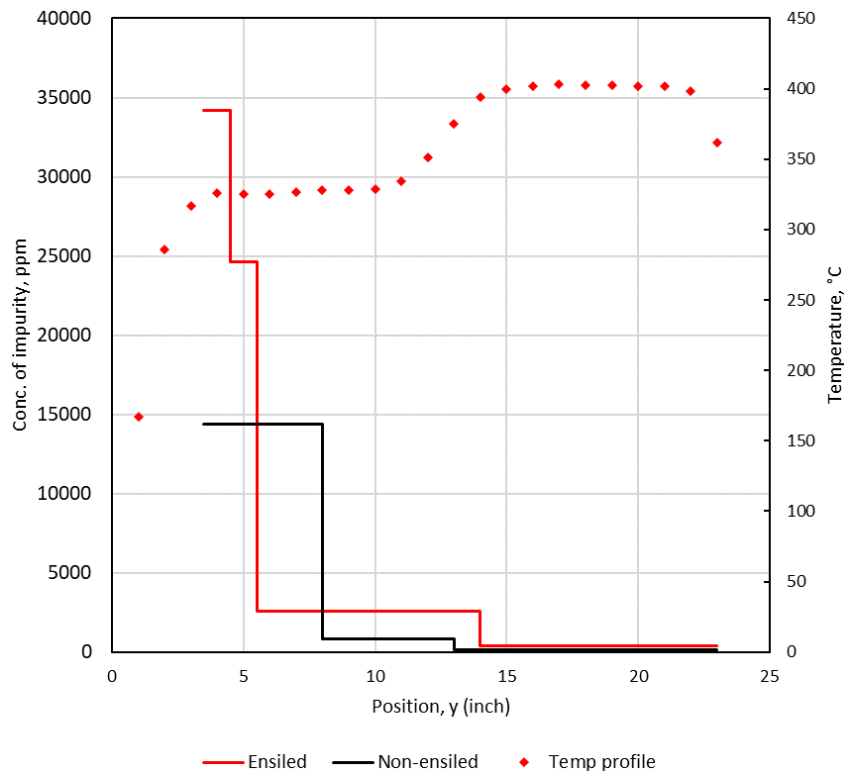
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removal as ammonia by increasing both the Brønsted acid and Lewis acid sites to assist in breaking the carbon–nitrogen bond [24] [25]. With increasing nitrogen loading in the feed, the process severity is expected to increase non-linearly, as nitrogen removal involves a multi-step reactions that requires the breaking of more bonds per molecule of nitrogen compared to oxygen or sulfur removal as pointed by Prado et al [35]. Consequently, this will result in increased consumption of hydrogen and possibly increased saturation of the product. Furthermore, increased ammonia production in the off-gas needs to be properly scrubbed and purged so its concentration in the recycle gas does not increase. In the second strategy, increasing severity is a commonly employed technique used to improve heteroatom removal. For example, lowering the LHSV is a common technique employed to target increased HDN activity [25]. This study employed a higher space velocity of 0.357 L/L/h due to recent success in improving yields (g/g dry biocrude basis) experienced in earlier studies; however, the trade-off to poorer product quality was evident in this study when high-nitrogen (>4 wt%) containing feed was used. Moreover, improvements to HDN can be made if the LHSV is decreased. In earlier studies by Elliott et al. [22] in which lower LHSVs were used (0.14–0.2 L/L/h), the nitrogen level was reduced to below detection limit (<0.05 wt%) from starting nitrogen concentration of 4.7 wt%. This represents >99% nitrogen removal for biocrude derived from *Nannochloropsis* sp.

However, the focus of this work has been to achieve a balance of yield and product quality using a commercial HDS catalyst with well-known conditions for biocrude upgrading [2] [22] [36]. Further optimization is needed to achieve improvement in quality fuel by employing an optimum catalyst composition/processing condition to effectively target low content in the final fuel.

### 3.8 *Catalyst deactivation and plugging by inorganic build-up on the guard catalyst bed*

As expected, presence of inorganics in the biocrude resulted in gradual deposition of material starting from the top of the guard bed. Ultimately, the restriction caused an increased pressure drop across the reactor bed to more than 100 psig, resulting in involuntary shut-down of the ensiled feed run. This limit was set to enable both solvent rinse (acetone) and hydrogen gas to still pass through the bed, thus enabling washing and drying to ease removal of the catalyst bed. The most prominent plug was from 1–5.5 inches from the top of the bed and occupied 45% of the total guard bed. The rest of the reactor bed, including the high temperature bed, was relatively clean and catalyst flowed freely from the reactor. The profile of metal deposition is shown in Figure 7.



**Figure 7. Profile of metal deposition in the reactor (impurity consisted of Fe, Na)**

The temperature of the pretreatment bed was designed to be operated at optimum hydrometallization (HDM) as earlier work at PNNL demonstrated demetallization at a milder HT temperature of 325°C, and as expected, the plug was successfully replicated and developed at the guard bed portion rather than at the main hydrotreater bed. [18]. The catalyst plug was removed from the reactor to be analyzed by inductively coupled plasma-optical emission spectroscopy. The plug material then was analyzed and was found to consist mostly of iron and sodium. For the ensiled feed, iron deposited in the plug at a higher concentration (30,000 ppm) than in the non-ensiled feed (14,000 ppm). Given the source of the iron are from the algae feed, the difference can be explained by the fact that the run with ensiled feed operated at much longer TOS of 156 h,

versus 86 h for the non-ensiled feed, so there is predictable rate of deposition of iron on the reactor bed of 162–192 ppm/h of iron on the catalyst bed for both tests.

Furthermore, the ensiling process does not affect the content or composition of inorganic elements within the biomass [9], and as discussed in-depth by Jarvis et al. [26], the inorganic material present in the biomass is not easily removed by physical separation methods (i.e., air classification or washing) as the iron is present in metal-organic complexes, such as porphyrin and metalloenzymes. Moreover, in that study, pure algal-sourced biocrude would contain 100,000–115,000 ppm of iron that ultimately led to the deactivation of the HDM catalyst in the pretreatment/guard bed.

However, in addition to buildup inorganics in the catalyst, there could be other catalyst deactivation mechanisms occurring, which will be the focus of the future work. Formation of gum from acid-base reactions that occur when basic nitrogen compounds such as pyridines and amines react with carboxylic acid to form a heavier molecule is an area of concern in petroleum refineries. Consequently, this acid-base chemistry also results in production of organic salts that may contribute to plugging in the catalyst bed [35] especially at extended TOSs. This concern also will be a subject of study in the future. In the present study, we did not observe clear formation of gum or buildup or organic salts downstream in the reactor. This can be attributed mostly to the shorter test durations of our tests.

For this work, the HT reactor included a non-optimized pretreatment bed that proved to be incapable of extended TOSs. An improved and optimized pretreatment bed is needed because deposition of iron and sodium on the catalyst leads to fouling and decreased performance and costly premature catalyst deactivation in the main bed. One strategy for effective HDM was discussed by Parkash et al. [25] to mitigate this problem is employing a larger pore-volume catalyst

and a permutable reactor system configuration to enable use of a multiple fixed guard that would allow improved continuous metal adsorption, resulting in more smooth and efficient operations without needing to shut down the process and no drop-off of throughput.

#### **4. Conclusions**

Production of a hydrocarbon fuel from blended and stored biomass feedstock presents an opportunity to add flexibility to our energy supply by providing a robust feedstock supply throughout the year. Achieving a year-round supply of biomass requires implementation of stabilization methods to provide adequate feedstock quality. Ensiling is a promising preservation method from a life cycle assessment perspective. The wet storage approach to algal biomass stabilization significantly reduces greenhouse gas releases compared to an approach that uses natural-gas-based drying for biomass stabilization.

The HTL-HT pathway enables evaluation of the suitability of ensiled biomass as a feedstock for HTL conversion to biofuels. The final yields and quality of fuels obtained from ensiled and unstored algae-FPR blends through the HTL-HT pathway were similar and differences observed are minor. Light acids are formed from fermentation and decomposition of hemicellulose in ensiled biomass and is from the aqueous phase during HTL. As a result, biocrude upgrading yielded a final fuel with lower oxygen content and a higher proportion of diesel and gasoline fraction compounds that consumed less hydrogen than fuel produced from unstored biomass blends. The impact of impurities, such as high nitrogen, iron, sodium, and silica on catalyst performance and useful lifetime represents a significant challenge to the development of an efficient, economical process for converting algae-FPR blends to fuels. Future research will

address this limitation by developing an optimized pretreatment bed to reduce the impact of these impurities.

Finally, techno-economic and life-cycle analyses must be performed to quantify the cost and benefit of using ensiling as a preservation strategy for the HT-HTL pathway. The current results suggest that quality and overall yield of the final fuel blendstock are not compromised as a result of storage.

#### **Statement of informed consent, human/animal rights**

“No conflicts, informed consent, human or animal rights applicable”.

#### **Declaration of authors**

All the participants are authorship of this work and agree to submit the manuscript for peer review to Algal Research.

#### **CRedit authorship contribution statement**

Daniel M. Santosa was responsible for writing-original draft preparation, data curation, formal analysis, visualization. Lynn M. Wendt was responsible for conceptualization, methodology, writing-original draft preparation, data curation, formal analysis, visualization. Bradley D. Wahlen was responsible for conceptualization, methodology, writing - review & editing, data curation, formal analysis. Andrew J. Schmidt was responsible for methodology, data curation, formal analysis. Justin Billing was responsible for methodology, data curation, formal analysis. Igor V. Kutnyakov was responsible for investigation, data curation. Richard T. Hallen was responsible for methodology, validation, supervision. Michael R. Thorson was responsible for

formal analysis, visualization. Tessa L. Oxford was responsible for investigation, visualization. Daniel B. Anderson was responsible for project administration, funding acquisition.

#### **Declaration of competing interest**

The authors declare any potential financial or other interests that could be perceived to influence the outcomes of the research.

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