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Richland, Washington 99354

Summary

A preliminary techno-economic analysis (TEA) was developed for the fiscal year 2020 state of technology (SOT) assessment to evaluate the benefits and risks for a large-scale microalga hydrothermal liquefaction (HTL) system based on most recent testing results. The focus of the study is directed toward the conversion system, which consists of five processes: two-stage sequential HTL (SEQHTL), biocrude upgrading to final fuels, bioprocessing for co-product generation, hydrogen generation, and steam cycle. In this system, algae biomass with corn stover supplement during the lower algae productivity seasons (winter, fall, and spring) to match the maximum algae seasonal production rate in summer is employed to maintain a constant plant capacity in all the seasons. Algae only (summer season) or algae/corn stover blended feedstock (other seasons) are sent to a two-stage SEQHTL process. In stage I, the carbohydrates in the feedstock are extracted and separated from the residual solid. The residual solid from stage I is further converted to biocrude in the SEQHTL stage II step. The biocrude is upgraded to final fuel products in an upgrading process. The extract stream from HTL stage I is sent to the bioprocessing section for co-product generation via fermentation of carbohydrate. Lactic acid (LA) is assumed to be the co-product based on current bioprocessing testing results.

In 2020, bench-scale continuous experimental work was conducted for SEQHTL processing of algae only and algae/non-algae blended feedstock. The testing results demonstrated effective carbohydrates extraction at stage I and high biocrude yield for stage II. The lab-scale bioprocessing testing was also conducted and successfully demonstrated LA production from fermentation of algae HTL carbohydrate extract. Algae cultivation testing using HTL recycled aqueous and precipitated solid waste streams shows strong growth in multiple tested algae strains. These testing results provide a solid design basis for this TEA study.

Table 1 summarizes the major changes of the 2020 SOT case compared to the 2019 SOT case and describes the purpose/potential benefits of these changes. These changes result in a reduction in the conversion costs (not including feedstock cost) from \$0.88/GGE for 2019 SOT to -\$0.33/GGE in 2020 SOT. The major reason for this cost reduction is the credits from the generation and sale of the co-product lactic acid.

Table 1. Major changes of 2020 SOT compared to 2019 SOT case

Major changes	2019 SOT	2020 SOT	Purpose/effects
HTL conversion	Single-stage HTL; slurry feed containing 20 wt% solid, medium temperature and high pressure, biocrude generation	Two-stage sequential HTL: Stage I - slurry feed containing 10 wt% solid, low temperature and pressure, carbohydrate extraction; Stage II - Medium temperature and high pressure, biocrude generation	To enable flexible co-products generation from stage I carbohydrate extractives; cost benefits resulting from lower feed flow rate to stage II; lower dewatering cost for algae feedstock because of lower required solids content of the slurry feed.
Bioprocessing for co-product generation	No co-product generation	A bioprocessing step is added to convert the extracted carbohydrates from SEQHTL stage I to biochemical co-product	Extra co-product credits and additional capital cost for bioprocessing compared to 2019 SOT
Feedstock	Microalgae with wood as the supplement feedstock in non-summer seasons; The conversion throughput is 598 US tons/d ash-free dry weight (AFDW); The algae feedstock cost is $670/ton AFDW.	Microalgae with corn stover as the supplement feedstock in non-summer seasons; The conversion throughput is 698 US tons/d AFDW The algae feedstock cost is $590/ton AFDW.	Corn stover demonstrated higher carbohydrates extraction than wood in prescreening tests; Capital cost reduction through economies of scale; Lower algae feedstock cost leads to lower overall feedstock cost and lower variable operating cost.

In this report, the following major elements are included: the system evaluated in this study is overviewed and the major TEA methodology and basis are first introduced. The major experimental achievements are summarized, which provides the design basis for this study. A previous study for potential co-products selection is briefly described. Detailed information for the process design and simulation and cost estimation are provided. TEA results of this study are presented and compared to the previous single-stage HTL SOT. Sensitivity analysis results and sustainability metrics from simulation outputs are also provided. Future research and development work for algae HTL systems related to the key cost drivers are expected to help further improve performance and reduce production cost. The potential improvements include using low-cost algae feedstock, optimizing HTL and bioprocessing conditions, identifying high-value co-products and improving co-product yield.

Acronyms and Abbreviations

AFDW	ash free dry weight
ANL	Argonne National Laboratory
APEA	Aspen Process Economic Analyzer
BETO	Bioenergy Technologies Office
BPSD	barrels per stream day
Btu	British thermal unit
CHG	catalytic hydrothermal gasification
CSL	corn steep liquor
DAP	diammonium phosphate
DOE	U.S. Department of Energy
FCI	fixed capital investment
FY	fiscal year
GGE	gallon gasoline equivalent
HHV	higher heating value
HT	hydrotreating
HTL	hydrothermal liquefaction
HCSD	high-carbohydrate *Scenedesmus*
ISBL	inside-battery-limits
LA	lactic acid
LAB	lactic acid bacteria
LHSV	liquid hourly space velocity
MFSP	minimum fuel selling price
MHTLS	modular HTL system
MVR	mechanical vapor recompression
NABC	National Advanced Biofuels Consortium
NAABB	National Alliance for Advanced Biofuels and Bioproducts
MM	million
NREL	National Renewable Energy Laboratory
PNNL	Pacific Northwest National Laboratory
SEQHTL	sequential hydrothermal liquefaction
SCF	standard cubic foot
SSCF	simultaneous saccharification and fermentation
TCI	total capital investment
TDC	total direct cost
TEA	techno-economic analysis
YE	yeast extract

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1.0 Introduction

The goal of the U.S. Department of Energy (DOE) Bioenergy Technologies Office (BETO) is to develop commercially viable bioenergy and bioproduct technologies to:

- Enable sustainable, nationwide production of biofuels that are compatible with today's transportation infrastructure, can reduce greenhouse gas emissions relative to petroleum-derived fuels, and can displace a share of petroleum-derived fuels to reduce U.S. dependence on foreign oil.
- Encourage the creation of a new domestic bioenergy and bioproduct industry (DOE 2016).

To meet national goals to increase the production of renewable fuels, products, and power from biomass, techno-economic evaluations have been developed for both biological and thermochemical pathways for converting biomass to fuels and co-products.

1.1 Background

Hydrothermal liquefaction (HTL), as a direct conversion method of biomass to liquid fuel, has been investigated for decades (Elliott 2016; Goudriaan and Peferoen 1990; Rust International Corporation 1982). HTL involves processing biomass feedstocks in hot subcritical water to produce an intermediate biocrude organic phase, which is separable from the aqueous phase (Elliott et al. 2015). The HTL biocrude can be further upgraded via catalytic hydrotreating (HT) (Duan and Savage 2011). Catalytic HT removes heteroatoms such as oxygen and nitrogen while also increasing the hydrogen-to-carbon ratio of the organic product. The hydrotreated hydrocarbon product may be suitable as a fuel blendstock or a standalone fuel after further processing (e.g. isomerization) to meet all fuel specifications.

HTL technology was initially investigated for the conversion of lignocellulosic biomass to liquid fuel. In recent years, microalgae have received increasing interest for advanced biofuel production due to higher growth rates, areal yields, and photosynthetic efficiency as compared to terrestrial biomass (Biller and Ross 2011, Barreiro et al. 2013, Weissman et al. 2018). Considering the high moisture nature of microalgae, HTL avoids the energy consumption for biomass feedstock drying and eliminates the energy penalty for water vaporization during the process compared to gasification and pyrolysis pathways (Elliott 2016). In addition, HTL converts the whole algae cell, including most of the lipid and a portion of the protein and carbohydrate fractions, to biocrude or other fuel precursors, and thus the feedstock for HTL is not constrained to high-lipid algae strains. Under the temperature and pressure conditions of hydrothermal liquefaction, microalgal biomass is converted to biocrude and other products containing numerous types of compounds. Reported HTL conditions for microalgae conversion typically range from 250 to 375°C, 10 to 20 MPa, the reaction time from 5 to 180 minutes, and microalgae feedstock with 5–20% dry biomass fraction in the slurry feed. The maximum biocrude yields can be as high as 64.0 wt% on a dry feedstock basis (Barreiro et al. 2013; Alba et al. 2012).

Initial HTL processing of microalgae has focused on single-stage high-temperature conversion pathways. However, as demonstrated by our experimental work and other published studies, the biocrude from a single-stage HTL usually has significantly higher oxygen and nitrogen contents than conventional crude oil (Duan and Savage 2011; Elliott 2016; Jazrawi et al. 2015). The high oxygen and nitrogen contents of biocrude pose problems with upgrading because of catalyst poisoning and deactivation and thus more work is needed to investigate the oxygen and nitrogen tolerant limits of conventional refineries (Jones et al. 2014a; Costanzo et al. 2015). The nitrogen content in biocrude comes from the protein fraction of algae and the oxygen content mainly comes from the carbohydrate fraction. Another limitation of single-stage HTL is its inability to allow the concurrent carbohydrates extraction and biocrude production. Therefore, two-stage sequential HTL (SEQHTL) conversion technology was developed to remove part of the nitrogen and oxygen from the feedstock by extracting carbohydrate and protein fractions in the first stage, thereby sending less nitrogen and oxygen to the second stage, while also enabling co-product generation from the first stage extract (Miao et al. 2012; Jazrawi et al. 2015; Costanzo et al. 2015; Selvaratnam et al. 2015).

In the SEQHTL process, a portion of the carbohydrate and protein in the feedstock are extracted at the first stage of HTL at low temperature and pressure. The residual solid is then converted to biocrude at the second stage with high pressure and temperature, which are similar to the conditions of the single-stage HTL process. Another important development in recent years is blending algae with other feedstocks as feedstock for HTL conversion. This is an alternative option to algae drying or wet storage in order to eliminate the seasonal algae productivity variation impacts on the conversion plant. This method can also increase the conversion plant capacity via adding non-algal feedstock. The investigated non-microalgae blending feedstocks include wood, starch-rich biomass, plastic, sugar beet pulp, rice husk, and macroalgae (Torr et al. 2018; Yang et al. 2019; Wang et al. 2019; Wu et al. 2017; Sintamarean et al. 2017; Brilman et al. 2017; Gai et al. 2015; Jin et al. 2013; Jarvis et al. 2018; Billing et al. 2019; Zhu et al. 2018).

To support the BETO goal of developing commercially viable bioenergy and bioproduct technologies, teams at Pacific Northwest National Laboratory (PNNL) have conducted multiple experimental and techno-economic analysis (TEA) studies for algae HTL processing. Since 1976, PNNL has been actively engaged in research activity for the biomass liquefaction process (Rust International Corporation 1982). From 2010 to 2013, PNNL, under the National Advanced Biofuels Consortium (NABC) in collaboration with other research organizations, conducted a series of bench-scale HTL and upgrading tests for woody biomass and corn stover (Schmidt et al. 2012; Elliott et al. 2015). The HTL team demonstrated a baseline continuous-flow process of loblolly pine and corn stover, and examined the influence of process conditions (temperatures and residence time) and the recycle of aqueous product to increase biocrude yields and decrease wastewater generation. HT of the biocrude product was also tested to construct material balances and to evaluate upgraded fuel quality. A reactor configuration combining a small continuous stirred tank reactor and a plug flow reactor was developed in the testing. In 2012, the PNNL experimental team began the research and development work for algae feedstock HTL processing and biocrude upgrading under the National Alliance for Advanced Biofuels and Bioproducts (NAABB) program (Zhu et al. 2013). Multiple aspects of algae HTL technologies have been explored by PNNL in recent years, including different algae strains and algae/non-algae blended feedstock, single and two-stage HTL conversion methods, HTL aqueous phase treatment, nitrogen and phosphorus nutrient recycling, aqueous phase valorization via co-product generation, and HTL biocrude hydrotreating.

The experimental work conducted by PNNL provides a solid and reliable basis for a TEA of HTL and upgrading technologies. TEA studies by PNNL have evaluated multiple HTL conversion systems, which mainly include HTL conversion and upgrading systems with different feedstock (lipid-extracted algae, woody biomass, whole microalgae, microalgae/non-algae blended feedstock, wet waste) and different aqueous phase treatment methods (Jones et al. 2014a&b; Albrecht et al. 2016; Zhu et al. 2013, 2014, 2018, 2019, 2020a&b). In 2014, a design case for whole microalgae single-stage HTL with a biocrude upgrading system was developed (Jones et al. 2014a). The HTL products (biocrude, solid, aqueous, gas) are separated and the biocrude is hydrotreated to form diesel and naphtha range fuel blendstocks. The HTL aqueous phase is catalytically treated via catalytic hydrothermal gasification (CHG) to recover the carbon content. Process offgas may be used to generate hydrogen, heat, and/or power. A hydrogen source is assumed to provide hydrogen for on-site HT. Nutrient recovery is accomplished by recycling treated water, carbon dioxide containing flue gas, and treated solids back to the algae ponds. This design case estimated that the minimum selling diesel price is \$4.77/gallon (2011 constant dollars) or \$4.49/gasoline gallon equivalent (GGE) with a projection year of 2022 (Jones et al. 2014a). Note that approximately 74% of this price is the cost of the algae feedstock. In 2018, several changes were applied to the 2014 design case, including updating the cost year (from 2011 to 2016), income tax rate (from 35% to 21%), and algae flow rates based on the National Renewable Energy Laboratory's (NREL) 2030 projection (Davis et al. 2020). The updated design case minimum fuel selling price (MFSP) for the 2030 projection is $4.45/GGE and it is $5.30/GGE for the 2025 projection (Zhu et al. 2020).

As indicated by the previous experimental work and TEA studies, further technology improvements and associated conversion cost reductions are limited for the single-stage HTL and biocrude upgrading system. Therefore, PNNL proposed and tested sequential two-stage HTL to explore further cost improvement opportunities for the algae HTL pathway. An initial simplified TEA for two-stage sequential HTL (SEQHTL) based on experimental data and literature values indicated the potential to achieve the BETO 2030 goal for modeled MFSP at $2.5/GGE via high value co-products generation. Therefore, for the fiscal year 2020, an SOT case based on the current best available testing results was developed. The purpose is to incorporate the current experimental development into the process design and cost estimation and thus provide the benefits and risks evaluation for applying these improvements to large-scale algae HTL conversion systems. The details of the process simulation and cost analysis of this SOT case are described in this report.

1.2 System Overview

A block diagram of the algae/corn stover (CS) blend feedstock conversion via HTL and biocrude upgrading investigated in this study is shown in Figure 1. The conversion system includes all processes inside of the dashed line in the figure. All processing unit operations are assumed to be co-located at the algae farm.

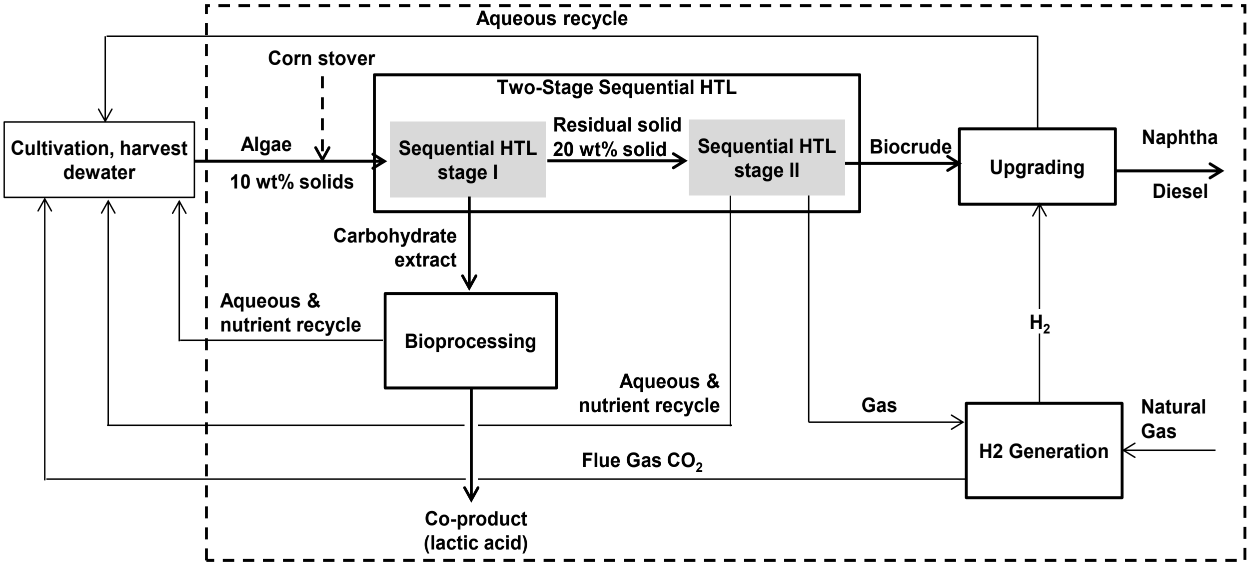


Figure 1. Block diagram of algae with corn stover supplement based SEQHTL and biocrude upgrading system.

The conversion system includes five major processes:

- **Hydrothermal liquefaction (HTL):** The conversion process takes the algae biomass produced at the farm after it has been harvested and concentrated to ~10% weight solids. As algae productivity varies by seasons, corn stover is assumed to be blended with algae biomass during lower algae productivity seasons (winter, fall, and spring) to match the maximum algae seasonal production rate in summer. In the system, algae only (summer season) or algae with CS supplement in non-summer seasons is pumped to the HTL conversion stage, which features a continuous two-stage process. In stage I, carbohydrates in the feedstock are extracted at low temperature and pressure. The carbohydrate stream is used to make co-products via bioprocessing. The residual biomass from stage I conversion is further processed in stage II at higher temperature and pressure to make a biocrude along with aqueous, gas, and mineral solids waste streams. The mineral solids stream is treated by acid digestion for nutrient element recovery. The digestate and the stage II aqueous streams are assumed to be recycled to provide nutrients for algae cultivation.

- **Bioprocessing of HTL stage I carbohydrate extract:** In this process, the extracted carbohydrates from HTL stage I are converted to co-product. The aqueous stream containing extracted carbohydrates is concentrated by evaporation and then sent to an enzymatic hydrolysis unit to convert sugar polymers to monomers. The stream with simple sugars is then fermented to produce chemicals as co-products for this system. The stream from the fermentation unit is then purified via filtration, evaporation, and distillation to generate the high-purity final co-product. In this study, lactic acid is assumed to be an example co-product from sugar fermentation and selection of LA as the co-product is based on a screening analysis of potential co-products (see Section 1.4) and our current testing work.
- **Biocrude upgrading:** The biocrude from the HTL process is sent to the upgrading process. In this process, hydrotreating reactions remove oxygen, nitrogen, and sulfur contents in the biocrude. The hydrotreated oil is then stabilized by removing butane and lighter components in a lights-removal column. The stable oil is further separated into gasoline and diesel-range fuels, and into a heavy fraction based on their boiling points. The heavy oil is cracked to produce additional gasoline and diesel range liquid fuels and some light fractions in a hydrocracking unit. These products are blended with the gasoline and diesel products from the HT process to form the final fuel products.
- **Hydrogen plant:** The offgas from HTL and the upgrading processes plus makeup natural gas, are used to generate hydrogen and heat in a steam reforming unit. The hydrogen plant is assumed to be co-located with the upgrading process to provide hydrogen required by the HT and hydrocracking reactions. The process flue gas is assumed to be recycled to the algae farm as a CO_2 source for algae growth.
- **Steam cycle:** Steam generation is assumed via heat recovery from hot process streams. A steam turbine uses part of the generated superheated steam for power generation. A gas-fired boiler is used to generate medium and low-pressure steam to provide heat for the bioprocessing step.

For the system, the aqueous steams and flue gas from different processes are assumed to be recycled to the algae farm for algae cultivation purpose. The individual processes, including HTL, hydrotreating, bioprocessing and aqueous phase recycle, have been tested in this study. Hydrogen generation and steam cycle are assumed to be based on conventional technologies. The fully integrated algae HTL system as proposed in this study needs to be tested at pilot or larger scales in the future.

1.3 Techno-Economic Analysis Approach and Assumptions

The approach to developing techno-economics for a conversion process is similar to that employed in previous conceptual design reports produced for BETO (Jones et al. 2014; Davis et al. 2018; Humbird et al. 2011). Process design and economic analysis are based on experimental results from completed and ongoing research at PNNL and other research organizations, as well as information from commercial vendors for mature and similar technologies. With the design basis developed, a process flowsheet for the biomass HTL and upgrading system was built in Advanced System for Process Engineering Plus (Aspen Plus), which is a deterministic steady-state chemical process simulator (AspenTech 2017). Unit operation blocks in Aspen Plus are used to simulate the actual pieces of equipment in the system. These blocks are connected by using material, heat, or work streams to simulate fluid flows and energy transfer between unit blocks. Input assumptions are specified for each unit block and inlet streams are based on information from the design basis. Final product yields, energy efficiency, and other performance indicators of the system are estimated based on the modeling results.

The material and energy balances from the process simulation model are used to estimate the capital and operating costs. Cost estimation for conventional equipment (such as pumps, heat exchangers, and tanks) is based on the operating conditions specified for the equipment such as temperature and pressure, and size information such as inlet flow rates. The Aspen Process Economic Analyzer (APEA) is used to calculate conventional equipment costs (AspenTech 2017). Non-standard equipment costs (e.g., HTL reactor, HT and hydrocracking reactors, and hydrogen plant) were estimated by scaling base equipment costs from literature references using the desired parameter (e.g., flow, duty) and applying an appropriate scaling factor. These are assembled in a Microsoft Excel spreadsheet employing a discounted cash flow analysis to estimate the MFSP. This approach is summarized in Figure 2 for the conversion process.

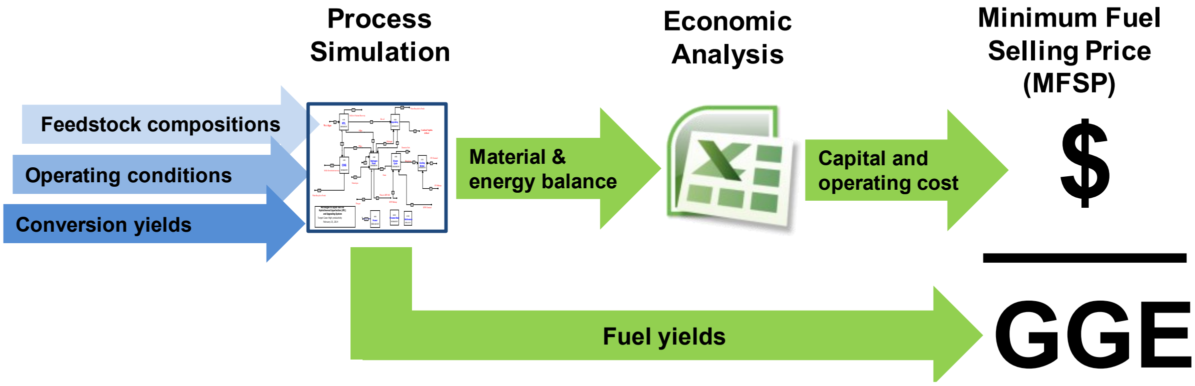


Figure 2. Techno-economic analysis approach.

A standard reference basis common to the conceptual design studies, known as the nth of a kind plant design, is used. These assumptions do not account for additional first of a kind plant costs, including special financing, equipment redundancies, large contingencies, longer startup times necessary for the first few plants and low on-line availability. For nth plant designs, it is assumed that the costs reflect a future time when the technology is mature and several plants have already been built and operated. The details of process simulation and economic analysis are described in the following sections.

1.4 Screening Study for Co-Products Selection

As described in the previous section, the carbohydrate extract from the HTL stage I process is assumed to be bioprocessed to produce a co-product. Various products can be produced from sugars or carbohydrates. In 2019, we developed a prescreening TEA to investigate the most significant factors of the carbohydrate bioprocessing for the algae HTL system cost. As shown in Figure 3, four parameters were selected for sensitivity analysis, including co-product price, carbohydrate bioprocess capital and operating cost, and co-product yield from carbohydrate. The most significant factors are co-product yield from carbohydrate and co-product price. The carbohydrate processing capital cost and operating cost are also significant but have relatively smaller impacts than the other two factors. The sensitivity analysis was implemented for lactic acid, acrylic acid, succinic acid, and L-lysine. The sensitivity analysis in Figure 3 was based on acrylic acid as it was our first research target. Since the sensitivity analysis used relative changes with wide variation ranges for co-product prices and other parameters, the results about key impacting factors also applies to other co-products and are not constrained to specific one.

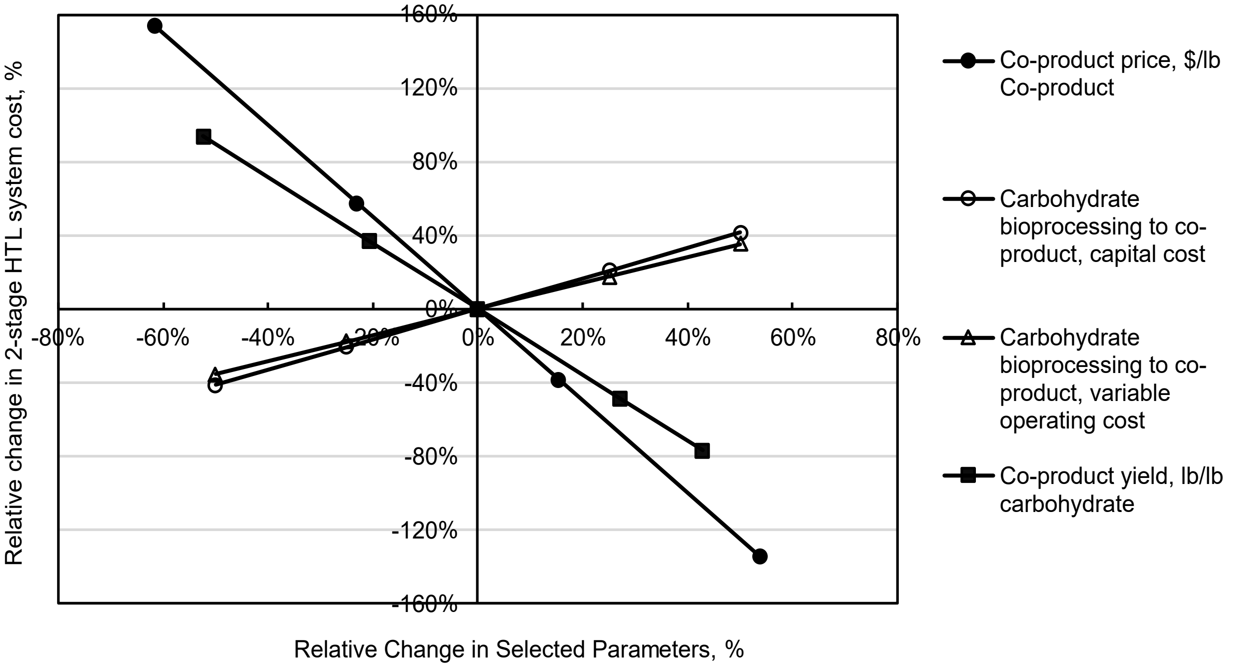


Figure 3. Relative changes in HTL system cost with variation in selected co-product generation parameters.

Market and production cost information for different co-products was also collected, as shown in Figure 4, to determine feasible co-product targets for commercial application. The collected information is mainly from industry database and literature or web sources (de Oliveira et al. 2018; GlobeNewswire 2019; Biddy et al. 2016; Grand View Research 2016). Due to the limited availability of conversion cost data, only seven potential products, which can be produced from glucose, were selected here for the market and production feasibility comparison.

As shown in the figure, some products have a high market price but a low price in terms of $/lb glucose. The price in unit of $/lb glucose is calculated by multiplying the product market price ($/lb product) by its conversion yield (lb product/lb glucose), which combines the two most significant factors based on the above sensitivity analysis for the production cost. The highest three market prices in $/lb glucose are for acrylic acid (AA), lactic acid (LA), and succinic acid (SA). L-lysine is also attractive because of its low conversion cost, despite a slightly lower market price in $/lb glucose compared to LA and AA. Comparing the market sizes, LA, AA, and L-lysine look more attractive than SA due to its very small market size. Both AA and L-lysine have higher market sizes than LA. However, based on literature searches for the technology readiness and our current testing work, LA is selected as the co-product from algae carbohydrates conversion in this study. However, AA and L-lysine from microalgae or its extract should be considered as promising co-product targets from algae. In addition, due to limited market and production information available for this screening study, very limited candidates were evaluated here and other candidates that can be produced from microalgae carbohydrate conversion should be considered in future work. The selection of LA for this study should be viewed as an example co-product from the algae carbohydrate bioprocess, but may be not the final or optimal choice. Other co-products choices should be investigated and evaluated in future research.

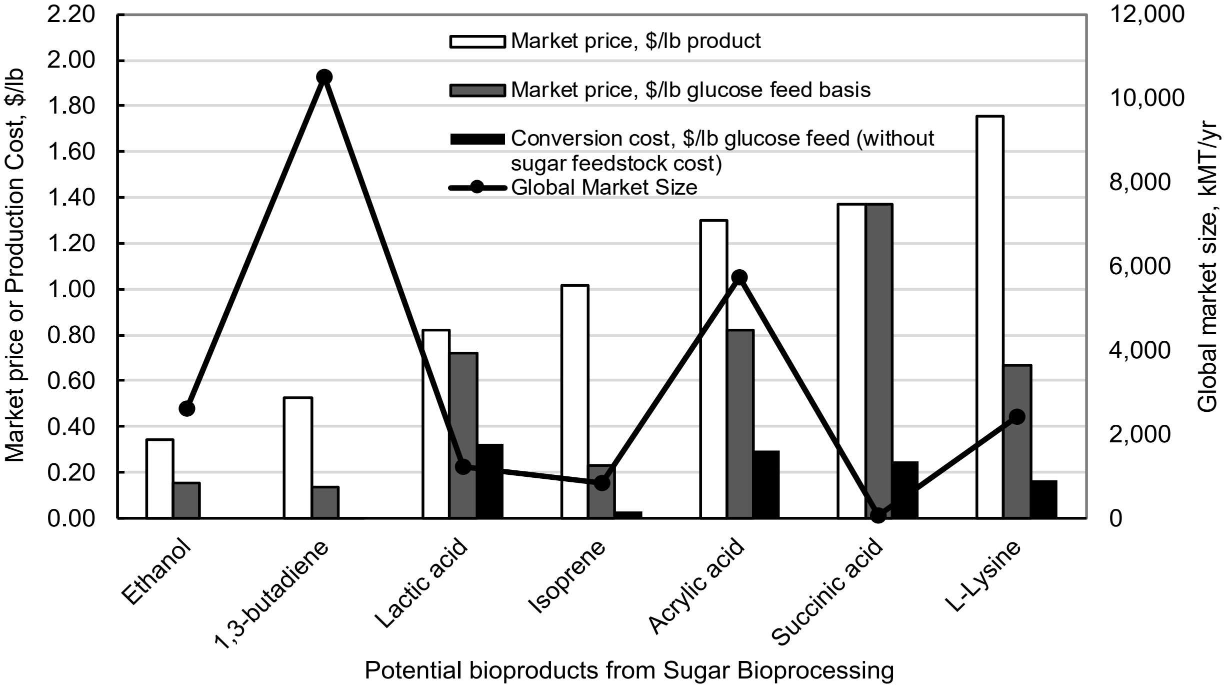


Figure 4. Market information for selected potential bioproducts from sugar bioprocessing.

Table 2 lists the basic information for LA as a commercial product. LA has wide application in different industries and its market size has grown rapidly. LA industrial production is mainly from chemical synthesis or microbial fermentation with the fermentation pathway comprising 90% of the total LA production (Komesu et al. 2017; de Oliveira et al. 2018). However, one of the biGGEst challenges for industrial LA fermentation process economics is the price of the sugar feed and food competition (de Oliveira et al. 2018). LA fermentation by using untreated or pretreated microalgae as substrates has been investigated at lab-scale (Nagarajan et al. 2020; Niccolai et al. 2019; Nguyen et al. 2012; Talukder et al. 2012; Ike et al. 1997). Although only limited studies of using microalgae for LA fermentation are reported, these published works provided a good starting point for researching the algae SEQHTL stage I extract as the substrate for LA fermentation. Use of the HTL stage I carbohydrate extract from microalgae as the substrate for LA fermentation can potentially solve the food competition challenge of the LA fermentation industry and help to meet the rapid growth in LA product demand.

Table 2. Lactic acid price and market information

Lactic Acid	Values	Source
Commercial concentration	88 wt%	National Research Council (2003)
Chemical purity	Sulphated ashes (%): max. 0.05; Heavy metals (ppm): max. 0.001~ 10; Iron (ppm): max. 0.001 ~ 10	National Research Council (2003)
World production (MMtons/year)	1.22 in 2016; ~ 2.0 in 2025	de Oliveira et al. (2018)
Price range ($/kg)	U.S.: $1.6 to $2.9/kg; Global: $1.1 to $2.9/kg (2010 to 2018)	de Oliveira et al. (2018), Industry database
Projected growth rate	16.2%	de Oliveira et al. (2018)
Major application	Personal and home care, biodegradable plastics, biodegradable polymer, food and beverage, pharmaceuticals	de Oliveira et al. (2018)

2.0 Experimental Work in Fiscal Year 2020

Beginning in 2018, PNNL has conducted bench-scale testing of a two-stage sequential HTL (SEQHTL) conversion process. Testing included HTL stage I and II and bioprocessing of stage I carbohydrate extract for valorization into co-product. The major research efforts by PNNL for algae HTL conversion to biofuels and biochemical in FY2020 are described in this section.

2.1 Two-Stage Sequential HTL

In this process, biomass feedstock slurry was sent to the HTL stage I reactor. In this reaction step, algal biomass was converted to decant and residual solids. The stage I decant is available for co-product generation via bioprocessing of the extracted carbohydrates. The wet residual is sent to the HTL stage II reactor and converted to biocrude, aqueous, gas, and solid products. A high-throughput batch system has been used to explore the impacts of alternative feedstocks (algae, wood, corn stover, algae/wood, and algae/corn stover blends), the use of additives (e.g., H_2SO_4) in stage I, and different reaction conditions (space velocity and temperatures). Confirmation tests have been conducted in the continuous flow bench system based on identified favorable reaction conditions. In 2020, scalable testing using a plug flow configuration has been conducted. A testing material flow diagram is shown in Figure 5.

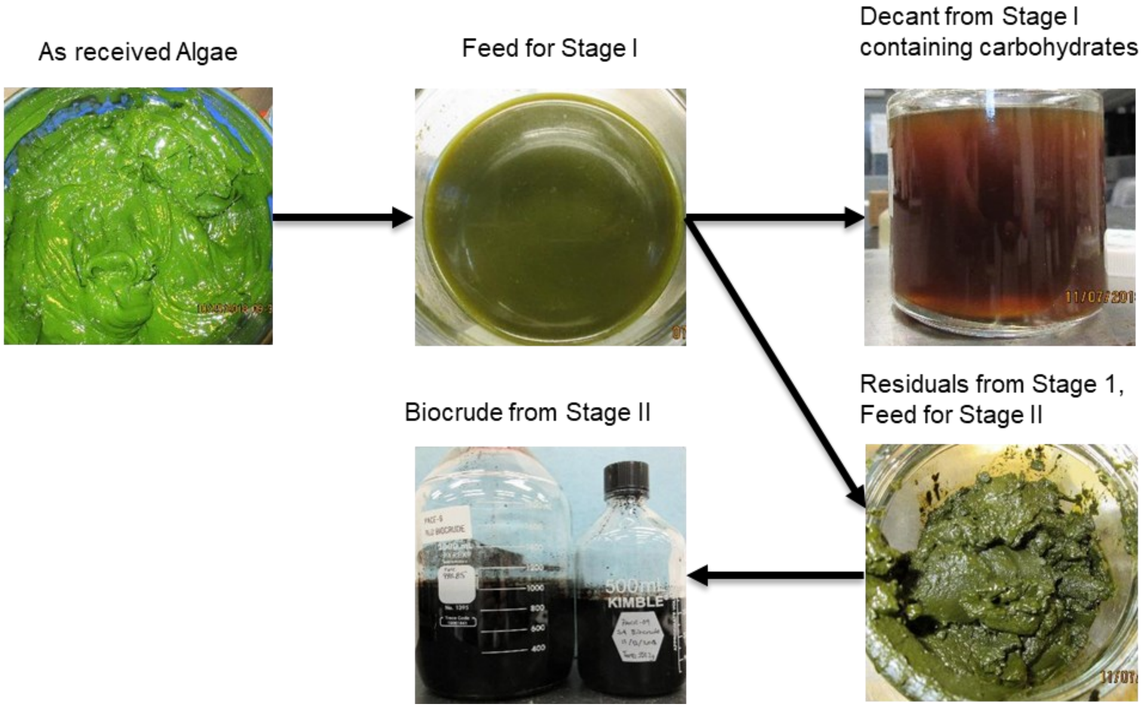


Figure 5. Experimental material flow diagram of SEQHTL testing.

The major experimental results for the HTL stage I carbohydrate extraction for the algae only and blended feedstock (50% algae/50% corn stover) are shown in Figure 6 and Figure 7. The bench-scale stage I experimental work investigated combinations of different reaction conditions, including temperatures (150 to 190 °C), sulfuric acid concentrations (0, 1, 2.5 wt% in total slurry feed), and liquid hourly space velocity (LHSV) (1.8 to 4). When sulfuric acid is used in the HTL stage I, the optimal temperature for carbohydrate extraction is found to be 160 °C. The optimal temperature findings are consistent with research by Miao et al. (2012) and Chakraborty et al. (2012). They found that the carbohydrate in algae is mainly polysaccharide, which is a homopolymer of glucose but not cellulosic in nature and therefore the

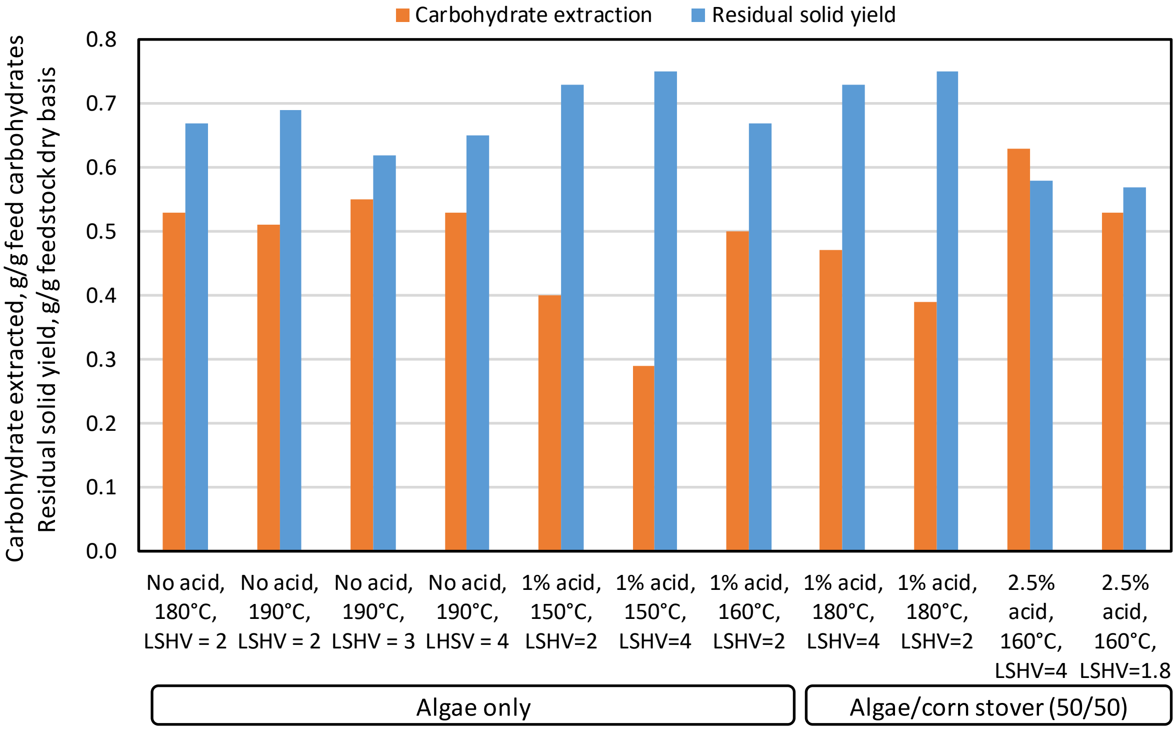


Figure 6. Experimental results of carbohydrates extraction and residual solid yields for SEQHTL stage I processing

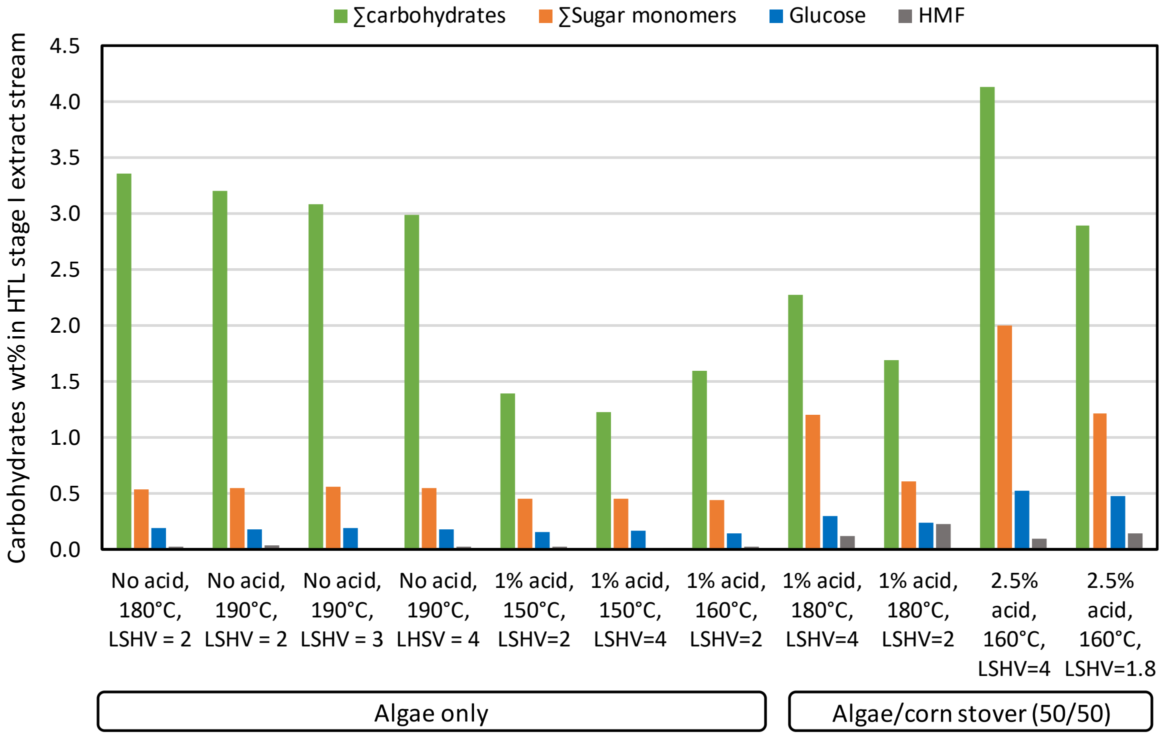


Figure 7. Experimental results for sugar concentrations in SEQHTL stage I extract stream

hydrolysis of the non-cellulosic carbohydrate is initiated at much lower temperature, such as 160 °C. The testing of different sulfuric acid concentrations shows that higher sulfuric acid concentration leads to higher carbohydrate extraction. However, the generation of sugar degradation products, such as HMF, also increases with increased sulfuric acid concentration. The testing results demonstrated that a lower reaction temperature or shorter residence time can reduce the formation of sugar degradation products. The optimal reaction conditions based on current testing results is a temperature of 160°C, LHSV of 4 and a 2.5 wt% acid concentration.

The HTL stage II testing employed the same reaction conditions as previously developed for single-stage HTL conversion, which uses pressure at 3000 psia and temperature at 350°C. The major testing results for the biocrude and other product yields for algae only and algae/corn stover blended feedstock SEQHTL stage II processing are shown in Figure 8. The solid yield from the blended feedstock is higher than for pure algae feedstock due to more carbon conversion to tar for the former. If this part of carbon can be converted to biocrude, the biocrude yield can be increased to about 57%. Additional testing work is needed to optimize the stage II processing conditions for improving the biocrude yield.

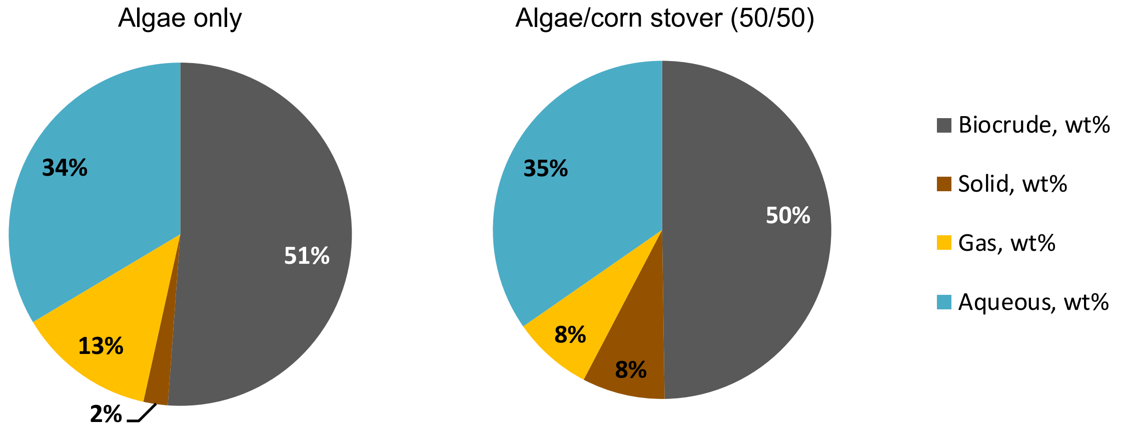


Figure 8. Experimental results for SEQHTL stage II products mass yields (ash-free dry basis)

The major biocrude testing information for the single-stage HTL and SEQHTL with different feedstock (algae only, algae/wood, and algae/corn stover blended feedstock) are listed in Table 3. Compared to single-stage HTL, the biocrude yields from SEQHTL stage II processing is much higher. As investigated by Biller and Ross (2011), the biocrude yield from the lipid fraction is much higher than those from protein and carbohydrates fractions of algae feedstock. With the extraction of carbohydrates and protein at HTL stage I, the residual feedstock has higher lipid content and thus higher biocrude yield than untreated algae, which has been demonstrated in our current testing work. The elemental compositions of biocrude is greatly affected by the feedstock composition. For both single-stage and two-stage sequential HTL, the biocrude from blended feedstock tend to have lower nitrogen, sulfur and iron contents than the pure algae because corn stover used in the blend has low protein and low ash contents. Biocrude from SEQHTL has slightly higher density and viscosity compared to that from single-stage HTL. Also, the moisture content of biocrude from SEQHTL is lower than that from single-stage HTL. This feature is beneficial for downstream upgrading since lower moisture content leads to lower heating requirement in upgrading.

Table 3. Comparison of single-stage HTL and SEQHTL stage II testing results for biocrude product

HTL process			Single stage	Single stage	SEQHTL	SEQHTL	SEQHTL
Feedstock			Algae only	Algae/wood	Algae only	Algae only	Algae/CS
Acid use					No acid	No acid	2.5% acid
Biocrude yield		g/g feed, AFDW	0.4 to 0.43	0.46	0.51	0.49	0.50
C yield to biocrude		%	60%	67%	70%	69%	65%
Biocrude composition		AFDW					
	C	wt%	79%	81%	79%	76%	78%
	H	wt%	10.6%	8.4%	10.1%	9.9%	9.1%
	O	wt%	3.7%	6.3%	6.0%	7.2%	9.6%
	N	wt%	5.6%	3.9%	4.5%	6.1%	3.5%
	S	wt%	1%	0%	0.4%	0.5%	0%
Fe content		ppm	985	566	1495	1497	467
Density		g/ml@40ºC	0.96	1.06	0.98	0.99	1.02 (@60ºC)
Viscosity		cSt@40ºC	295	10,235	646	746	800 (@60ºC)
Moisture		wt%	12.00%	11.60%	2.60%	3.40%	8.50%
Ash		wt%	0.50%	0.10%	0.26%	0.00%	0.80%

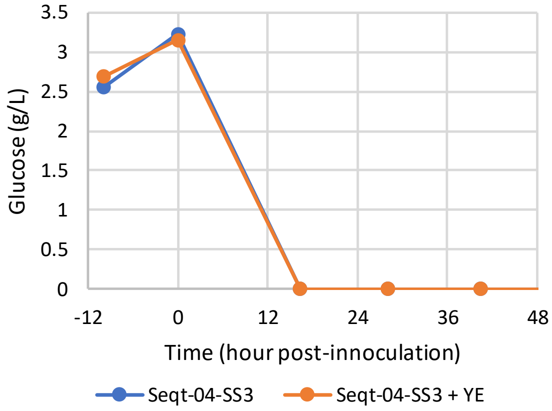
2.2 Bioprocessing of HTL Carbohydrate Extract

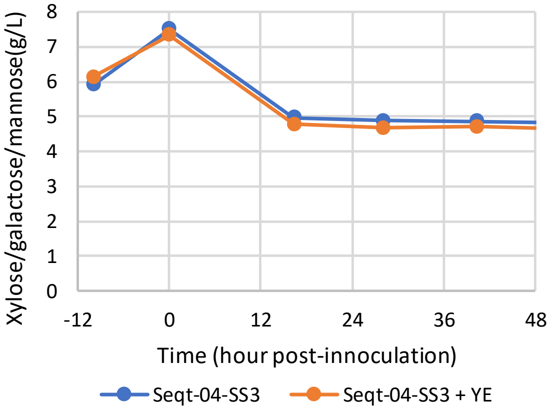
Preliminary screening tests were conducted to evaluate the bioconversion potential of the carbohydrate extracted from sequential two-stage HTL testing of pure algae feedstock. In 2020, more bench-scale testing was conducted using industrial microbes for fermentation to assess their potential for profitable production of commodity chemicals from HTL stage I carbohydrate extract. This testing primarily focused on the fermentation of carbohydrate extract to generate lactic acid (LA).

Different bioprocessing conditions were investigated, including with or without enzymatic hydrolysis prior to fermentation, different lactic acid bacteria, different carbohydrate concentrations, and different alkali options. Anaerobic fermentations of lactic acid producing bacteria (*Lactobacillus pentosus and Lactobacillus rhamnosus*) were conducted in sealed culture tubes to test the direct conversion of HTL stage I carbohydrate extract (CE) from algae only and algae/corn stover blended feedstock. *L. rhamnosus* produced lactic acid and converted both glucose and xylose while producing minimal cell mass without the need for enzymatic hydrolysis or removal of suspended solids from the CE, whereas *L. pentosus* was sensitive to untreated CE and produced more biomass and less lactic acid than *L. rhamnosus*. Although lactic acid production was about 30% higher with enzymatic pretreatment with cellulase, hemicellulase, and amylase, this increase appeared to be solely due to increased glucose availability.

Based on the testing results for different reaction conditions, *L. rhamnosus* bioconversion of CE in batch bioreactor fermentations was conducted. In this work, *L. rhamnosus* inoculum was first grown in flasks on sterilized (autoclaved) CE amended with rich MRS media that is widely used for laboratory cultivation of *Lactobacillus* strains. Bioreactor fermentations were carried out in parallel under anaerobic conditions using a media composed of raw (not autoclaved) CE with pH adjusted to 5.5 via NaOH addition and with or without supplementation with 5 g/L of sterile yeast extract (YE). The cultures were inoculated with the preculture broth at a 1:10 volume ratio with the fresh CE medium in the bioreactor vessels. As shown in Figure 9, glucose was rapidly consumed in both bioreactor cultures (with or without YE supplementation) and was completely exhausted from the medium by the time of the first sampling at 16.3 hours after inoculation (HAI) (productivity = 0.46 g/Lh). The lactic acid concentration at inoculation in both cases was about 7 g/L due to carryover from the inoculum preculture, but then rapidly rose to a near maximum an average of about 14 g/L by 16.3 HAI. The xylose concentration in both cultures declined modestly from about 7.4 g/L to about 4.8 g/L at 16.3 HAI, after which time little if any xylose appeared to be consumed. The measured xylose levels, however, may not reflect the actual xylose levels in the cultures since galactose and mannose co-elute with xylose with overlapping peaks using the HPLC method that was used in this case. Nonetheless, the yield of lactic acid from total consumed sugars was 82%. The overall lactic acid yield is about 0.37 g/g total carbohydrates from the algae/corn stover blended feedstock HTL stage I processing.

As shown in Figure 9, no practical difference was seen in sugar consumption and LA production when comparing the fermentation with or without YE supplementation by using HTL stage I CE from algae/corn stover blends (50/50) conversion. Two explanations appear plausible for the lack of difference: 1) Nutrients and nitrogen in the CE were in excess of what was required to support cell growth and product synthesis such that the carbon substrate (bioavailable sugars) was the limiting input to the culture; or 2) Sufficient nutrients and nitrogen were carried over from the preculture inoculum to be in excess of what was required to fully consumed the available carbon substrates in both the YE(+) and YE(-) cultures. Additional laboratory analysis of samples from theses cultures are needed to answer this question. Considering the preculture broth is only 10% in volume compared to the fresh CE medium in the main bioreactor vessels, the first explanation seems reasonable. It is consistent with the testing results by Ike et al. (1997) and Nagarajan et al. (2020). The testing by Ike et al. (1997) demonstrated that algae biomass was rapidly fermented by *L. amylovorus* without any addition of nutrients, which meant nitrogen, phosphate, and other inorganic components in algae are sufficient for bacterial fermentation. However, for different algae feedstock with different compositions, such as high carbohydrate and low nitrogen algae or blending with non-algae feedstock with such compositions, external nutrients might be needed than those with higher nitrogen contents. Experimental work is needed to decide if external nutrients addition is needed or not for CE from different feedstock HTL conversion.





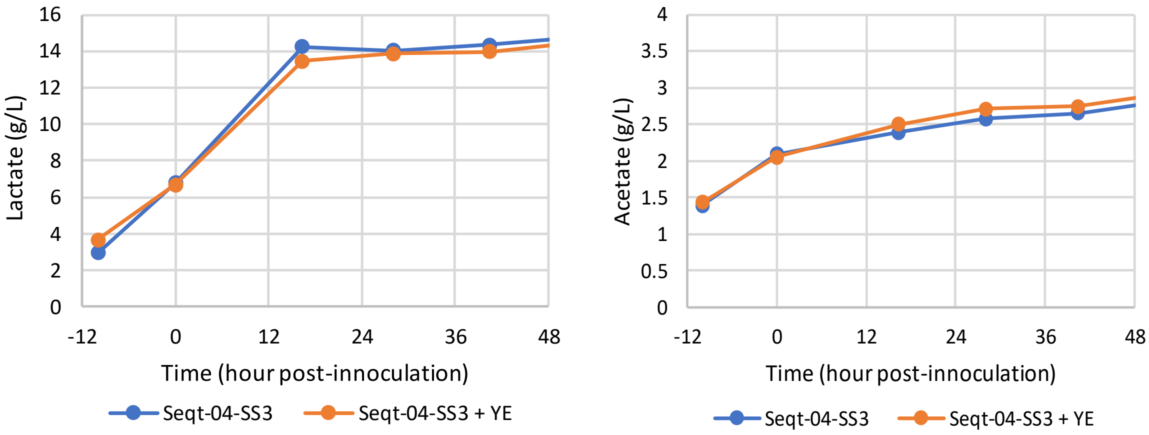


Figure 9. Batch fermentation testing results with *L. rhamnosus* for the algae/CS (50/50) blended feedstock HTL stage I carbohydrate raw extract (not autoclaved) without and with yeast extract (YE) added

Different target chemicals from sugar fermentation and different microorganisms will be tested by the experimental team in future work. As described in Section 3.0, LA is selected as an example target product for this study. With the development of the bioprocessing experimental work, alternative co-product options will be considered in future work.

The above experimental results provide the major design basis for the 2020 SOT case for the algae HTL conversion for biofuel and biochemical production system.

2.3 HTL Aqueous and Nutrient Recycle for Algal Cultivation

In 2020, the algae cultivation team continued the testing work for using nutrients derived from HTL aqueous and precipitated solids recycle streams for algae growth cultivation. The testing work also included growth and harvest of algae for HTL thermal conversion studies.

The growth of several of the most productive algae strains from the DISCOVR (Development of Integrated Screening, Cultivar Optimization, and Verification Research) project was tested in photobioreactors with media derived from HTL waste streams. Strains tested were ones that have made it through the initial stages of the DISCOVR screening pipeline and have some relevance to outdoor open pond cultivation. The best performing DISCOVR strains then compete via sustained areal biomass productivity testing at the Arizona Center for Algae Technology and Innovation (AzCATI) to be the DOE-BETO algae production SOT strain. The testing results of maximum specific growth rates of algae in a laboratory-grade, chemically defined control medium (DISCOVR, 3.5 mM N and 0.09mM P) were compared with a medium that was derived from HTL aqueous and solid waste components (Figure 10). The HTL-derived medium used in these tests replaced all nitrogen, phosphorus, and iron with components derived from the aqueous (nitrogen) and solid (iron and phosphorus) phase HTL processing wastes. It has approximately equivalent nitrogen (45 ppm N) and phosphorus (2.8 ppm P) as the DISCOVR medium, but provided by the HTL-derived aqueous phase (0.642% v/v) and solid extracts (0.228% v/v). A modified f/2 trace metals solution, which omitted iron, was added based on previous maximum specific growth rate testing using HTL-recycled nutrients (Edmundson et al. 2017). The major findings of this testing work are that most of the phylogenetically diverse DISCOVR strains can use the recycled aqueous and N and P nutrients streams for growth with no adaptation required, typically with only minor reductions in maximum specific growth rates, and occasionally (for *Nannochloropsis* and *Porphyridium*) an improvement in maximum specific growth rate. In addition, there is great potential to further improve the productivities for each individual strain via optimizing the growth medium containing HTL recycle streams. Importantly, a slight reduction in maximum specific growth rate does not necessarily translate to a reduction in areal biomass productivity as growth rates in pond cultivation systems are often light limited and do not approach maximum specific growth rates as seen in flask cultivation. These multi-strain testing results resolve a major knowledge gap highlighted by BETO and many other researchers as our previous work only demonstrated that *Chlorella sorokiniana* could tolerate the HTL recycle stream for complete replacement of nitrogen and phosphorus inputs (Edmundson et al. 2017).

Additional cultivation work tested the direct recycle of HTL aqueous wastes from a blended algae and wood feedstock at a 200x dilution ratio on the growth of a top summer DISCOVR strain (*Acutodesmus obliquus* UTEX393). Nutrient recycling biocompatibility with using mixed feedstock combining wood and algae at two blend ratios (50:50, 38:62) were tested. After removing char particles by centrifugation, *A. obliquus* UTEX393 was tolerant to the mixed feedstock HTL aqueous phase at a concentration of 0.5% v/v (200x dilution) with stable growth (Figure 11A) and increased biomass yield compared to the control medium (f/2), indicating that toxicity is not expected from the recycling of nutrients derived from mixed terrestrial feedstock materials (Figure 11B). Further research is needed to optimize nutrient recycle in a mixed feedstock co-liquefaction strategy, but preliminary evidence presented here gives reasonable assurance of a pathway to nutrient recycling and recovery. More details of the HTL-derived medium compositions for the algae HTL screen testing will be provided in our manuscripts, which are in preparation.

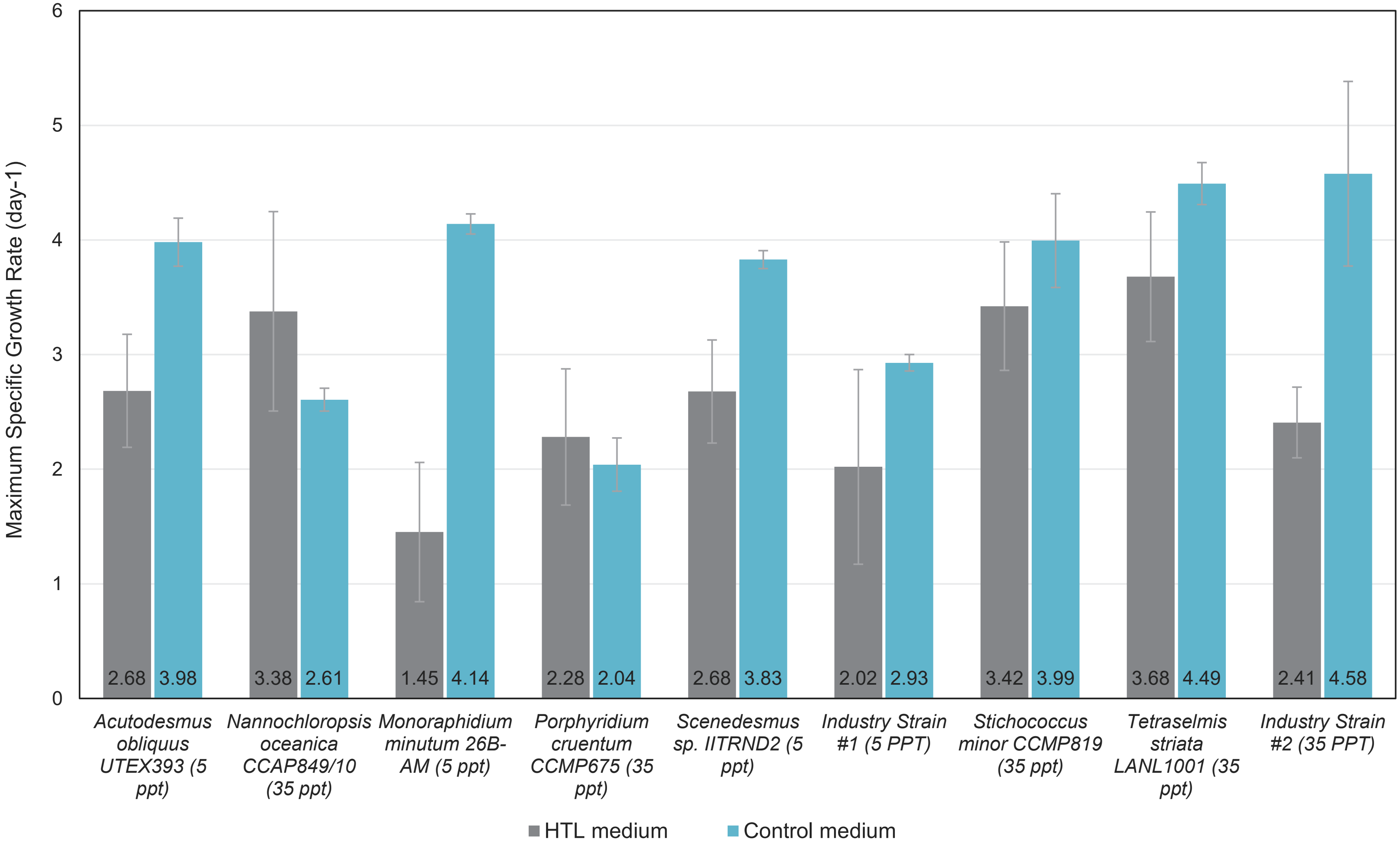


Figure 10. Maximum specific growth rates of algae in control media (DISCOVR) and HTL-derived media. Error bars represent the standard error of the mean, n= >3, except for *Monoraphidium minutum* 26B-AM, n=2.

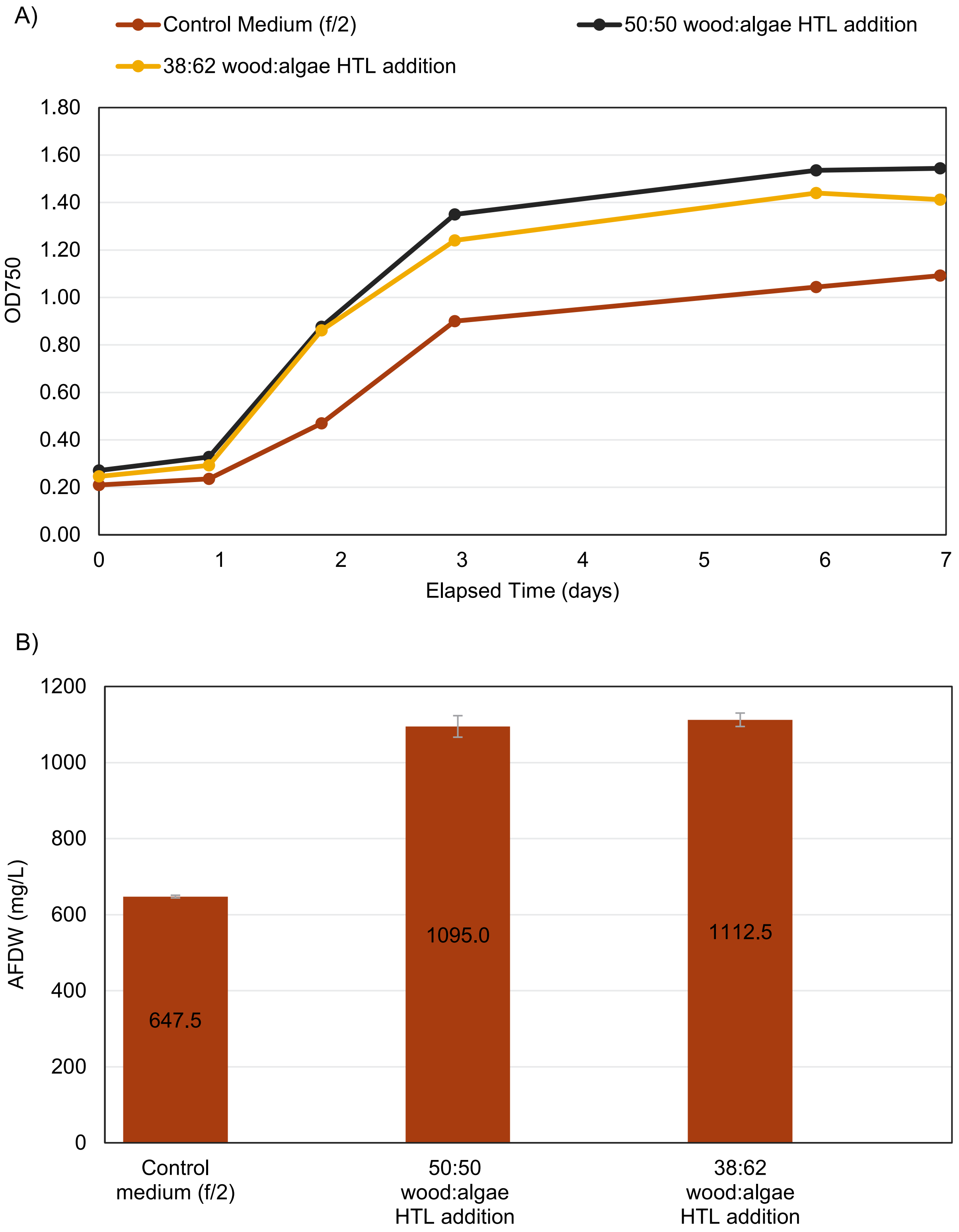


Figure 11. Biocompatibility tests showing the **A)** growth curve and **B)** biomass yield after seven days for *Acutodesmus obliquus* UTEX393 with additions of HTL aqueous phase from different wood:algae feedstock blends.

3.0 Process Design and Simulation

This section describes the major process design assumptions and simulation details.

3.1 Feedstock

Algae productivity varies by seasons, thereby driving variability in production rates to the conversion plant. To maintain a constant feedstock flow rate to the HTL conversion plant, one can either use algae drying or wet algae storage during high-productivity seasons for later use or blend in non-algae biomass feedstock in low-productivity seasons to maintain stable conversion capacity. Compared to drying and storing algae for later use, blended feedstocks have the following advantages: elimination of the extra cost for algae drying in summer/spring seasons, increased annual plant throughput, and reduced feedstock cost by introducing a lower cost feedstock. Considering these advantages for using blended feedstock, PNNL has conducted HTL testing with algae blending with wood and other non-algae feedstock (Zhu et al. 2020). Effective feedstock conversion to biocrude has been demonstrated by this work. The algae with corn stover supplement in non-summer seasons is assumed to be the feedstock in this study. Corn stover demonstrated higher carbohydrates extraction than wood in prescreening tests and thus is assumed to be the supplemental feedstock is this study. The 2020 SOT seasonal algae flow rates to conversion plants and the associated minimum biomass selling price (MBSP) for dewatered algae (80 wt% moisture) for a 5000-acre open pond model from NREL inputs are shown in Table 4.

Table 4. Algae biomass seasonal productivity and minimum biomass selling price (MBSP) encompassing growth, harvest and dewatering from NREL FY20 SOT

Seasonal flow rates to the conversion facility (kg/hr, AFDW)	Summer	Fall	Winter	Spring	Annual Average	MBSP ($/ton, AFDW) - 20 wt% solid
Ponds with Florida-based evaporation	26,376	12,520	6,946	15,406	15,312	603 (unlined); 772 (lined)
Ponds with ASU-based evaporation	26,376	12,520	6,946	15,406	15,312	683 (unlined); 853 (lined)

The conversion plant throughput in this study matches the algae production rate in summer, which has the highest productivity. For seasons with lower production rates, corn stover is added until the summer flow rate is met to maintain a constant plant capacity for all seasons. Based on the case of algae ponds with Florida-based evaporation, the feed flowrates of algae and supplemental corn stover to the conversion plant at seasonal and annual average basis are calculated, as shown in Figure 12. The annual average feedstock flow rate is 698 U.S. ton/d at AFDW basis, equal to the summer algae flow rates. The annual average mass ratio for algae/corn stover feedstock is 58/42.

In this study, based on the HTL stage I testing, the feedstock slurry feed moisture is required to be 90% or above for better pumpability and heat transfer. Based on the NREL algae farm model (Davis et al. 2016), dewatered algae containing 90% moisture is approximately 2% lower in cost compared 80% moisture algae, due to lower dewatering energy consumption and capital cost. Therefore, the dewatered algae MBSPs provided by NREL (Table 4), which are for algae with 80% moisture, were adjusted with a 2% reduction, which results in a $590/ton AFDW cost for the baseline case (unlined ponds with Florida-based evaporation) of this study. The 2019 SOT corn stover feedstock cost, $81.37/dry ton (or $85.65/ton at AFDW basis) is assumed, which includes the cost for pretreatment, such as milling (DOE 2020).

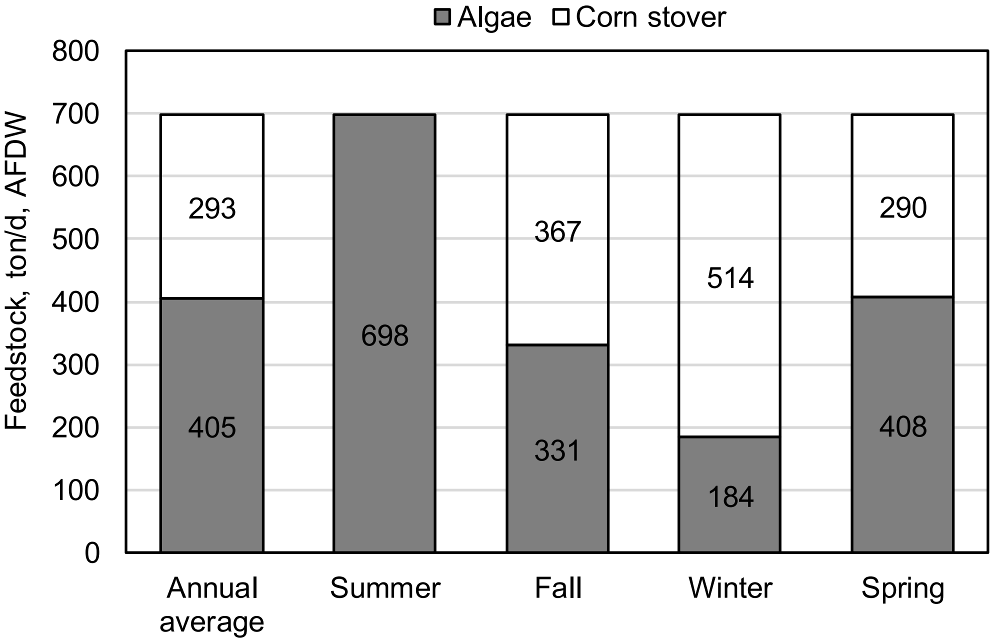


Figure 12. Feedstock seasonal and annual average flow rates.

Table 5. lists the elemental compositions and higher heating values (HHVs) of microalgae and supplemental corn stover tested. This data was used directly in the process modeling to specify the feedstock compositions assumed in this study. The tested algae strain (*Scenedesmus sp.*) demonstrated high productivity in our algae cultivation testing with using recycle HTL aqueous stream and therefore it is assumed as the feedstock in this study. The HHVs for algae and corn stover are estimated by using the Boie equation (Annamalai *et al.* 1987).

Table 5. Elemental and biochemical compositions for microalgae and supplemental feedstock in non-summer seasons

Feedstock	Microalgae	Corn stover (supplement to algae in non-summer seasons)
Elemental analysis, wt% ash free dry weight (AFDW)		
Carbon	53.5	49.1
Hydrogen	7.11	6.0
Oxygen	28.6	44.2
Nitrogen	8.41	0.67
Sulfur	2.38	0.0
Total	100	100
Ash, wt% dry basis	10.5	6.91
Phosphorus (in ash)	1.12	0
Biochemical composition, wt% AFDW		
Carbohydrates	19.8	93.8
Fat	7.37	0.69
Protein	72.9	5.55
Total	100	100
Higher heating value, Btu/lb, AFDW	10,430	8,150

Compared to previous work for algae-only systems with consistent feedstock flow rate and composition for different seasons, this study needs to consider the seasonal variations in feedstock blend ratios and the corresponding variations in feedstock compositions. To facilitate analysis of such a system, a key consideration is to specify input parameters accommodating seasonal variations in algae production rates. The blend ratios for each season are specified based on the algae seasonal production rates and their differences between summer and non-summer seasons. The feedstock compositions in different seasons are calculated based on the mass blend ratios of algae/corn stover and the compositions for algae only and corn stover only. With the parameters for each season specified, the parameter assumptions on an annual average basis are calculated and input to the process simulation to estimate the system mass and energy balance.

3.2 Hydrothermal Liquefaction

The major design assumptions for the two-stage sequential HTL process were developed based on the best available testing results. The details of process design and simulation are described in this section. The capital cost estimation for this process is also summarized.

3.2.1 Process Design and Simulation

A simplified process diagram for the two-stage SEQHTL conversion is shown in Figure 13. The blended feedstock slurry containing 10 wt% solid (AFDW basis) is mixed with sulfuric acid at 2.5 wt% (whole slurry basis) and pumped to 250 psia. The slurry is preheated by the SEQHTL stage I and then the stage II outlet streams to 160 °C. The heated stream is sent to the stage I HTL reactor. In this reaction step, the carbohydrate in the feedstock is partially extracted. The product slurry is pH-adjusted with sodium carbonate from pH 0.5 to 4.5, which is required for the stage II HTL reaction. The product stream is then cooled by the inlet stream and depressurized to release CO_2, which is sent to the downstream bioprocessing process. The cooled product stream is filtered by a vacuum filter to form a wet residual solid steam and a carbohydrate extract stream. The carbohydrate extract stream is sent to bioprocessing for co-product generation. The filtered wet cake with up to 28 wt% dry solid is mixed with the cell biomass from the bioprocessing process. Makeup water, recycled from the bioprocessing condensate, is added to the residual solid stream to dilute it to about 20 wt% solid (dry basis), which is based on the pumpable solid content constraint demonstrated in the bench-scale testing (Note: It is anticipated that higher solids concentration can be pumped in scaled up HTL systems). The slurry is then pumped to 3,000 psia and heated by hot oil to 350 °C. The hot slurry is sent to the stage II reactor. In this step, the slurry feed is converted, and the solid part (primarily mineral ash and char) is separated from the product stream. The solid product is assumed to be sent to an acid digestion unit for nutrient recovery, mainly phosphorus. After acid digestion, the digestate containing recovered phosphorus compounds is recycled to the algae farm. The remaining hot liquid product stream is cooled by heating the heat transfer oil and the stage I inlet stream. The cooled product stream is then depressurized and separated to biocrude, aqueous and gas phases by a three-phase separator. The aqueous phase (including dissolved organics) is cooled by an air cooler and then directly recycled to the algae farm together with the digestate from the solid acid digestion unit. The gas stream from stage II is assumed to be used as fuel gas for process heating and hydrogen generation. The biocrude is then sent to the upgrading process for final fuel generation.

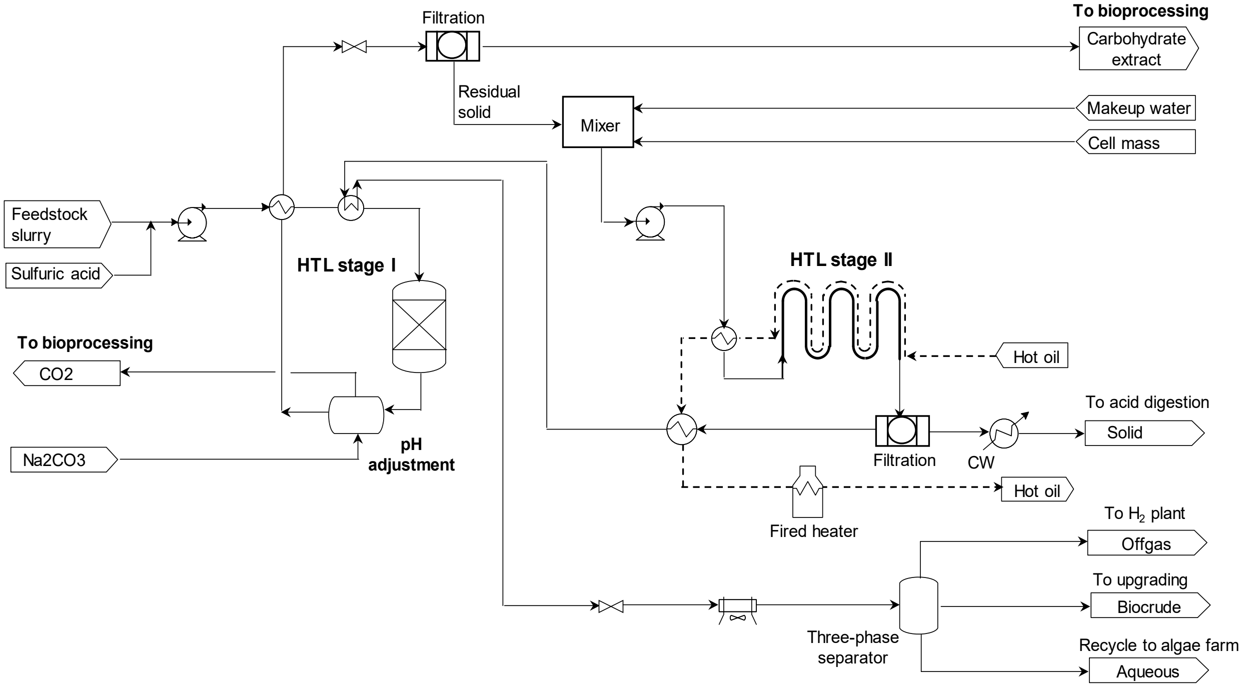


Figure 13. Process flow diagram of two-stage SEQHTL process.

Table 6 lists the major process assumptions (annual average basis) and the corresponding experimental results for two-stage SEQHTL process of this study. The primary purpose of stage I is to extract carbohydrate fraction from the feedstock. Therefore, the reaction conditions, including a temperature at 160 ºC, 2.5 wt% sulfuric acid addition and a LHSV of 4 are selected based on the best available experimental results (see section 2.1). Based on the testing configuration, the stage I HTL reactions are performed in the liquid state at the reaction conditions and it is simulated by a RSTOIC unit block in the model. Based on the testing results, the stage I residual solid product is simulated by using a non-conventional compound and its elemental compositions are specified based on the related testing results. The compounds in the stage I extract stream mainly include acetic acid, lactic acid, ethanol, butanol, sugar monomers and oligomers, sugar degradation products, and amino acids from protein extraction. Their mass yields are specified in the model based on the High Performance Liquid Chromatography (HPLC) testing results. The sugar monomers are represented by using two compounds, glucose and xylose, in the model. The compound xylose is used to represent all the other sugar monomers, except glucose, including xylose, galactose, mannose, fructose and arabinose, presented in the stage I extract stream based on the testing results for algae/corn stover blended feedstock. The testing results demonstrated that about 40% to 65% of total feed nitrogen is extracted to the stage I carbohydrate extract steam and it results from the protein extraction. The major extracted nitrogen compounds are simulated by using amino acids compounds in the model.

The SEQHTL stage II operating conditions are essentially the same as those for a single-stage HTL reactor. The stage II biocrude yield for the blended feedstock is assumed to be 0.51 g/g solid feed to stage II, as supported by the experimental data. It is also assumed that the cell mass from the fermentation of the stage I carbohydrate extract is recycled and combined with the stage I residual solid to be processed by HTL stage II for biocrude generation. Based on the simulation, the cell mass amount is lower than 2 wt% of the stage I residue solid and thus it is assumed that the recycle of cell mass to stage II increases the solid feed mass flow, but does not change the biocrude yield at g/g solid feed basis. The stage II

Table 6. Major design assumptions and experimental results for two-stage SEQHTL process.

SEQHTL process	Model assumptions	Experimental data
HTL stage I		
Solid wt% in feed slurry, AFDW	10	~10
Temperature, °C	160	160
Pressure, psia	250	250
Liquid space hourly velocity (LHSV), L/L/h	4	4
Sulfuric acid addition, wt% of the slurry	2.5%	2.5%
Carbohydrate extraction, % of feed carbohydrates to stage I extract stream	58	Algae only: 80 to 98%; Algae/corn stover (50/50): 49 to 67%; Corn stover: 11 to 32%
Products yields, g/g feedstock, ADFW		
Residual solid	0.57	0.56 to 0.58
Stage I extract	0.43	
Sugar monomers wt% in total extracted carbohydrates	55%	Algae only: 40 to 65%; Algae/corn stover (50/50): 30 to 50% Corn stover: 30 to 45%;
Elemental analysis of residual solid product, wt% AFDW		Algae only; Algae/corn stover (50/50) AFDW normalized
Carbon	59	62; 52
Hydrogen	6.7	8.1; 6.6
Oxygen	28	22; 35
Nitrogen	4.7	7.1; 2.7
Sulfur	0.87	0.5; 4.2 (a)
HTL stage II		
Feed slurry solid wt%, AFDW	20	15 to 19
Temperature, °C	350	350
Pressure, psia	3000	3000
LHSV, L/L/h	3.5	2.6 to 3.5
Products yields, g/g feed to stage II, AFDW		Algae only; Algae/corn stover (50/50)
Biocrude	0.51	0.51; 0.50
Aqueous	0.33	0.34; 0.35
Gas	0.08	0.13; 0.08
Solid	0.08	0.02; 0.08
Elemental analysis of biocrude, wt% dry basis		Algae only; Algae/corn stover (50/50)
Carbon	78	79; 77
Hydrogen	9.2	10; 9.0
Oxygen	8.8	6.0; 9.5
Nitrogen	3.6	4.5; 3.5
Sulfur	0	0.4; 0

(a) The sulfur content of the testing results for algae/CS blended feedstock contains sulfur from sulfuric acid used in the stage I.

reactor is simulated by using a RYIELD unit block in the model. The biocrude product mainly contains C16 to C18 fatty acids and amides, cyclic organics (such as phenols, substituted benzenes and naphthalene), heavy components, and a small fraction of moisture. The compound yield distributions are specified based on the experimental results for products yields and their compositions and meet the inlet/outlet mass and elemental balances. Compared to the biocrude from single-stage HTL, the biocrude from SEQHTL stage II demonstrated higher density based on the testing results. A possible reason is that part of carbohydrates in feedstock have been extracted in stage I and thus the short-chain carbon species, mainly from carbohydrates conversion, in stage II biocrude has less amounts than that of a single-stage HTL without carbohydrates removed, and thus the SEQHTL biocrude has higher amounts of long-chain or heavy compounds. Therefore, in the simulation, although similar compounds used for the single-stage HTL biocrude are assumed, the wt% of heavy compounds are increased to match the higher density for the biocrude from SEQHTL.

Based on the testing results, 50% to 60% ash from the feedstock is extracted in SEQHTL stage I and goes to the carbohydrate extract stream. Therefore, in the model, 60% of the phosphorus (P) of the feedstock ash is assumed to be extracted and flows to the bioprocessing unit. The remaining P going to stage II and all of it goes to the solid product. For the solid acid digestion, 90% of P in the solid stream is assumed to be extracted and recycled to the algae farm together with the acid digested product stream. As P element is not simulated in the process model, P element balance and sulfuric acid consumption for the solid acid digestion are calculated in the cost model based on the experimental results.

3.2.2 HTL Capital Cost

The SEQHTL stage I reactor cost is estimated by using Aspen Process Economic Analyzer (APEA) with size calculated based on the inlet flowrate and the assumed space velocity. Considering the HTL stage I operates completely at liquid state with moderate pressure level, high LHSV and low pH environment, an agitated tank with glass-lined carbon steel material is assumed to be used as the stage I reactor. The cost for the stage I solid/liquid separation is also estimated by using APEA for a vacuum filter. The stage II capital cost are mainly based on a detailed engineering analysis with vendor budgetary estimates from for a wood HTL system under the National Advanced Biofuels Consortium (NABC) (Knorr et al. 2013). The original NABC cost data were scaled to the feedstock flowrate of this SOT case. The stage II reactor is a jacketed serpentine pipe with heating medium in the annular space and this design was based on the heating requirement of the reaction and also its high operating pressure condition. This is similar to a double pipe heat exchanger or the serpentine reactors used for low density polyethylene manufacturing (Exxon 2014). The metallurgy of the NABC cost data (316 stainless) is the same as that used in the experimental work. The cost of acid digestion process is estimated by using APEA and the main reactor is assumed to be an agitated glass-lined tank.

The capital costs for the SEQHTL system are shown in Table 7. A single-stage HTL process capital cost is also listed for comparison purpose. Both HTL processes assumed the same feedstock flow rates. Since the single-stage HTL reactor has the same operating temperature and pressure as the stage II of the SEQHTL, the single stage HTL reaction system capital cost is listed together with the SEQHTL stage II reactor. The two HTL processes have similar capital cost. For the SEQHTL stage I, the heat exchange and liquid/solid separation cost contributed over 50% of the stage I capital cost and these costs reduced the cost advantages resulting from the moderate reactions conditions of stage I reactor compared to a single-stage HTL reactor. For the SEQHTL stage II, its feed is the residual solid from stage I processing, which has much lower flow rates than the unprocessed feedstock, and thus it leads to a much lower capital cost for the stage II than the one for the single-stage HTL with unprocessed feedstock as the feed. Therefore, the extra cost for stage I processing and the lower cost for stage II results a similar capital cost for SEQHTL compared to a single-stage HTL with the same feedstock assumptions.

Table 7. Capital cost for SEQHTL and single-stage HTL process.

Installed cost (million $)	SEQHTL	Single-stage HTL
SEQHTL stage I reaction system (pumps, heat integration, stage I reactor, and filter)	10.3	n/a
SEQHTL stage II or single-stage HTL reaction system (pumps, heat integration, reactor, products separation)	29.6	38.2
Hot oil system	2.64	3.39
Solid product acid digestion	0.96	1.48
Total	43.5	43.0

3.3 Bioprocessing of HTL Stage I Carbohydrate Extract

Fermentation technology has been predominantly used in industrial production of LA, especially for pure optical LA isomers (Vaidya et al. 2005). Microorganisms commonly used for industrial production of LA are lactic acid bacteria (LAB). Fermentation conditions are typically at 28 to 62 °C with a pH of 5 to 6.5 (Vaidya et al. 2005; Komesu et al. 2017). LA fermentation from different sugars, including glucose, cellobiose, sucrose, xylose, and arabinose, have been investigated with demonstrated yields ranging from 0.8 to 0.97 g LA/g sugar and productivities ranging from 0.3 to 5.4 (mostly over 1) g/L/h (Komesu et al. 2017; Talukder et al. 2012; de Oliveira et al. 2018). The majority of LA production uses LAB, but fungi and yeast have also been tested for LA production as yeasts and fungi are more tolerant to acid than LAB (Komesu et al. 2017; Manandhar and Shah 2020; de Oliveira et al. 2018; Sauer et al. 2010). Depending on the microorganism used, LA fermentation conditions can be anaerobic/microaerobic for bacteria or aerobic for fungi and yeast. Research on LA fermentation with flexible reaction conditions and alternative microorganism choices provides a good basis for further developing the algae SEQHTL stage I carbohydrate extract fermentation technology.

Although LA fermentation using sugar-rich feedstock has been widely investigated, research on fermentation of microalgae or their derivatives to produce LA is still very limited. Nguyen et al. (2012) reported the production of L-lactic acid by *Lactobacillus paracasei* from a substrate of the freshwater microalga *Hydrodictyon reticulum*. They investigated a simultaneous saccharification and fermentation (SSCF) process with microalgae slurry as the substrate and the optimal concentration is 80 g/L algae with 47.5% reducing sugars. The SSCF at 45 °C produced 37.11 g/L of LA with a productivity of 1.03 g/l/h and an optical purity of 95.7% for L-LA. Talukder et al. (2012) investigated LA production and lipid extraction from *Nannochloropsis salina* using *Lactobacillus pentosus*. In their testing, acid-pretreated algae were mixed with hexane for lipid extraction and then filtered. The liquid phase after filtration was fermented for 48 h resulting in a 96% conversion of sugar (xylose and glucose) with an LA yield of 0.9 g/g converted sugars and a productivity of 0.45 g/L/h. Nagarajan et al. (2020) investigated the LA fermentation of renewable feedstocks with poly(vinyl alcohol)-Immobilized *Lactobacillus plantarum* 23. They demonstrated batch fermentation testing of microalgae (*Chlorella vulgaris* ESP-32) hydrolysate with a final LA concentration of 40.3 g/L, a maximum productivity of 6.72 g/L/h, and yield of 0.97 g/g. Their continuous fermentation testing showed a productivity of 12.6 g/L/h. The use of microalgae hydrolysate as the carbon source presented the highest LA productivity among all the renewable feedstocks tested in their study. Collectively, the above studies show microalgae carbohydrates can be a promising carbon source for LA fermentation.

Based on the above studies for LA fermentation by using microalgae as the feedstock, PNNL testing team developed LA fermentation by using the carbohydrates extract stream from the SEQHTL stage I processing of algae/corn stover blended feedstock. This type of carbon source used for LA fermentation has not yet been reported by other investigators. As the experimental work is still in very early phase, the current testing conditions have not been optimized for LA generation and productivities. Additional work is needed to improve the performance. The process design of the fermentation is based on the currently best available testing information. Since we did not do the testing for LA product purification, the process design of this process is mainly based on literatures. The details of process design and cost estimation are described in the next section.

3.3.1 Process Design and Simulation

The process flow diagram for bioprocessing is shown in Figure 14. The HTL stage I carbohydrate extract stream with 3.7 wt% carbohydrates is cooled and sent to a batch anaerobic fermentation process. In this step, the monomer sugars are converted to LA and a small fraction is converted to cell mass. Sodium hydroxide (NaOH) together with sodium bicarbonate ($NaHCO_3$) are added to control the pH value of the fermentation process and the LA product is converted to sodium lactate ($NaC_3H_5O_3$). After fermentation, the broth is sent to an ultrafiltration step to remove cell mass. The removed wet cell mass is assumed to be recycled to the stage II of HTL process for additional biocrude generation. The permeate stream from the filtration step is concentrated by using a mechanical vapor recompression (MVR) vacuum evaporation unit to increase the concentration of lactate. This stream is further concentrated in a vacuum crystallization step to move large portion of salts, mainly sodium sulfates resulting from ash extraction and sulfuric acid use in the HTL process. The crystalized salts are assumed to be disposed as solid waste. The lactate in the concentrated stream is then converted to LA by adding compressed CO_2 in the acidification step. Sodium bicarbonate ($NaHCO_3$) is generated in this step and it is filtered from the stream and recycled to the fermentation reactor as a makeup for pH control. The raw LA stream is sent to a reactive distillation process. In the first column, the LA is converted to ethyl lactate (LA ethyl ester) via esterification reaction with ethanol. The LA ester is removed from the top of the column and the impurities, mainly including remaining salts and unconverted sugars are removed from bottom. The overhead stream from the esterification column mainly containing ethyl lactate and water is then sent to a hydrolysis column. In this column, hot water is injected to convert the ethyl lactate to ethanol and LA. Ethanol and water are removed from the overhead stream of the column and high purity LA is collected at the bottom stream. The ethanol and water steam are then sent to the recovery unit to separate ethanol from water via normal distillation and the separated ethanol is recycled back to the esterification column. The high-purity LA is further concentrated to 88 wt% in a vacuum evaporator and then cooled to be sold as the final co-product.

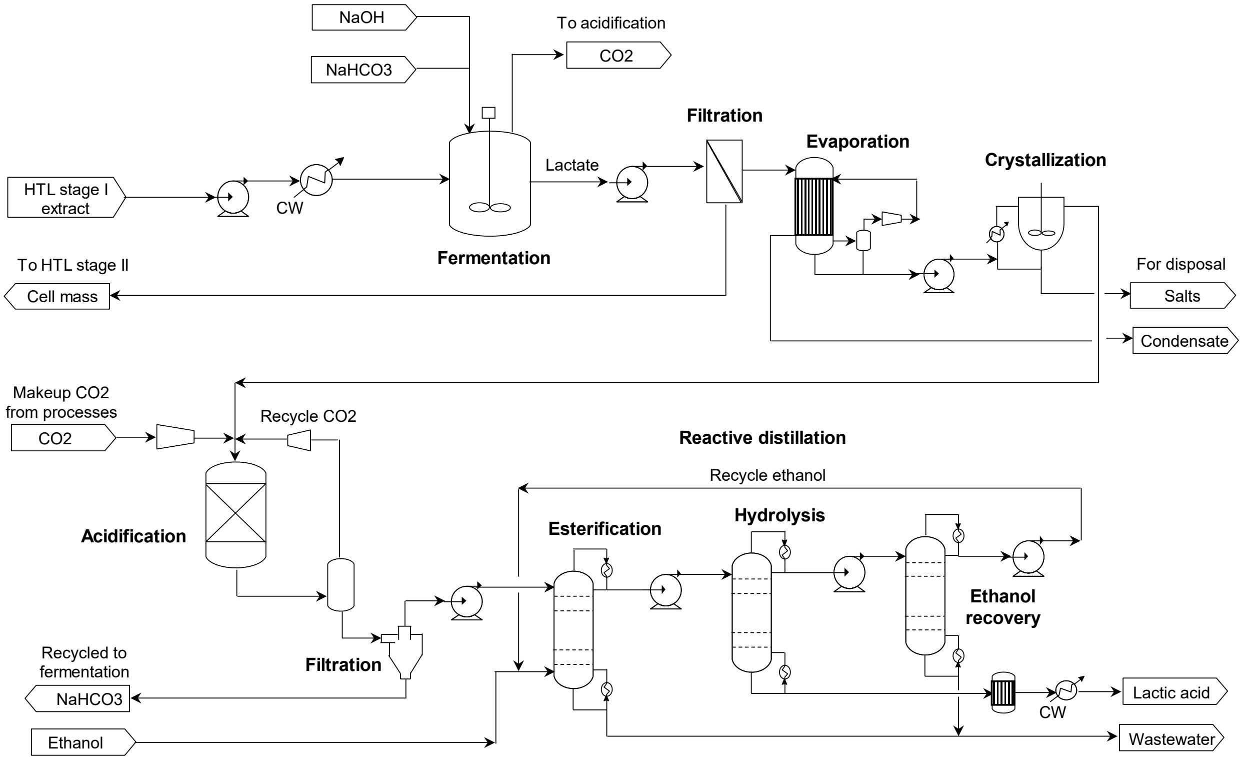


Figure 14. Simplified process flow diagram of the bioprocessing of HTL stage I carbohydrate extract

Table 8 lists the process assumptions for the conversion of carbohydrates to lactate process. The design of the fermentation process is mainly based on our bioprocessing testing results, which has been described in Section 2.2. The HTL stage I carbohydrate extract stream initially has 30 g/L total carbohydrates based on the process simulation. Sugar monomers contained in the SEQHTL stage I extract are primarily glucose, xylose, mannose, galactose, and arabinose based on the testing information. The microorganism, *Lactobacillus rhamnosus*, was tested for the fermentation. For pH control, NaOH was used and in the simulation, NaOH with $NaHCO_3$ as a makeup base is assumed. The $NaHCO_3$ is recycled from the downstream product purification process. Based on the LA production rate and the testing productivity results , the residence time in the fermenter is about 22 hrs. Compared to typical LA productivities in the literature, which ranges from 0.3 to 5.4 (mostly over 1) g/L/h (Komesu et al. 2017; Talukder et al. 2012; de Oliveira et al. 2018), the LA productivity, 0.46 g/L/h, achieved in our testing is close to the lower bound and thus there is great potential to optimize the productivity in future work. For LA fermentation from different sugars, the conversion efficiency ranges from 85 to 100% for glucose, 30 to 93% for xylose, 50 to 100% for arabinose, and 83 to 90% for cellobiose based on our bioprocessing testing results and literatures information (de Oliveira et al. 2019, Ma et al. 2016, Nguyen et al. 2012). Compared to the literature values, the testing work showed a much lower LA conversion efficiency for sugar monomer other than glucose, mainly including xylose, galactose and mannose. Therefore, future testing work is needed to improve the productivity and the LA conversion of xylose and other sugar monomers except glucose. Based on the testing work by Ma et al. (2016) and de Oliveira et al. (2019), *B. coagulans* is potentially the most promising choice, which has a high conversion of xylose to LA and also a bio-detoxification function for removing HMF and furfural during fermentation.

The bioprocessing testing demonstrated that no external nitrogen source is needed for the main fermentation. Based on SEQHTL testing work, the algae SEQHTL stage I extract contains about 40 to 65% of total feed nitrogen and most of it is organic nitrogen comes from protein in the feedstock. It also contains phosphate and other inorganic components extracted from the ash part of algae. These extracted nitrogen and phosphorus compounds act as nutrients for the LA fermentation, which has been verified by the bioprocessing test. As shown in Section 2.2, fermentation testing without use of external nitrogen source has no significant impact on performance compared to testing with additional YE. Therefore, in this study, it is assumed that no external nutrients are used for the main fermentation.

Table 8. Major design assumptions for the fermentation process of SEQHTL stage I carbohydrate extract

Processes	Model assumption	Experimental data
Fermentation	Batch/anaerobic	Batch/anaerobic
Initial sugar loading, wt%	2.7	2 to 4
Microorganism	*Lactobacillus rhamnosus*	*Lactobacillus rhamnosus*
Temperature, °C	37	37
pH control	NaOH and $NaHCO_3$, pH = 5.5	NaOH, KOH; pH = 5 to 5.5
Productivity, g/L/g	0.46	0.46
Sugar monomers conversion % and selectivity	Glucose: 100%; Xylose (representing other sugar-monomers): 36%; LA selectivity: 82% of consumed sugars	Glucose conversion: 100%; Xylose/galactose/mannose conversion: 36% (overall); LA selectivity: 82% of consumed sugars Overall LA yield: 0.37 g/g total carbohydrates
Nutrients	No external nutrients used for main fermentation	No significant changes in LA yields with/without external nutrients
Seed culture preparation	Anaerobic	Anaerobic
Inoculum level, vol% of fermentation broth	10	10
Residence time, h	12	12
Nutrients	15 g/L CSL	5 g/L yeast extract

The detailed sugar fermentation yields assumptions are specified based on our current experimental results and listed in Table 9. In the simulation, the compound glucose is used to represent glucose and the compound xylose is used to represent other sugar monomers except glucose. The major fermentation product is LA with acetic acid as the major byproduct based on testing results. A small fraction of sugars is assumed to be converted to cell mass. The cell mass formula is assumed to be $CH_{1.8}O_{0.5}N_{0.2}$ based on the average biomass formula developed by Roels (1980). It is assumed that amino acid from the protein extraction by the SEQHTL stage I processing of algae is the major organic nitrogen source for the cell mass formation. This assumption is consistent with our testing work and the findings by Nagarajan et al. (2020).

Table 9. Fermentation reactions assumption.

Reaction	Reactants	% of Reactants Converted
Glucose ($C_6H_{12}O_6$) → 2 LA ($C_3H_6O_3$)	Glucose	88
Glucose ($C_6H_{12}O_6$) + 3 amino acid → 15 cell mass + 4.33 H_2O	Glucose	5
Glucose ($C_6H_{12}O_6$) → 3 acetic acid ($C_2H_4O_2$)	Glucose	7
3 Xylose ($C_5H_{10}O_5$) → 5 LA ($C_3H_6O_3$)	Xylose	24
Xylose ($C_5H_{10}O_5$) + 2.5 amino acid → 12.5 cell mass + 3.61 H_2O	Xylose	5
2 Xylose ($C_5H_{10}O_5$) → 5 acetic acid ($C_2H_4O_2$)	Xylose	7

The bioprocessing testing used 10% (v/v) of the carbohydrate extract stream mixing with de Man, Rogosa and Sharpe (MRS) broth for the seed growth medium. The MRS broth contains glucose, YE, and other nutrients. Although most reported fermentation work used MRS broth only for seed culture preparation, Aulitto et al. (2019) found using wheat straw hydrolysate as seed growth medium has the microorganism pre-adaptation advantage with higher LA productivity compared to the hydrolysate-free medium. Based on the testing work, a 10% (v/v) carbohydrate extract stream is assumed as the seed growth medium in the model. In addition, CSL is assumed to replace YE in MRS broth used in the testing as the nutrient source for seed growth. Studies indicated that although higher CSL concentration than YE is needed to achieve similar LA yields, the cost for using CSL is still much lower than using YE (Lee 2005). The possible reason for higher CSL usage is the lower amino nitrogen in CSL than YE and/or inhibition of cells growth by the impurities in CSL (Tan et al. 2016; Lee 2005). The CSL composition is assumed to be 50% water, 25% LA, and 25% protein based on Humbird et al. (2011). Based on the literatures, a 15 g/L CSL is assumed to be used to replace 5g/L YE used in the testing.

The process design and simulation for the product purification are based on literatures (Vener and Thompson 1950, Dubois and Fouache 2002, Manandhar and Shah 2020, Cellulac 2020, Baniel et al. 1996, Barve et al. 2011). An ultrafiltration step is assumed to be used to remove cell mass and protein, which is assumed to have a permeate flux at 67 $kg/m^2/hr$ based on Davis et al. (2018). Wet cell mass is assumed to be removed from the fermentation outlet stream and sent to the HTL stage II for biocrude generation. The permeate from ultrafiltration containing 80% water is first concentrated to have 50 wt% water by using a vacuum evaporation unit. For the large-scale system assumed in this study, MVR vacuum evaporation is used to simulate the evaporation process and its simulation is based on literatures (Monceaux and Kuehner 2009; Davis et al. 2018). Using MVR can reduce the fresh steam use for evaporation by recompressing and recycling the evaporation vapor to heat the inlet stream. The stream after evaporation has about 30% sulfate salts, mainly sodium sulfate formed from sulfuric acid and sodium carbonates use and ash extraction in SEQHTL stage I, and this high concentration facilitates the downstream crystallization operation. The solubility of Na_2SO_4 in water for the crystallization process is specified based on Vener and Thompson (1950). It is assumed 90% of the sulfate salts is crystallized and sold as a byproduct in this system. The mother liquor from the crystallizer containing about 30 wt% lactate is sent to a reactive distillation system to further purify the product. For the acidification unit, compressed CO_2 is assumed to be used to convert lactate to LA and generate sodium bicarbonate (Cellulac 2020):

$$C_3H_5NaO_3 + CO_2 + H_2O \xrightarrow{\qquad} C_3H_6O_3\ (LA) + NaHCO_3 \tag{1}$$

Although many methods can be used for LA purification, considering the complicated impurities of the raw LA stream, such as salts, sugar and organic impurities, reactive distillation is selected in this study to achieve both high final product purity and feasible application for large scale system. The design of the reactive distillation is based on literatures (Manandhar and Shah 2020; Gezae Daful and Görgens 2017; Su et al. 2013). In this process, ethanol reacts with LA to form ethyl lactate in the first step. Ethyl lactate is very volatile and is easily separated from the heavy impurities, which are removed from the bottom of the column. In the second column, the ethyl lactate reacts with hot water and is hydrolyzed back into LA and ethanol. LA is collected in the bottom stream of the hydrolysis column and the ethanol-water solution is collected in the overhead stream. The ethanol-water solution is then distilled to separate ethanol from water and the ethanol stream is recycled to the first esterification column. The reactions for the esterification and hydrolysis processes are represented as (Gezae Daful and Görgens 2017):

$$C_3H_6O_3\ (\text{LA}) + C_2H_6O\ (\text{ethanol}) \underset{\text{Hydrolysis}}{\overset{\text{Esterification}}{\rightleftarrows}} C_5H_{10}O_3\ (\text{ethyl lactate}) + H_2O \tag{2}$$

The LA stream from the hydrolysis column is sent to a vacuum evaporator to concentrate the stream to have 88 wt% LA. The final LA product has over 99% purity and meets purity requirement for a commercial LA product.

3.3.2 Bioprocessing Capital Cost

The major equipment costs in this process – including enzyme hydrolysis, fermentation, pumps, heat exchangers, crystallizer, tanks, filters, evaporators and boilers – are estimated by using APEA with sizing inputs based on the process simulation results. The capital costs for membrane separation processes are estimated by scaling the base cost from Davis et al. (2018) with new sizes from the process simulation results. Part of the cost estimation for the reactive distillation process is based on the information from Su et al. (2013). Auxiliary equipment not simulated in the model, such as hold and storage tanks and some pumps, is added to the equipment list based on Davis et al. (2018). The capital costs for LA production and purification processes are listed in Table 10. Although LA fermentation has been commercialized, algae for LA fermentation is still at lab-scale scale. There are expected cost uncertainties when applying this technology to large-scale systems. A 25% equipment contingency is assumed to address the expected uncertainties in the cost when applying these technologies to large commercial scale plants.

Table 10. Capital cost for the bioprocessing of HTL stage I extract.

Process	Installed Cost (million $ in 2016 U.S. dollars)	Source
Fermentation	14.9	APEA cost estimation, Davis et al. (2018)
Product purification	25.2	APEA cost estimation, Davis et al. (2018); Su et al. (2013).
Contingency, 25% of the total cost	10.0	User assumption
Total	50.1	

3.4 Biocrude Upgrading and Other Processes

Other processes in the system process simulation also includes biocrude upgrading, hydrogen generation, steam cycle and cooling water processes.

Algae HTL biocrude can be upgraded via catalytic HT to remove heteroatoms such as oxygen, nitrogen, sulfur and iron, while increasing the hydrogen-to-carbon ratio of the HTL biocrude (Albrecht et al. 2016). Upgrading of biocrude can improve its quality for application as a transportation fuel blendstock or a standalone fuel after further processing (e.g., isomerization) to meet all fuel specifications. Currently, only single-stage HTL biocrude HT testing has been conducted. However, based on suGGEstions of the biocrude upgrading experts, there are no obvious risks or reactions conditions changes for upgrading the SEQHTL biocrude compared to the single-stage HTL one. Therefore, in our simulation, we used the same assumptions for the upgrading conditions and hydrotreated oil compounds as the single-stage HTL system (Jones et al. 2014a&b, Zhu et al. 2020). The hydrotreated oil yield is assumed to be 0.86 g/g dry biocrude feed, which is the average value of the range of 0.83 to 0.90 g HT oil/g dry biocrude for a single-stage HTL system (Zhu et al. 2020). The yields for gas and aqueous products are adjusted to meet the inlet/outlet elemental and mass balances. In the biocrude upgrading process, the biocrude is pretreated in a guard bed to remove iron and thus prevent plugging in the downstream hydrotreater. The guard bed used sulfided $CoMo/Al_2O_3$ catalyst and its catalyst life is assumed to be 6 months for algae only and is higher when non-algae feedstock is used since iron is mainly from algae feedstock. The pretreated biocrude is then sent to a main bed to generate hydrotreated oil, wastewater, and offgas streams. The main bed used sulfided $NiMo/Al_2O_3$ catalyst and its catalyst life is assumed 2 years. The hydrotreated oil is first stabilized by removing butane and lighter components in a lights-removal column. This column also serves to adjust the initial boiling point of the gasoline fraction. The overhead gas containing light organics is combined with the PSA tail gas. The stable oil is then fractionated into three boiling point cuts: naphtha range, diesel range, and heavy oil range material. The heavy oil is sent to a hydrocracking unit to generate additional gasoline and diesel. The details of the design assumptions for this process have been described in our previous reports (Jones et al. 2014a&b, Zhu et al. 2020). Testing work for the SEQHTL biocrude upgrading is needed in future to verify the hydrotreated products yields estimation, hydrogen consumption, and also optimize the HT process.

Offgas from the HT process contains mainly C_1 to C_4 hydrocarbons, which can be used for hydrogen generation via steam reforming. A co-located hydrogen plant is assumed in this study to maximize the use of offgas from biomass sources and thus to minimize the use of petroleum-based hydrogen or natural gas. In this study, the hydrogen plant is simulated based on a conventional steam reforming process. The major process simulation assumptions and cost estimation basis for the hydrogen generation process of this study were provided in our previous design report (Jones et al. 2014a).

Superheated steam at 650 psia and 700 °F is generated by recuperating heat from the steam reformer process and hot flue gas from other processes fired heaters. Part of the superheated steam is used in the steam reformer as a reactant, and the remaining steam is expanded in a steam turbine for electricity generation. Part of the condensate from the bioprocessing process is used as the makeup water for the HTL stage II feed slurry to reach the required solid wt%. The remaining condensate is used as makeup water for the cooling water system. A boiler is used to provide medium- and low-pressure steam for the distillation step of the bioprocessing process. The boiler makeup water is assumed to be fresh water. The balance of plant includes equipment for cooling water system, chemicals storage tanks, nutrients and aqueous recycle pumps and storage tanks, and storage tanks for final and intermediate products.

3.5 Nutrients Recycle

In this system, several processes, including HTL, upgrading, bioprocessing, and hydrogen generation, have aqueous or condensate products. Some of these streams contain significant amounts of organic carbon and nitrogen, which must be recovered for their nutrient and economic values. Catalytic hydrothermal gasification (CHG) was originally developed by a PNNL experimental team for microalgae HTL aqueous phase treatment (Jones et al. 2014b). It can achieve almost 100% chemical oxygen demand removal based on experimental testing results. However, the capital cost to treat the HTL aqueous phase by CHG is significant. In addition, the precious metal catalyst used in the CHG is susceptible to sulfur poisoning and the cost to remove sulfate compounds prior to CHG is high. Therefore, the concept of directly recycling HTL aqueous phase for algae cultivation was proposed as this option not only eliminates the aqueous phase treatment costs but also reduces the nutrient demand for algae cultivation.

Direct aqueous phase recycle to the algae farm is based on the assumption that the algae ponds can act like a natural bioreactor, in which the nutrient elements, such as organic nitrogen (N), phosphorus (P), and carbon (C), in the recycle stream can be biodegraded by naturally occurring fungi and bacteria in algae ponds, making those nutrients available for algae growth. Several studies on algae HTL aqueous phase recycling for algae cultivation have concluded that this offers a promising route to reduce nutrient demand in algae growth (Alba et al. 2013; Bagnoud-Velásquez et al. 2015; Biller et al. 2012; Du et al. 2012). Researchers at PNNL conducted lab-scale semi-continuous cultivation testing by using the recycled HTL aqueous stream and solid acid digestate from HTL processing (Edmundson et al. 2017). The test results demonstrated that the HTL recycled streams do not show obvious negative impacts on the growth of the tested algae strains. Therefore, the bioavailability of the recycled nutrients from algae HTL has been verified. TEA studies for a single-stage algae HTL system with direct aqueous phase recycle design have been conducted and it concluded using direct aqueous phase recycle improved the overall system performance and cost compared to the CHG option (Zhu et al. 2019&2020).

Algae cultivation testing for the SEQHTL stage II aqueous phase have been conducted and it was found multiple algae strains showed strong growth in HTL derived media. The algae cultivation by using wastewater from the fermentation process has not been tested. As the wastewater from the fermentation process mainly include the unreacted sugars and carbohydrates, amino acids, and salts, based on discussion with our testing team for algae cultivation, these compounds should not have significant negative impacts on algae growth. Therefore, in this study, the aqueous streams from the SEQHTL stage II, bioprocessing, biocrude upgrading, and hydrogen generation processes are assumed to be directly recycled to the algae cultivation farm. The HTL stage II solid acid digestate containing part of P from the feedstock ash is also assumed to be recycled together with the aqueous streams from HTL and other processes. The organic carbon in the recycled aqueous streams is assumed to be bio-available for algae growth as CO_2 derived from the respiration of heterotrophic microbes (e.g., fungi and bacteria). Considering potential losses during a recycle process, such as leakage or volatilization, a 10% recycle loss is assumed for water and nutrient elements in the recycle streams. The flue gas from the hydrogen plant and fired heaters contains a large amount of CO_2, which is also assumed to be recycled to the algae farms to reduce the external pipeline CO_2 use for algae production. The C, N, P elemental balances of the overall system are estimated based on process simulation results and experimental information (see 7.0Appendix A). The credits related to these elements recycle are estimated and the results are presented in Section 5.0.

4.0 Process Economics

This section describes the calculation methods and results for the capital and operating cost for the system.

4.1 Capital Cost

All costs in this report are on a 2016 constant U.S. dollar basis. The original cost reflects the year of the cost quote or estimate, and the scale of the equipment. All capital costs are adjusted to an annualized 2016 basis using the *Chemical Engineering* (CE) magazine's published indices:

$$\text{Cost in 2016 \$} = \text{Cost in quote year} \times \left(\frac{\text{2016 index}}{\text{Quote cost year index}}\right) \tag{1}$$

The capital costs of standard equipment, such as pumps, compressors, and heat exchangers, were estimated using APEA. Non-standard equipment costs (e.g., HTL stage II, membrane separation, HT system, and hydrocracking reactor) were estimated by scaling base equipment costs from vendor budgetary estimates or literature references based on the appropriate metric (e.g., flow, duty) and applying an appropriate scaling factor (Peters and Timmerhaus 1980):

$$\text{Cost}_{\text{new}} = \text{Cost}_{\text{base}} \left(\frac{\text{Capacity}_{\text{new}}}{\text{Capacity}_{\text{base}}}\right)^{\text{scaling factor}} \tag{2}$$

where the base cost is associated with a base size parameter and the new equipment cost is a function of the base cost and the ratio between new and base capacities. The scale factor accounts explicitly for economies of scale, which refers to the cost changes with different equipment sizes.

Once the equipment is scaled and adjusted to the common cost year, factors are applied to calculate the total capital investment. The installed costs were estimated based on the purchased equipment costs and their installation factors, which are from APEA results or vendors. The total direct cost is the sum of all the installed equipment costs, plus the costs for buildings, additional piping, and site development, which are calculated based on the inside-battery-limits (ISBL) equipment costs according to heuristics given in Davis et al. (2018). Indirect costs are estimated as 60% of the total installed costs. The sum of the direct and indirect costs is the fixed capital investment. The total capital investment is the fixed capital plus working capital and land costs. The capital cost results for the SOT case evaluated in this study are listed in Table 11. The bioprocessing area represents the largest cost fraction, 36%, of the total installed cost and the second largest one is the HTL area. Therefore, reducing the capital cost of the bioprocessing area is important for reducing the overall system capital cost.

Table 11. Capital cost results.

Installed cost	million $ (2016 US$)	% of Total installed cost
Hydrothermal liquefaction	43.5	31%
Bioprocessing of HTL stage I extract	50.2	36%
Biocrude upgrading	13.5	9.7%
Hydrogen generation	13.0	9.4%
Steam cycle	3.55	2.6%
Balance of plant	15.2	11%
Total installed cost (TIC)	139	100%
Warehouse (4% of ISBL)	4.81	--
Site Development (9% of ISBL)	10.8	--
Additional Piping (4.5% of ISBL)	5.41	--
Total direct cost (TDC)	160	--
Indirect cost		--
Prorated expenses (10% of TDC)	16.0	--
Home office & construction fees (20% of TDC)	32.0	--
Field expenses (10 of TDC)	16.0	--
Project contingency (10% of TDC)	16.0	--
Other costs (start-up, permits, etc.) (10% of TDC)	16.0	--
Total indirect cost	96.0	--
Fixed capital investment (FCI)	256	--
Working capital (5% of FCI)	12.8	--
Land – assumed to be included in the feedstock cost	0	--
Total capital investment (TCI)	269	--

4.2 Operating Cost

The operating cost includes variable and fixed operating cost. Variable operating cost was calculated based on the simulation results for the flow rates of raw materials (feedstock, chemicals, etc.), utilities and credits (co-product and recycled nutrients), and their unit prices from literature sources or vendor quotations. Table 12 lists their unit prices and the annual variable operating cost. The associated cost year is shown in parenthesis. Credits are shown as negative values. As discussed in the previous section, the recycled streams contain compounds that supply the carbon, nitrogen, and phosphorus elements needed for algae growth and they are assumed to be completely bio-available, excluding assumed losses. The cost benefits of these recycled nutrients for algae cultivation are estimated by calculating the credits corresponding to their nutrient equivalents: CO_2 for carbon, NH_3 for nitrogen, and diammonium phosphate (DAP) for phosphorus. The CO_2 and nutrients equivalent mass flow rates are estimated from the process simulation results. The unit cost of the CO_2 and nutrients used for algae cultivation are from Davis et al. (2016). The cost credits of the recycle streams are calculated from the carbon, nitrogen, and phosphorus nutrient equivalent chemical flow rates multiplied by their unit cost.

Table 12. Variable operating cost.

Raw Materials	Price (2016)	Units	Consumption (/GGE fuel)	Cost (MM$/yr)	Source
Blend feedstock cost	378	$/ton AFDW	0.013	87.2	Calculated based on annual blending ratio, algae and corn stover price (see Section 3.1)
Natural gas	3.51	$/million Btu	0.096	6.09	2016 industrial annual average, EIA (2017a)
H_2SO_4 (93 wt%)	0.043	$/lb	7.46	5.81	Davis et al. (2018)
Na_2CO_3	0.083	$/lb	4.32	6.46	Industry database
Corn steep liquor	0.034	$/lb	0.30	0.19	Davis et al. (2018)
NaOH	0.238	$/lb	0.20	0.84	Davis et al. (2018)
Ethanol	2.40	$/gal	0.029	1.25	Industry database
Ethylene glycol	0.39	$/lb	0.048	0.34	Industry database
Reactive distillation catalyst (Amberlyst resin)	70.4	$/lb	0.001	1.62	Davis et al. (2018)
Hydrogen plant catalyst	2.03	¢/1000scf H_2	0.10	0.04	Industry database
Hydrotreating main bed catalyst	10.4	$/lb	0.001	0.22	Industry database
Hydrotreating guard bed fill	16.5	$/lb	0.002	0.52	Industry database
Hydrocracking catalyst	16.5	$/lb	0.00002	0.01	Industry database
Sum				**111**	
Waste disposal	37.9	$/ton	0.003	2.02	Humbird et al. (2011)
Sum				**2.02**	
Utilities					
Water makeup	0.37	$/MT	0.003	0.03	Dutta et al. (2011)
Electricity	6.76	¢/kwh	3.44	2.56	2016 industrial annual average, EIA (2017b)
Sum				**2.57**	
Credits					
Lactic acid (co-product)	0.97	$/lb	3.02	-52.9	Industry database, 5-year average price
NH_3 equivalent (N recycle)	0.41	$/lb	1.25	-9.26	Davis et al. (2016)
CO_2 equivalent (C recycle)	0.02	$/lb	32.8	-12.8	Davis et al. (2016)
Diammonium phosphate (DAP) equivalent (P recycle)	0.33	$/lb	0.63	-3.80	Davis et al. (2016)
Sum				**-78.8**	
Total Variable Operating Costs				**36.4**	

The fixed operating costs mainly include the maintenance and labor costs, which are shown in Table 13. Salaries and the factors for benefits and maintenance, and insurance and taxes are the standard assumptions used for BETO design cases (Davis et al. 2018).

Table 13. Fixed operating cost.

Position	Number	Total Cost (2016) (MM$/yr)
Plant manager	1	0.16
Plant engineer	2	0.16
Maintenance supr	2	0.13
Lab manager	2	0.13
Shift supervisor	5	0.27
Lab technician	5	0.22
Maintenance tech	6	0.27
Shift operators	30	1.34
Yard employees	4	0.13
Clerks & secretaries	1	0.04
Subtotal		2.84
Labor burden (90%)	90% of labor & supervision	2.56
Maintenance - conversion	3% of ISBL	3.61
Insurance & taxes	0.7% of FCI	1.79
Total fixed operating costs		**10.8**

4.3 Minimum Fuel Selling Price (MFSP)

The final production cost was calculated as MFSP by using a discounted cash flow rate of return (DCFROR) calculation method. It is the selling price of the fuel that makes the net present value of the process equal to zero with a specified internal rate of return over the overall plant life. The methodology is identical to that used in Jones et al. (2014) and other TEA studies (Davis et al. 2018; Zhu et al. 2019). The MFSP is represented by a gasoline-equivalent price in unit of $/GGE (gallon gasoline-equivalent) for the final product, which is calculated to compare the lower heating values (LHV) of the fuel product and generic commercial gasoline and the MFSP of the fuel product:

$$\text{MFSP (\$/GGE)}=\frac{\text{MFSP of fuel product} \times \text{gasoline LHV}}{\text{Final product LHV}} \tag{3}$$

This method provided a consistent comparison of prices for fuel with different heating values.

Table 14 gives the economic parameters used to calculate the MFSP. Note that the assumption of 90% on-stream factor or 330 operating days per year at full capacity may be optimistic given the potential for seasonal disturbances (summer flooding, winter storm, etc.) and maintenance requirements (corrective or breakdown maintenance, scheduled maintenance, preventive maintenance, and predictive maintenance).

Table 14. Economic parameters for MFSP calculation

Parameters	Value
Internal rate of return	10%
Plant financing debt/equity	60% / 40% of total capital investment
Term for debt financing	10 years
Interest rate for debt financing	8% annually
Plant life	30 years
Income tax rate	21%
Working capital cost	5% of fixed capital investment
Depreciation schedule	7 years
Construction period	3 years (8% 1st yr, 60% 2nd yr, 32% 3rd yr)
Startup time	6 months
On-stream factor	90%
Total indirect cost	55% of total direct cost
Cost year	2016 US$

5.0 Results and Discussion

The major cost analysis results for baseline SOT case and sensitivity analysis for selected parameters and alternative scenarios are described in this section.

5.1 Cost Results

Table 14 lists the production cost breakdown results for the SOT and projected cases. All the 2017 to 2019 SOT cases assumed single-stage HTL process for biofuel generation and the 2020 SOT case assumed a two-stage SEQHTL process. Compared to other SOT cases, the FY20 SOT has much lower fuel yields and extra co-product generation because only part of the feedstock is used for fuel generation and the remaining is used for co-product generation. Therefore, although the FY20 SOT case has lower algae feedstock cost in unit of $/ton AFDW than the FY19 case, its feedstock cost at $/GGE fuel basis is much higher because of the much lower fuel yield. For the same reason, the capital cost at $/GGE fuel basis for the SEQHTL of FY20 SOT is also higher than other SOT cases. But more importantly, because of the use of sulfuric acid and sodium carbonate in the SEQHTL process, the operating cost for the SEQHTL process is much higher than the single-stage HTL process. Therefore, the total production cost for HTL of FY20 SOT is much higher than other SOT cases. The decrease in the HTL biocrude upgrading cost of FY20 SOT mainly comes from the lower fixed operating cost, which results from its lower capital cost contribution to the total cost compared to other SOT cases due to the high capital cost of the bioprocessing process. The bioprocessing process contributes 32% of the total cost. The cost of the balance of plant for FY20 SOT is much higher than the FY19 SOT because extra equipment is needed for the chemicals and products storage for the SEQHTL and bioprocessing process, higher cooling water flow rates and larger boiling water system. The FY20 SOT also has extra co-product credits and much higher nutrient recycle credits since it has higher C, N and P recycle flow rates than other SOT cases. The higher C recycle flow rates results from the higher natural gas use and the use of sodium carbonate compared to other SOT cases. In addition, the feedstock used in FY20 SOT (see Table 5) has higher N and P contents than the feedstock used in FY17 to 19 SOT cases (Zhu et al. 2020). FY20 SOT has 10% lower MFSP than the FY19 SOT case, which mainly results from the larger plant scale, lower feedstock cost in unit of $/ton, extra co-product credits and higher nutrients recycle credits.

Table 15. Cost contribution for the microalgae HTL system SOT and projected cases

Production Cost Breakdown, $/GGE ($2016)	2017 SOT	2018 SOT	2019 SOT	2020 SOT	2025 projected	2030 projected
Feedstock	$6.66	$5.61	$4.10	$4.81	$5.91	$4.80
Algae drying (summer & spring only)	$0.00	$0.00	$0.00	$0.00	$0.00	$0.00
HTL biocrude production	$0.95	$0.84	$0.75	$1.54	$1.62	$1.53
HTL biocrude upgrading to finished fuels	$0.69	$0.59	$0.42	$0.30	$0.32	$0.30
Bioprocessing for co-product generation	$0.00	$0.00	$0.00	$1.43	$1.43	$1.45
Balance of plant	$0.61	$0.57	$0.49	$0.74	$0.79	$0.76
Co-product credits	0.00	0.00	0.00	-2.92	-$3.41	-$4.08
Nutrient recycle credits	-0.86	-0.78	-0.78	-1.43	-$1.67	-$1.62
Total	$8.05	$6.83	$4.98	$4.48	$5.00	$3.13

The SOT cases cost breakdown is depicted in Figure 15. For the 2020 SOT case of this study, 91% of the feedstock cost is contributed by algae feedstock and the remaining 9% is from corn stover based on their individual cost and the annual average blend ratio (see Section 3.1). Note that the MFSP for the 2025 projected case is higher than the 2020 SOT. This is due in part to the fact that the algae cultivation 2025 projected case has a lower summer productivity than the 2020 SOT, which is 27.7 g/m^2/d for the 2025 case and 31.6 g/m^2/d for the 2020 SOT (DOE 2019). The summer productivity rate sets the HTL plant scale, so lower summer productivity means smaller scale, which increases capital and conversion costs. Also, the 2025 algae pond case has a smaller gap between the summer and other seasonal productivities than the 2020 SOT. Therefore, less corn stover is needed in the non-summer seasons for the 2025 case, which results in a higher annual average algae/corn stover blend ratio and higher feedstock cost.

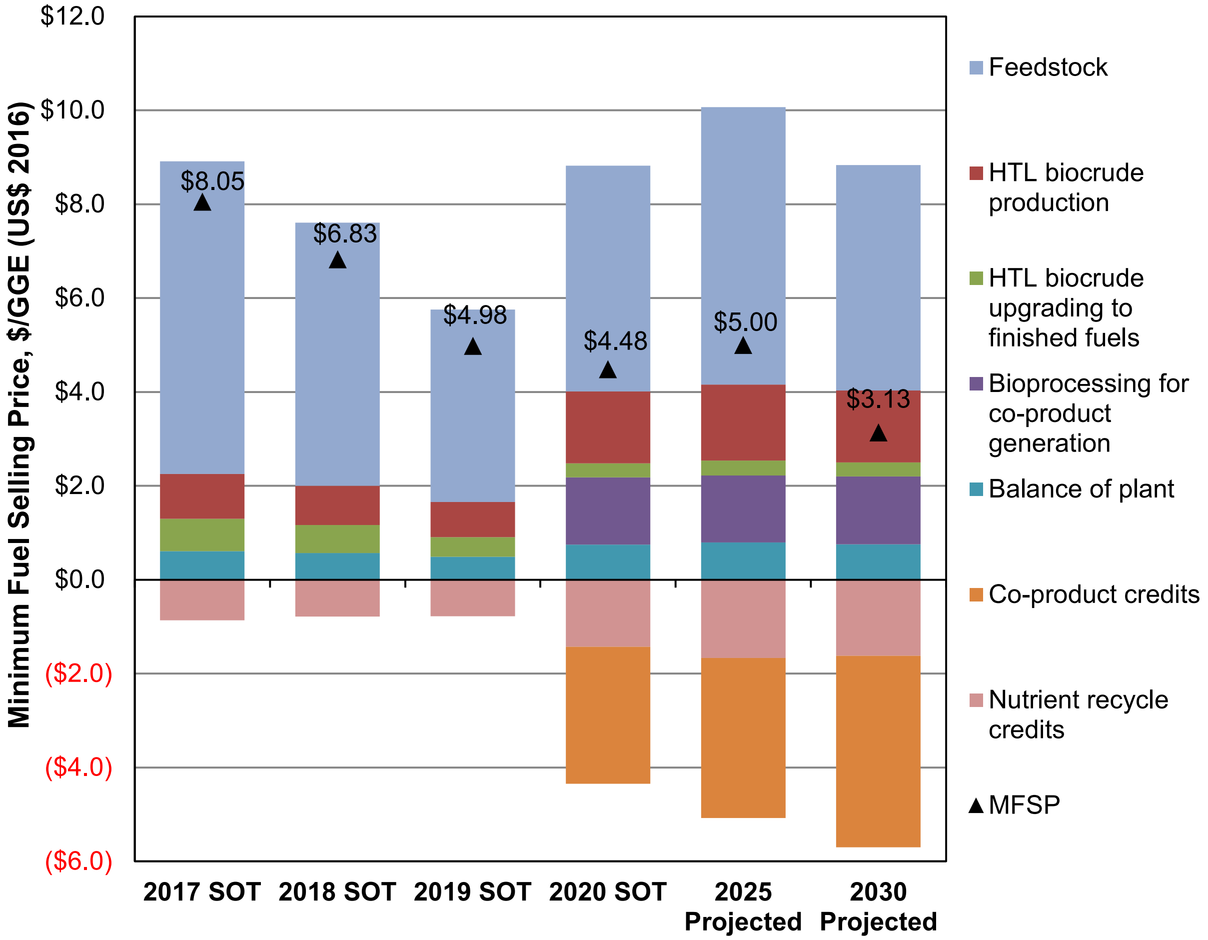


Figure 15. Cost contribution for the microalgae HTL system SOT and projected cases

Figure 16 shows the conversion cost contributions to MFSP for algae-based biofuel produced via the HTL pathway. While the addition of the SEQHTL configuration bioprocessing section for the 2020 SOT increases the overall plant capital cost, co-product credits significantly reduce the overall conversion cost contribution to the MFSP. Improved carbohydrate yields assumptions for the 2025 and 2030 cases (see Appendix B) further reduce conversion costs.

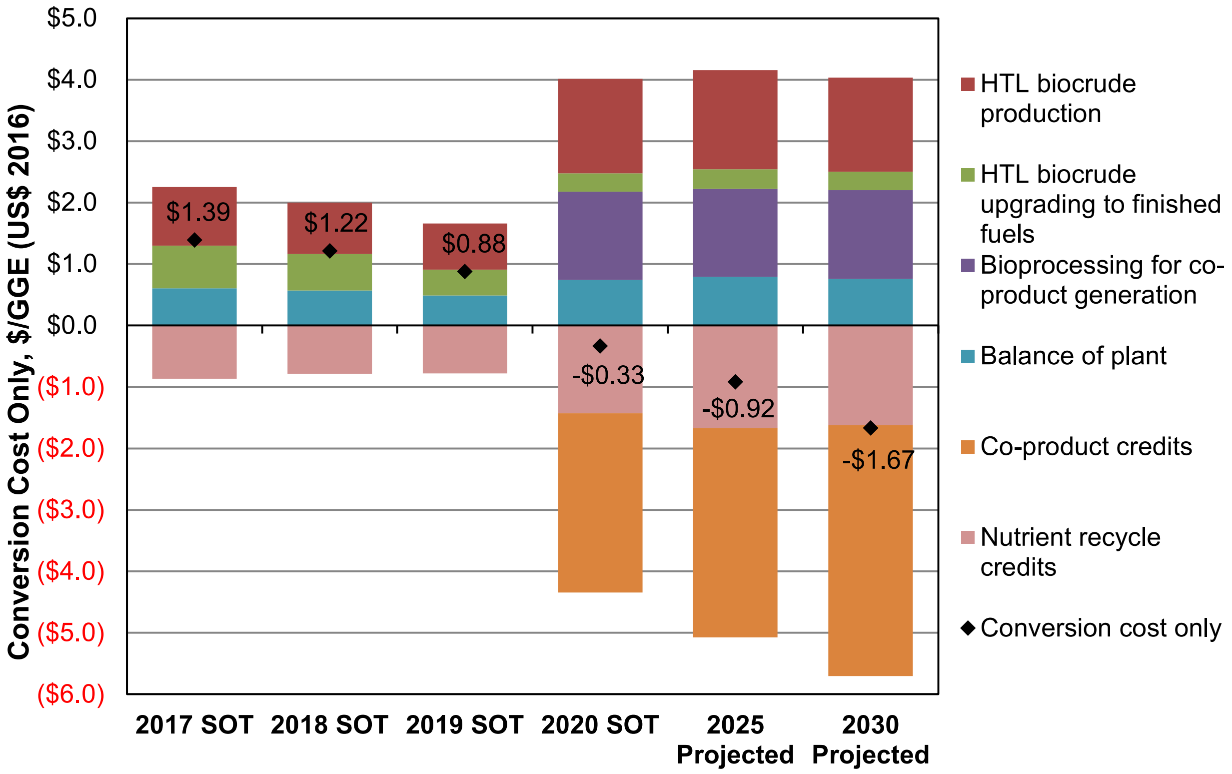


Figure 16. Conversion cost only allocation for the microalgae HTL system SOT and projected cases

It is evident from Figure 15 that costs for the AHTL pathway are dominated by algae feedstock production costs and even with co-product credits from the SEQHTL configuration and projected improvements in the process and algae productivity. The projected 2030 case does not meet the BETO 2030 target of fuel production cost ≤$2.5/GGE. For this reason, a pivot to low-cost algae feedstocks will be made in FY21 and moving forward. These may include algae used for water clean-up or remediation (e.g., turf scrubber), nuisance algae blooms, or macroalgae.

5.2 Sensitivity Analysis

The sensitivity analysis for selected process parameters and different scenarios are discussed in this section.

5.2.1 Cost Impacts of Selected Parameters

The cost impacts of selected parameters are shown in Figure 17 and the purpose is to identify the key parameters for the overall system cost. For this sensitivity analysis, significant interactions between the investigated parameter and other parameters are considered. These interactions generally lead to trade-offs between the final fuels and the co-product generation since the feedstock carbon is distributed between the final fuels and co-product via SEQHTL processing.

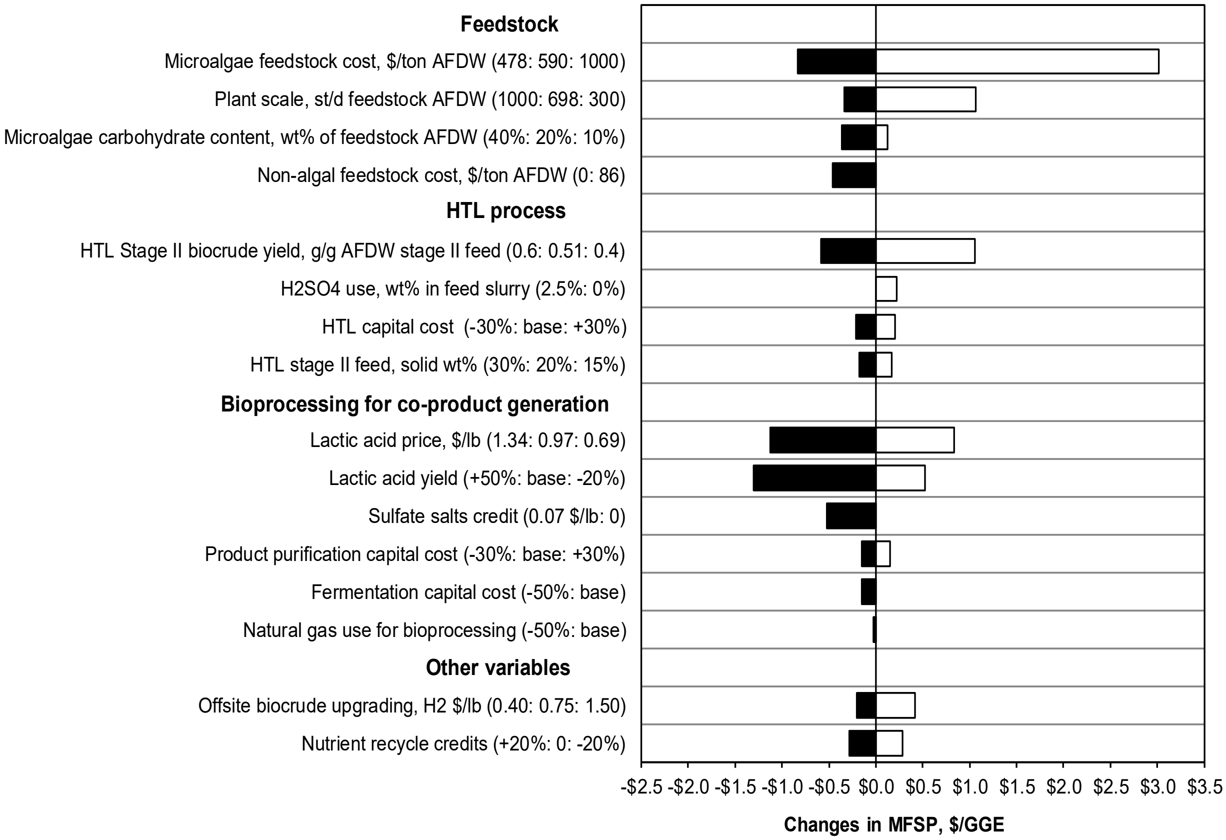


Figure 17. Changes in MFSP based on variations in selected parameters for the microalgae SEQHTL system 2020 SOT case

For the feedstock related variables, the algae feedstock cost and plant scale are identified as significant factors for the system cost. The low end value for the algae feedstock price is assumed to be the 2030 projected algae price with 2% cost saving due to lower dewatering requirement (DOE 2020). With the specified algae feedstock cost variation, the relative change in MFSP is -19% to +67% of the baseline value, which is $3.65 to 7.50/GGE for the MFSP. For the plant scale, the variation range leads to MFSP relative changes from -7.6% to +24%. For the algae feedstock carbohydrate content variation, the interaction between the carbohydrate content and the HTL stage I residual solid yield is considered. Higher carbohydrate content leads to higher carbohydrates extract yield and thus lower residual solid yield at HTL stage I. The higher carbohydrate extract yield leads to higher co-product yield. The lower HTL stage I residual solid yield leads to lower biocrude yield and thus lower final fuel production. When the algae carbohydrate content is 10 wt%, the trade-off between higher fuel yield and lower LA production leads to a 2.9% increase in MFSP. When the algae carbohydrate content increases to 40%, the MFSP reduces relatively 8.1% because the cost benefits from higher LA yield exceed the cost penalty from the lower final fuel yields. Therefore, algae feedstock with higher carbohydrate content is preferred for the system investigated in this study. The impact of non-algae feedstock cost on MFSP depends on its mass fraction in the overall feedstock use and its unit price. For the system investigated in this study, if the non-algae feedstock cost is 0, the MFSP can be 10% lower than the baseline value.

For the HTL process, the stage II biocrude yield is identified as a significant factor. The changes in biocrude yield from 0.6 to 0.4 g/g stage II AFDW feed lead to -13% to +24% of the baseline MFSP. The stage II biocrude yield is affected by several factors, including the fat contents of feedstock, the HTL stage II reaction conditions and the aqueous/oil products separation performance. The sulfuric acid use directly affects the carbohydrate extraction efficiencies, sodium carbonates use, and the residual solid yields from HTL stage I. The interactions between variables (carbohydrate extraction efficiency vs. residual solid yield, sulfuric acid use vs. sodium carbonates use) are descried in the cost model via liner regression equations developed based on testing results in order to ensure dependent variables are adjusted automatically when an independent variable is changed. The interactions between sulfuric acid use and carbohydrates extraction efficiency are described by using discrete values for carbohydrates extraction efficiency based on testing results for different sulfuric acid use. Lower acid use leads to lower carbohydrates extraction efficiency and also lower base use for pH adjustment in HTL process and thus lower operating cost for acid and base. The interactions between these variables lead to a slightly higher MFSP for no acid use compared to the baseline case with 2.5% acid use. For future work, with the increase in the co-product yields from carbohydrates extraction, the cost advantage for higher acid use will increase.

The HTL capital cost variation of +/-30% have moderate impacts on the MFSP with +/-4.7% changes. The dry solid content of the stage II slurry feed also has moderate cost impacts. When the dry solid content in the slurry changes from 30% to 15%, the relative MFSP change is -4.0 to +3.8% of the baseline value. With higher dry solid wt% in the slurry feed to stage II, the slurry feed has lower water content and thus the HTL stage II has lower heat requirement. In addition, when the dry solid flow rate is constant, higher dry solid wt% leads to a lower slurry feed flow rate and thus smaller equipment size and lower capital cost for the HTL stage II process. Therefore, higher solid content of the stage II slurry feed is beneficial for reducing both capital and operating costs of HTL process.

The identified significant factors for the bioprocessing area include the LA price, LA yield, and sulfate salts credit. The LA range is chosen based on the LA price history in recent years. The changes in LA price leads to the MFSP varying from -25% to +19% relative to the baseline value. The variation range of the LA yield is specified based on the literature values. When the overall LA yield from the carbohydrate increases 50% compared to the baseline value, the MFSP decreases 29% to about $3.18/GGE. When the LA yield decreases 20% of the baseline value, the MFSP increases relatively 12%. For the current SOT case, the LA yield from non-glucose sugar monomers of the current SOT case is at the low end of the literature values. Therefore, there is great potential for cost improvements resulting from LA yield increase.

The current sulfate salts in the SOT case is assumed to be solid waste for disposal. In HTL stage I process, part of ash from the feedstock is extracted and form sulfate salts in the carbohydrate extract stream. These salts are mainly Na_2SO_4 from ash extraction and the reaction between sulfuric acid and Na_2CO_3, and also K_2SO_4 and $MgSO_4$ from ash extraction because the algae ash has large amount of Na, K and Mg elements based on the testing work. Therefore, the sulfate salts removed from the fermentation product stream is rich in Na_2SO_4, but also have other sulfate salts, mainly K_2SO_4 and $MgSO_4$. If assuming the sulfate salts is not disposed as waste but sold as raw Na_2SO_4 and has the same selling price as salt cake at $0.07/lb (Davis et al. 2018), the MFSP will decrease 12% to $3.95/GGE. The potential market and final use or treatment for the sulfate salt stream need additional investigation and discussion.

The capital cost changes in fermentation and product purification processes have insignificant cost impacts for the overall system. The cost impacts of natural gas use for bioprocessing also very small. The reason is that the changes in natural gas use not only change the operating cost for natural gas, but also change the nutrients recycle credits related to CO_2 recycle. When natural gas use decreases, the cost for natural gas use is lower, while the recycle CO_2 from the natural gas combustion is also lower and thus lower nutrients recycle credits. Based on the sensitivity analysis results, the capital cost for the bioprocessing process is not key factors for this system. The co-product price and yields from the extracted carbohydrates are very important. Therefore, the selection of co-products for the system needs to consider both its price and the yields. The bioprocessing testing should focus on improving the yields.

Offsite biocrude upgrading refers to leveraging existing infrastructure through HT at a conventional refinery plant. This eliminates the capital cost for the HT, hydrocracking, hydrogen generation, and the related natural gas consumption. However, this offsite option requires extra cost for biocrude transportation. The biocrude transportation cost to the refinery is assumed to be $10//barrel by rail based on the crude oil transportation cost (Frittelli et al. 2014). The cost related to hydrogen use in a specific refinery plant would be assumed as an internal hydrogen transfer price. The range of internal hydrogen cost is specified based on IEA (2019) for the hydrogen production cost by using natural gas steam reforming in the refinery industry. An internal transfer price at $0.75/lb hydrogen leads to the same MFSP as the baseline case. With the specified internal hydrogen cost, the offsite biocrude upgrading leads to a -4.9% to +9.0% change in the MFSP. This scenario needs more research work to investigate the HTL biocrude stability and potential chemical/physical hazards during shipping. The changes in nutrients credits are based on the possible variability in CO_2, NH_3, and DAP unit prices. A +/- 20% changes in nutrients credits leads to +/- 6.4% changes in MFSP.

5.2.2 Algae Only SEQHTL System

Cost analysis for an algae only SEQHTL system was implemented to investigate and the cost results are shown in Figure 18. Compared to the 2020 SOT case, which used algae with non-algae feedstock supplement in non-summer seasons, the algae only system has higher feedstock cost and extra cost for algae storage in summer and spring. The algae wet storage cost is estimated based on the algae seasonable flow rates and wet storage base cost from Davis et al. (2020). The algae only system has smaller plant scale compared to the 2020 SOT system due to extra corn stover (CS) feed. The algae only system has higher carbohydrate extraction and higher glucose content in the extracted sugar monomers than the system with algae and CS supplement based on the testing results. The higher carbohydrates extraction and higher glucose content lead to higher LA yield, but lower residual solid to stage II and thus lower fuel production. The overall effect is the algae only system has 48% lower fuel production rate in unit of GGE/hr than the 2020 SOT case. The algae only system also has 40% lower LA production rate resulting from no extra CS feed. However, the algae only system has higher co-product credits on a $/GGE basis than the 2020 SOT case because 100% algae has higher LA yield than the algae/CS blend. The lower feedstock flow rates or lower plant capacity lead to a 31% lower total capital cost for the algae only system compared to the 2020 SOT case. However, the smaller plant scale and lower fuel production rates of the algae only system lead to higher cost at $/GGE basis for each process compared to the 2020 SOT case. The conversion only cost for the algae only system is -0.45 $/GGE and it is -0.33 $/GGE for the SOT case. For an annual basis, the algae only system has a conversion only production cost at -4.24 million $/yr and it is -5.98 million $/yr for the SOT case. Therefore, the 2020 SOT case with corn stover as supplement feedstock has cost advantages over the algae only case in both feedstock cost and conversion only cost, although the algae only has higher carbohydrates extraction on a per unit feedstock basis.

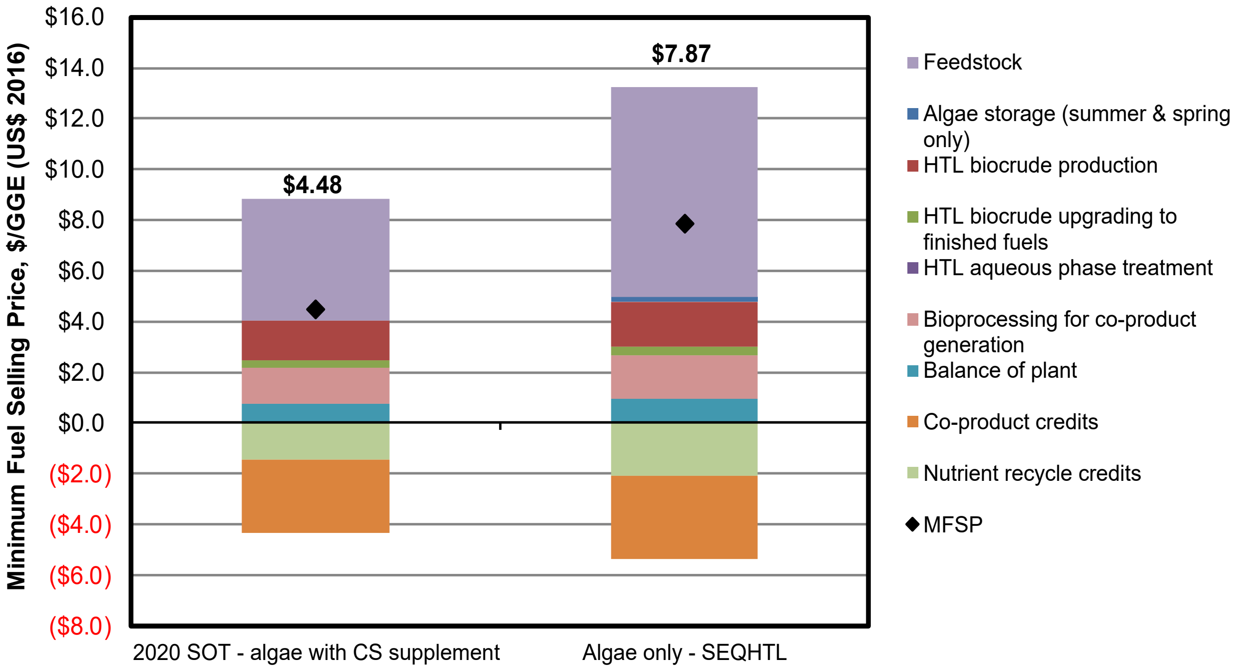


Figure 18. Microalgae SEQHTL system 2020 SOT compared to algae only case

5.3 Sustainability Metrics

Table 16 listed the conversion sustainability metrics for 2017 to 2020 SOT cases. Although the 2020 SOT has larger plant scale or feedstock flow rates than previous SOTs, its fuel yield at per unit feedstock basis is lower than other cases because only part of feedstock is used for fuel production. The remaining part of the feedstock is used for co-production generation. Assuming the algae HTL system is scaled up to meet a lactic acid global market size of 2.0 MMtons/year (Table 2), the biofuels yields from the system will become 32 million barrels/yr, which is about 0.1% of current global petroleum fuel production size (EIA 2021). Therefore, after reaching the co-product market size limits, the process needs to be reverted to making fuels alone without the coproduct or a co-product with larger market size can be considered in future work.

The annual natural gas consumption for the 2020 is higher than for the 2019 SOT. Although both cases have similar biocrude production rates (18 mmGGE/y for FY20 and 20 mmGGE/y for 2019), the HTL and HT offgas generation rates for 2020 are less than the FY19 based on the simulation results. Since the offgas together with natural gas are needed to meet the process heating and hydrogen generation requirement for fuel production, less offgas generation leads to a higher natural gas requirement. In addition, the biocrude from the 2020 has a higher oxygen content (see Table 3), which leads to higher hydrogen needs for the hydrodeoxygenation (HDO) reaction in the biocrude upgrading process. However, the hydrogen consumption of HT is also affected by the hydrotreated oil components. The 2020 SOT assumed similar hydrotreated oil components as 2019 because HT testing for biocrude from SEQHTL process was not conducted this fiscal year. Therefore, future testing work is needed to investigate the hydrotreating of the biocrude from the SEQHTL with blended feedstock. The testing results will help to verify and improve the TEA for the SEQHTL biocrude generation and upgrading system. The natural gas for bioprocessing is mainly used for process heating, evaporation and distillation. It contributes 37% of total natural gas use for 2020 SOT and is the major reason that 2020 SOT has a much higher natural gas consumption per unit feedstock and per unit fuel generation basis.

Table 16. Conversion sustainability metrics for microalgae HTL SOT cases

Input	2017 SOT	2018 SOT	2019 SOT	2020 SOT
Fuel yield, GGE fuel/ton AFDW feedstock	104	115	106	78.7
Co-product yield, lb/ton AFDW feedstock	0	0	0	238
Natural gas, mmscf/y				
To fuel production (HTL and hydrogen plant)	419	475	822	1,069
To bioprocessing	0	0	0	631
Total natural gas usage	419	475	822	1,701
SCF natural gas/ton AFDW feedstock	4,078	4,228	4,160	7,387
SCF natural gas/GGE final fuel	39.2	36.9	39.4	93.8
Makeup water, kg/GGE final fuel	5.16	4.70	5.23	2.99
Electricity, kwh/GGE final fuel	0.76	0.70	0.73	3.44
Carbon efficiency				
Fuel C/feedstock C, %	54	58	53	41
Fuel + co-product C/feedstock C, %	--	--	--	50
Overall products carbon efficiency, %	48	51	47	32
Energy efficiency				
Final products/feedstock only, % HHV basis	65	70	64	55
Overall efficiency, % HHV basis	54	57	52	44
EROI (energy return on investment), HHV basis	3.0	3.1	2.8	1.4

The 2020 SOT has a lower makeup water requirement than other SOT cases, the reason being that bioprocessing generates a large amount of condensate water via evaporation, part of which is used as cooling water makeup and thus lowers the demand for external makeup water. The FY20 SOT has much higher electricity consumption than other SOT cases. The major reason is the extra power consumption of the bioprocessing process compared to other SOT cases. Another contribution is from the cooling water process because the bioprocessing process needs a large amount of cooling water for its product purification units. The SEQHTL process also has slightly higher power consumption than the single-stage HTL resulting from the power consumption of the liquid/solid separation at HTL stage I.

The 2020 SOT cases have lower carbon efficiencies than other cases. The carbon efficiency of fuel C/feedstock C is lower because only part of feedstock is used for fuel production and the C in fuel products of 2020 SOT is lower than that of other cases at per unit feedstock C basis. The efficiency of the total fuel and co-product C/feedstock C is still lower than the fuel C/feedstock C efficiency of other cases because the co-product C yield from feedstock C is low, which is only 9% of feedstock C. With the improvement in co-product yield from the carbohydrate extract, this C efficiency can be improved. The overall products carbon efficiency is defined as C in fuel and co-products divided by total C in (feedstock, natural gas and chemicals). The 2020 SOT case has lower overall products carbon efficiency that other cases.

The 2017 to 2018 SOTs have comparable energy efficiencies. The 2019 SOT has slightly lower efficiency and EROI, which is calculated as the total energy output from products divided by the energy inputs from electricity and natural gas. The reason is that the 2019 SOT has a lower fuel yield at per ton feedstock basis resulting from a lower algae blend ratio compared to 2017 and 2018 SOT cases. The 2020 SOT has lower energy efficiency and EROI than other cases. Considering the energy inputs, the 2020 SOT has extra natural gas consumption for bioprocessing and high heating input for HTL due to the high moisture content of the feed slurry required by SEQHTL stage I, which is 90%, compared to the 80% of other SOT cases with single-stage HTL. Considering the energy outputs, the chemical co-product has much lower HHV than the fuel products and thus the total energy output from fuel and co-product is less than that from fuel only product at per ton feedstock basis. Therefore, there is a trade-off between the cost benefits from co-products generation and energy penalty due to extra energy input for co-product generation and lower energy output from co-products with low HHV than fuels.

Conversion plant sustainability metrics are not useful by themselves and need to be coupled to the farm life-cycle inventory (LCI), to account for aqueous recycle from the conversion plant back to the farm. An LCI for the conversion plant will be delivered to Argonne National Laboratory (ANL), who can then complete a full well-to-wheels lifecycle analysis using the farm inputs from NREL.

6.0 Conclusions and Future Work

The development of SEQHTL technologies enables separation of carbohydrates from other biochemical compounds of microalgae and conversion to targeted products. Stage I processing reduces solid flow rates, equipment size and cost for stage II via extraction of carbohydrates. More importantly, the stage I processing increases the fat content of the solid feed to stage II, leading to a higher biocrude yield on a per unit solid feed basis than single-stage HTL. Extracting the carbohydrates part from the feedstock enables the production of high-value biochemical via carbohydrates bioprocessing.

Compared to the single-stage HTL system for fuel generation only, the SEQHTL system has lower fuel production, but extra biochemical co-product generation, and the related extra cost for bioprocessing. The cost results show that the credits from co-products generation via bioprocessing of the extracted carbohydrates outweigh the extra cost for adding bioprocessing and the reduced fuel production value. Although LA fermentation has been commercialized and extensive research has been conducted, algae based LA fermentation is still at lab-scale and only limited studies are reported. In addition, it is the first time that bioprocessing of algae SEQHTL stage I carbohydrate extract has been investigated. Due to the limited knowledge and information available, there are expected uncertainties in the bioprocess cost estimation. As such, more experimental work for algae SEQHTL carbohydrates extracts bioprocessing is needed to improve our knowledge of this technology, optimize the process design, and reduce the uncertainties in the cost estimation.

Sensitivity analysis identified key cost drivers for the process, which provides guidance for research development in the future. With the current assumption for LA yield from carbohydrates bioprocessing, lower feedstock cost and larger plant scale have more cost benefits than higher carbohydrates extraction based on the comparison results between the SOT case and the algae only one.

Key recommendations for future experimental work and large-scale system development are summarized as follows:

- Feedstock: as shown by the 2030 projected case, with the target microalgae cost in 2030, the MFSP still does not meet the BETO goal of \$2.50/GGE. Therefore, low-cost algae feedstock, such as algae derived from waste treatment processes, needs to be considered in future work to reduce the impacts of high feedstock cost on the overall system. If non-algae feedstock is still needed for non-summer seasons, selecting low-cost feedstock is essential.
- Sequential HTL:
    a. HTL stage I:
        - Optimal reactions conditions (mainly temperature, acid use, residence time) should be investigated based on feedstock types and compositions. The selected conditions should optimize the carbohydrate extraction and sugar monomers generation and keep a minimum use of acid. If non-algae feedstock is used, the optimal blending ratio needs to be identified if possible.
        - Increasing slurry solid content or decreasing the moisture content of the slurry needs to be investigated in order to reduce the energy consumption of stage I and also reduce stage I reactor size.
        - With acid addition, the material corrosion issue for stage I needs to be investigated.
        - The identification and measurement of N compounds in the stage I extract will help to understand the nutrients needs in the bioprocessing step.

    - With significant sulfuric acid added, the S element from feedstock and sulfuric acid needs to be measured and sulfur-based compounds need to be identified.
    - The biochemical compositions (lipid/protein/carbohydrates wt%) of stage I residual solid needs to be measured in order to develop a correlation relationship between stage I residual solid compositions and the stage II biocrude yield. Impacts of different stage I conditions on the stage II biocrude yields can also be investigated via this approach.
  - b. HTL stage II:
    - Different reaction conditions (mainly solid wt% of the feed slurry and space velocity) need to be investigated to optimize the biocrude yields.
    - Testing for combined processing of residual solids from HTL stage I and recycled cell mass from bioprocessing is needed to provide information about the impacts of recycling cell mass on stage II biocrude and solid generation.
    - Additional work for the stage II biocrude characterization is needed to compare the differences between the SEQHTL biocrude and the single-stage HTL one. It will help reveal the underlying pretreatment requirements for the upgrading process. In addition, it also provides useful information for the refinery industry about the potential option of offsite centralized biocrude upgrading.
    - Larger scale (engineering or pilot) testing is needed to investigate if extra equipment or steps are needed to achieve the same or better performance than the lab-scale results and also identify performance uncertainties when scaling up.
- Bioprocessing:
  - For the main fermentation process, different reactions conditions and the selection of different microorganisms should be investigated to optimize the target product yields and productivity.
  - Low-cost nitrogen sources, such as CSL, should be tested for seed culture preparation.
  - A range of chemical target products should be considered and tested based on the features of the algae HTL stage I extract. Market size, price, and yields from the carbohydrates extract should be considered in the selection of the co-products.
  - Product purification testing should be conducted to validate the design basis for this process. In addition, reducing energy consumptions for product purification needs to be investigated.
  - Detailed characterization of the recycled cell mass for HTL processing and the wastewater streams recycled for algae cultivation are needed. The composition analysis for the cell mass can help to understand its potential biocrude generation in the HTL stage II process. The elemental and compounds analysis for the recycled wastewater stream from the bioprocessing unit is needed to fully understand its impacts on algae growth. In addition, a more complete understanding of the fate of phosphorus in the process is needed to validate assumptions around nutrient recycle.
- Biocrude upgrading: The upgrading of the biocrude from the SEQHTL process needs to be tested. The testing information is important for comparing the SEQHTL biocrude upgrading to the single-stage HTL one. The testing information should include hydrogen use, distillation curves, key upgraded oil properties, such as flash points, cold flow properties, and other related information.
- Aqueous and waste streams treatment:
  - Testing of combined nutrient recycle streams (i.e., aqueous streams from the SEQHTL stage II, bioprocessing, biocrude upgrading, and hydrogen generation processes) on the growth and

productivity of algal cultures should be investigated for negative or positive impacts from residual unreacted sugars and carbohydrates, amino acids, salts, and bacterial cell cultures.

  - For low-cost algae feedstock, the treatment or utilization of HTL and bioprocessing aqueous streams and solid waste streams need to be investigated. In addition, with sulfuric acid and base used in the current system, a large amount of sulfate salts, such as sodium sulfate, is generated and assumed to be a solid waste stream. To reduce the solid waste generation of the system, the treatment or use of the sulfate salt stream needs additional investigation and discussion.

For the overall system, engineering- or pilot-scale testing needs to be developed in the future to investigate the risks of integration of multiple process steps into a single system, examine the performance differences between lab-scale and large-scale applications, and explore whether extra equipment is needed to achieve similar performance to the lab-scale processes.

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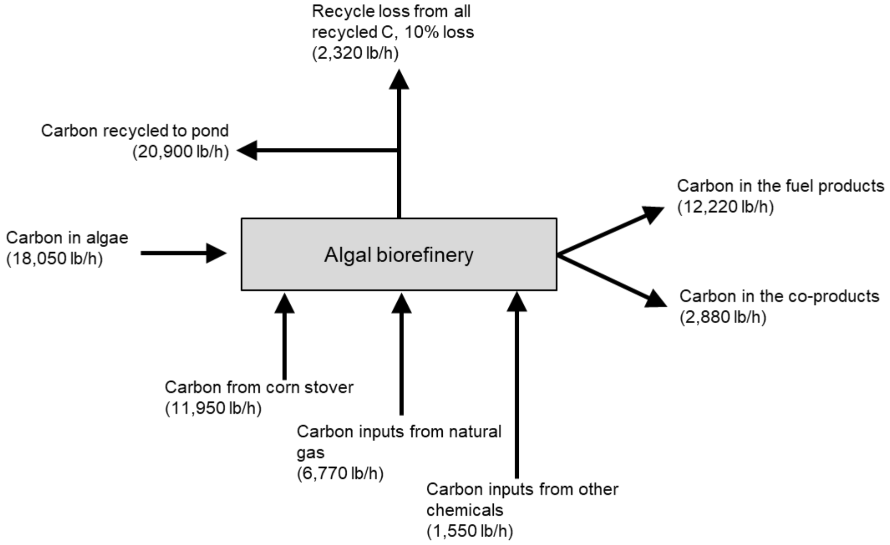
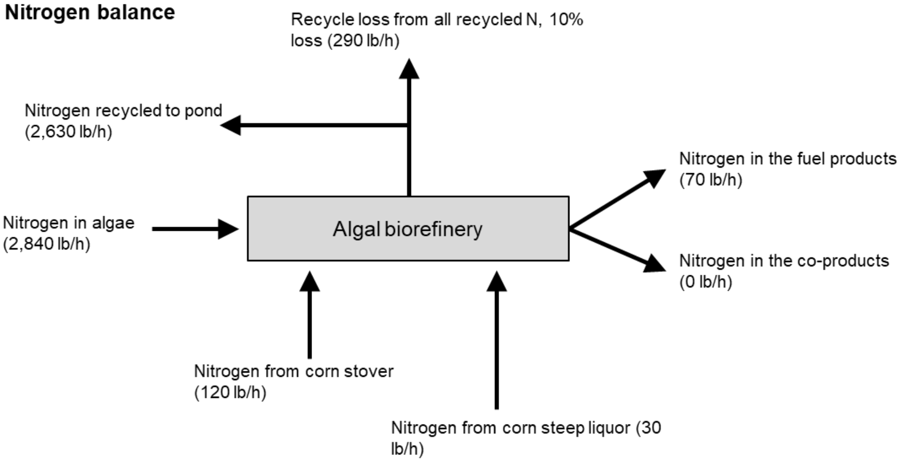
Appendix A – Nutrient Elements Balance

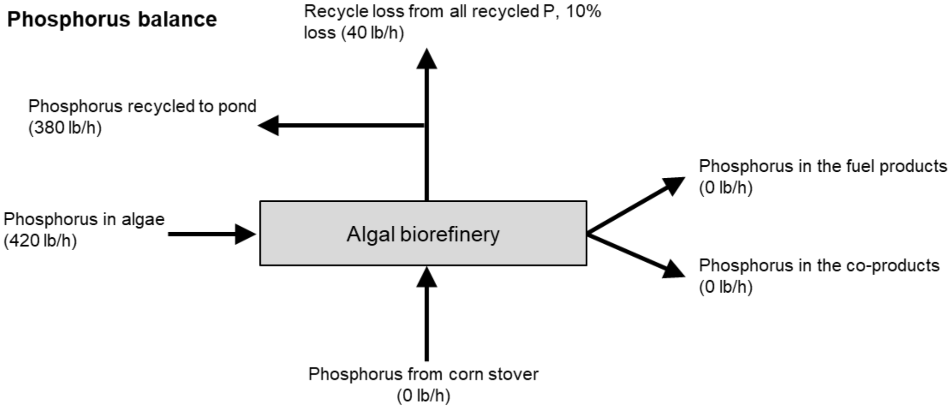
Carbon balance



Nitrogen balance



Phosphorus balance



Appendix B – Detailed SOT Costs

Processing Area Cost Contributions & Key Technical Parameters	**Metric**	**2017 SOT Florida - no liners**	**2018 SOT Florida - no liners**	**2019 SOT Florida - no liners**	**2020 SOT Florida - no liners**	**2025 Projected**	**2030 Projected**
Fuel selling price	$/gge	$8.05	$6.83	$4.98	$4.48	$5.00	$3.13
Conversion Contribution	$/gge	$1.39	$1.22	$0.88	($0.33)	($0.92)	($1.67)
Production Diesel	mm gge/yr	7.1	8.9	13.7	12	10.3	12.9
Production Naphtha	mm gge/yr	3.6	4.0	6.6	6.3	5.47	6.89
Diesel Yield (AFDW feedstock basis)	gge/US ton feedstock	69	79	70	51	49.7	49.8
Naphtha Yield (AFDW feedstock basis)	gge/US ton feedstock	35	36	33	27	26.5	26.5
Diesel Yield (areal basis)	gge/acre-yr	1,416	1,771	2,746	2,365	2,053	2,583
Naphtha Yield (areal basis)	gge/acre-yr	724	800	1,310	1,261	1,095	1,377
Co-product Yield (AFDW feedstock basis)	lb /lb feedstock	0	0	0	0.12	0.13	0.16
Natural Gas Usage-drying (AFDW feedstock basis)	scf/US ton feedstock	0	0	0	0	0.00	0.00
Natural Gas Usage-HTL, H2 gen, bioprocessing (AFDW feedstock basis)	scf/US ton feedstock	4,078	4,228	4,085	7,387	7,591	8,220
Carbon from Biomass in Fuels	%	54%	58%	53%	41%	39%	39%
Carbon from Biomass in Other Productsc	%	0%	0%	0%	10%	11%	13%
Feedstock							
Total Cost Contribution	$/gge fuel	$6.66	$5.61	$4.10	$4.81	$5.91	$4.80
Feedstock Type	Algae with non-algae feedstock supplement in non-summer seasons	*Algae with wood supplement*	*Algae with wood supplement*	*Algae with wood supplement*	*Algae with corn stover suppplement*	Algae with corn stover suppplement	Algae with corn stover suppplement
Feedstock Cost (AFDW basis)	$/US ton feedstock	$694	$643	$421	$379	$450	$366
Algae Drying (summer & spring only)							
Total Cost Contribution	$/gge fuel	$0.00	$0.00	$0.00	$0.00	$0.00	$0.00
Capital Cost Contribution	$/gge fuel	$0.00	$0.00	$0.00	$0.00	$0.00	$0.00
Operating Cost Contribution	$/gge fuel	$0.00	$0.00	$0.00	$0.00	$0.00	$0.00
HTL Biocrude Production							
Total Cost Contribution	$/gge fuel	$0.95	$0.84	$0.75	$1.54	$1.62	$1.53
Capital Cost Contribution	$/gge fuel	$0.56	$0.50	$0.47	$0.56	$0.58	$0.55
Operating Cost Contribution	$/gge fuel	$0.39	$0.34	$0.28	$0.98	$1.03	$0.99
Liquid Hourly Space Velocity (LHSV)	vol/h/vol	4.0	4.0	4.0	Stage I: 4; Stage II: 3.5	Stage I: 4; Stage II: 3.5	Stage I: 4; Stage II: 3.5
HTL Carbohydrate Extraction	%, extracted/carbohydrate in feedstock	0%	0%	0%	58%	66%	65%
HTL Biocrude Yield (AFDW)	lb /lb feedstock	0.41	0.45	0.41	0.30	0.29	0.29
HTL Biocrude Hydrotreating to Finished Fuels							
Total Cost Contribution	$/gge fuel	$0.69	$0.59	$0.42	$0.30	$0.32	$0.30
Capital Cost Contribution	$/gge fuel	$0.30	$0.27	$0.23	$0.17	$0.18	$0.17
Operating Cost Contribution	$/gge fuel	$0.39	$0.32	$0.19	$0.13	$0.14	$0.13
Mass Yield on dry HTL Biocrude	lb/lb biocrude	0.81	0.82	0.81	0.83	0.83	0.83
HTL Aqueous Phase Treatment							
Total Cost Contribution	$/gge fuel	$0.00	$0.00	$0.00	$0.00	$0.00	$0.00
Capital Cost Contribution	$/gge fuel	$0.00	$0.00	$0.00	$0.00	$0.00	$0.00
Operating Cost Contribution	$/gge fuel	$0.00	0.00	0.00	0.00	0.00	0.00
Bioprocessing for Co-product Generation							
Total Cost Contribution	$/gge fuel	$0.00	$0.00	$0.00	$1.43	$1.43	$1.45
Capital Cost Contribution	$/gge fuel	$0.00	$0.00	$0.00	$0.64	$0.59	$0.57
Operating Cost Contribution	$/gge fuel	$0.00	0.00	0.00	0.79	0.84	0.88
Fermentation Productivity	g/L-hr	0	0	0	0.46	1.00	1
Fermentation Process Yield	g product/g extracted carbohydrates	0	0	0	0.37	0.46	0.46
Balance of Plant							
Total Cost Contribution	$/gge fuel	$0.61	$0.57	$0.49	$0.74	$0.79	$0.76
Capital Cost Contribution	$/gge fuel	$0.29	$0.28	$0.23	$0.41	$0.44	$0.41
Operating Cost Contribution	$/gge fuel	$0.31	$0.29	$0.26	$0.34	$0.35	$0.35
Co-product Credits	$/gge fuel	$0.00	0.00	0.00	(2.92)	($3.41)	($4.08)
Nutrient Recycle Credits	$/gge fuel	($0.86)	(0.78)	(0.78)	(1.43)	($1.67)	($1.62)
Models: Case References		Blend-111317-17SOT-16$-FL-NL-R2	Blend-092018-18SOT-16$-FL-NL	Blend-092019-19SOT-16$-FL-NL	Blend-020821-SEQHTL-FY20SOT-FL-NL.xlsm	Blend-021421-SEQHTL-2025P.xlsm	Blend-021421-SEQHTL-2030P.xlsm

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