U.S. DEPARTMENT OF ENERGY

Process Design and Economics for the Conversion of Algal Biomass to Hydrocarbons: Whole Algae Hydrothermal Liquefaction and Upgrading

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Pacific Northwest
NATIONAL LABORATORY

NOTICE

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Executive Summary

The goal of the U.S. Department of Energy's Bioenergy Technologies Office (BETO) is to enable the development of biomass technologies to:

- Reduce dependence on foreign oil
- Promote the use of diverse, domestic, and sustainable energy resources
- Establish a domestic bioenergy industry
- Reduce carbon emissions from energy production and consumption. (DOE 2013)

To assist in realizing these goals, a number of techno-economic evaluations have been developed for both biological and thermochemical pathways for converting biomass to fuels. These conceptual evaluations, termed "design cases", provide a detailed basis for understanding the potential of various conversion technologies and help identify technical barriers where research and development could potentially lead to significant cost improvements. Consistent assumptions for items such as plant lifetimes, rates of return, and other factors are used in all design cases so the various conversion pathways may be assessed on a comparative basis.

The purpose of this report is to evaluate the economics of hydrothermal liquefaction (HTL) of whole algal biomass followed by the catalytic upgrading of the HTL oil to produce renewable diesel fuel. HTL is especially suited for conversion of wet feedstocks such as algae and the economics are more strongly influenced by improvements in algal biomass productivity rather than extractable lipid content. The focus of the report is directed towards the conversion process. The costs for algae growth, harvest and dewatering are not modeled here, but instead, treated as a single feedstock cost. The block flow diagram for the conversion process and the target carbon flows are shown in Figure ES-1.
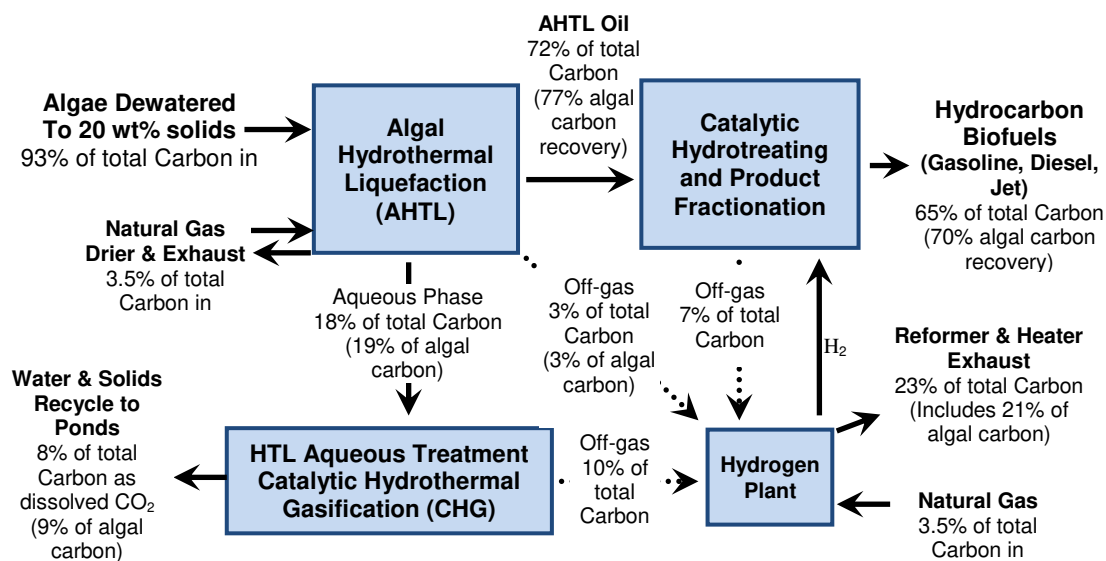
Figure ES-1 Block flow diagram of AHTL conversion process showing carbon balance
100% inlet carbon balance = 93% from algae, 3.5% from natural gas to drier, 3.5% from natural gas to hydrogen plant

AHTL is a thermal process that uses pressurized water in the condensed phase to convert whole, wet algae to primarily a liquid fuel product. Aqueous and solid phases are also formed from which nutrients and energy may be recovered. AHTL and upgrading of the AHTL oil to transportation fuels have only been demonstrated in the laboratory and on a small engineering development scale. Thus, the analysis does not reflect the current state of commercially-available technology but instead provides the basis for future research areas advancements that are likely to be achieved by 2022.

Experimental data were used to establish the economic and technical foundation for a future target AHTL plant. Using n^{th} plant assumptions (where costs reflect a future time when the technology is mature and several plants have already been built and are operating as opposed to first of a kind), and incorporating improvements to AHTL oil recovery, hydrotreating and wastewater treatment, suggest that the minimum selling diesel is $4.77 per gallon (2011 constant dollars) or $4.49/gasoline gallon equivalent (gge). This assumes a plant scale of 1340 U.S. tons per day of algae (dry and ash free basis) available at $430 per ton, 10% internal rate of return, and onsite upgrading of AHTL oil to diesel.

Meeting the long term goal of $3/gge will require a combination of strategies, potentially including co-feeding with lower cost lignocellulosic biomass and offsite upgrading at a larger facility or conventional petroleum refinery. Meeting the conversion costs projected in this report, and summarized in Figure ES-2, will require the following:

- Maximize yield and optimize oil quality through improved AHTL reaction conditions for a variety of different algal feedstocks,

- Optimize phase separation of the AHTL oil from the aqueous product, solids and gas,

- Optimize AHTL aqueous phase treatment to reduce costs and enhance carbon recovery, and,

- Better characterize the AHTL oil and hydrocarbon products.

Although outside the scope of this report, it is important to note that research improvements to algal growth, harvest and dewatering, and optimization of nutrients recycle to the farm from the conversion plant is critical to the overall success of this process given that the $430/ton aglal cost is 74% of the diesel production cost.

Figure ES-2 Summary economics

Liquid Fuels from Microalgae Hydrothermal Liquefaction and Upgrading
2022 Projection Incorporating Improvements to Current Technology
Feedstock Cost: **$430**   **$/U.S. ton algae (dry, ash free basis)**
delivered at 20 wt% solids

Minimum Diesel Selling Price (MFSP)	**$4.77**	$/gallon
MFSP Gasoline Gallon Equivalent	**$4.49**	$/gge

Naphtha	Diesel	
11.2	54	million gal/yr
1	7	trillion Btu/yr
25	122	gal/US ton AFDW algae
3	15	million Btu/US ton AFDW algae

Co-Product	0	tons/year
Internal Rate of Return (After-Tax)	10%	
Equity Percent of Total Investment	40%	
Cost Year	2011	

CAPITAL COSTS

Algae Cultivation, Harvest, Dewater	$0	0%
HTL Oil Production	$101,800,000	40%
CHG Water Treatment	$81,400,000	32%
HTL Oil Upgrading	$24,700,000	10%
Hydrocracking	$5,700,000	2%
Hydrogen Plant	$28,600,000	11%
Steam cycle	$3,600,000	1%
Balance of Plant	$6,800,000	3%
Total Installed Capital Cost	$252,600,000	100%
Building, site development, add'l piping	$34,900,000	
Indirect Costs	$158,100,000	
Working Capital	$22,300,000	
Land (included in feedstock cost)	$0	
Total Capital Investment (TCI)	$467,900,000	
Installed Capital per Annual Gallon Diesel	$5	
TCI per Annual Gallon Diesel	$9	
Total Capital per Annual GGE	$7	
Loan Rate	8.0%	
Term (years)	10	
Capital Charge Factor (computed)	0.054	

MANUFACTURING COSTS

Plant Hours per year	7920	
avg feed rate, dry ash-free algae	1,339	TPD to HTL reactor

	$/gal diesel	$/year	$/gge
Algae feedstock cost	3.51	$190,000,000	3.31
Natural Gas	0.12	$6,600,000	0.12
Catalysts & Chemicals	0.16	$8,500,000	0.15
Waste Disposal	0.00	$0	0.00
Electricity and other utilities	0.05	$3,000,000	0.05
Naphtha Credit	-0.67	-$36,300,000	-0.63
Fertilizer Credit	0.00	$0	0.00
Fixed Costs	0.38	$20,400,000	0.36
Capital Depreciation	0.28	$14,900,000	0.26
Average Income Tax	0.16	$1,800,000	0.15
Average Return on Investment	0.78	$8,600,000	0.73
	4.77		**4.49**

PERFORMANCE

Total Electricity Usage (KW)	5,451
Electricity Produced Onsite (KW)	4,755
Electricity Purchased from Grid (KW)	0
Electricity Sold to Grid (KW)	696
Net Electricity Use (KWh/gal product)	0.8
Overall Carbon Efficiency (Naphtha + Diesel)	
On algae + natural gas	65%
On algae	70%

Abbreviations

AFDW	Ash Free Dry Weight
AHTL	Algal Hydrothermal Liquefaction
ASTM	American Society of Testing and Materials
BETO	Bioenergy Technologies Office
BBL	Barrel (42 gallons)
BPSD	Barrel Per Stream Day
BTU	British Thermal Unit
CHG	Catalytic Hydrothermal Gasification
CSTR	Continuous Stirred Tank Reactor
CoMo	Cobalt Molybdenum
DOE	Department of Energy
FCI	Fixed Capital Investment
g	Gram
GGE	Gasoline Gallons Equivalent
GHG	Green House Gas
gpm	Gallons Per Minute
H_2A	Hydrogen Analysis Program
HDN	Hydrodenitrogenation
HDS	Hydrodesulfurization
HDO	Hydrodeoxygenation
HTL	Hydrothermal Liquefaction
IRR	Internal Rate of Return
kWh	Kilowatt hour
lb	Pound
LHSV	Liquid Hourly Space Velocity
m^2	Square meters
MFSP	Minimum Fuel Selling Price
MJ	Mega Joule
MYPP	Multi-Year Program Plan
NABC	National Advanced Biofuels Consortium
NAABB	National Alliance for Advanced Biofuels and Bioproducts
NREL	National Renewable Energy Laboratory
PNNL	Pacific Northwest National Laboratory
PFR	Plug Flow Reactor
PSA	Pressure Swing Adsorption
Ru	Ruthenium
SCF	Standard Cubic Foot
SCF/BBL	Standard Cubic Foot per Barrel
TCI	Total Capital Investment
TIC	Total Installed Cost
WGS	Water Gas Shift

Contents

Figures

Tables

1. Introduction

The goal of the Department of Energy's Bioenergy Technologies Office (BETO) as stated in the Multi-Year Program Plan (MYPP) is to enable the development of biomass technologies to:

- "Reduce dependence on foreign oil,
- Promote the use of diverse, domestic, and sustainable energy resources,
- Establish a domestic bioenergy industry,
- Reduce carbon emissions from energy production and consumption" [DOE 2013]

To assist in realizing these goals, a number of techno-economic evaluations have been developed for both biological and thermochemical pathways for converting biomass to fuels. These conceptual evaluations, termed "design cases", provide a detailed basis for understanding the potential of various conversion technologies and help identify technical barriers where research and development could potentially lead to significant cost improvements. Consistent assumptions for items such as plant lifetimes, rates of return, and other factors are used in all design cases so the various conversion pathways may be assessed on a comparative basis.

The purpose of this report is to evaluate the economics of hydrothermal liquefaction (HTL) of whole algal biomass followed by the catalytic upgrading of the resultant oil to produce primarily renewable diesel fuel. HTL is a thermal process that uses pressurized water in the condensed phase to convert whole, wet biomass primarily to useful fuel products. Aqueous and solid phases are also formed from which nutrients and energy can be recovered. Whole algae HTL (AHTL) and upgrading of the AHTL oil to transportation fuels have only been demonstrated in the laboratory and on a small engineering development scale. Hence, the analysis does not reflect the current state of commercially-available technology but includes advancements that might be achieved by 2022 with regard to algae conversion to fuels.

Some of the benefits of the algal cultivation and AHTL processing are as follows:

- Microalgae grown via autotrophic pathways have the potential to make sizeable contributions to renewable fuel mandates, particularly due to their rapid growth rates and other favorable cultivation characteristics relative to terrestrial biomass feedstocks.

- Converting the whole algae allows all parts of the biomass (carbohydrates, proteins, lipids) to contribute to fuel production. Thus it is not necessary to promote lipid accumulation.

- HTL in general is especially suited for conversion of wet feedstocks such as algae since the feed to the conversion unit is water based slurry.

- The overall economics for hydrocarbon biofuels are more strongly influenced by improvements in algal biomass productivity rather than extractable lipid content from the biomass.

- Hydrocarbon fuel can be produced by hydrotreating AHTL oil under relatively mild conditions.

- AHTL results in mid-distillate range hydrocarbons rather than gasoline replacements

1.1.   Overall AHTL Process Summary

Algal processing differs from lignocellulosic-based biomass refineries in that feedstock production and conversion to fuels or fuel intermediates are co-located and interdependent. However, for the purposes of this report, the cost for algae cultivation, harvest and dewatering is represented as a single feedstock cost. As shown in Figure 1, algae is harvested from the farm and dewatered to approximately 20 wt% solids. Condensed phase liquefaction then takes place in the AHTL reactor through the effects of time, heat and pressure. The resulting AHTL products (oil, solid, aqueous, gas) are separated and the AHTL oil is hydrotreated to form diesel. The AHTL aqueous phase is catalytically treated to recover the carbon content and allow water recycle back to the ponds. Process off gas may be used to generate hydrogen, heat and/or power. A hydrogen source is needed if hydrotreating is performed on-site as opposed to transporting the AHTL oil to a centralized upgrader. For simplicity, the preliminary target case assumption in this report is that hydrotreating is co-located with the algae ponds and AHTL conversion. This assumption should be revisited in next few years, as use of existing infrastructure becomes better understood. Nutrient recovery is accomplished by recycling treated water, carbon dioxide containing flue gas, and treated solids back to the algae ponds.
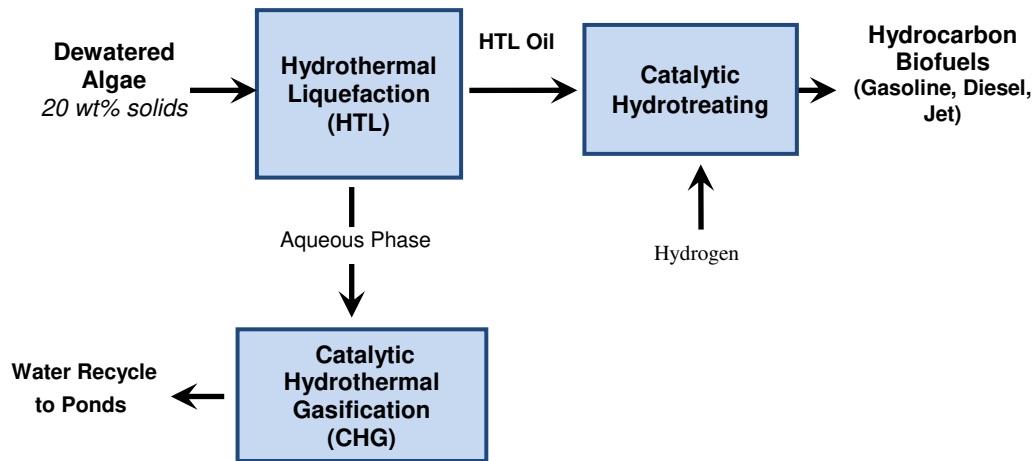
Figure 1 Block diagram for the overall conversion process

Although outside the scope of this report, it is important to note that research improvements to algal growth, harvest and dewatering, and optimization of nutrients recycle to the farm from the conversion plant are critical to the overall success of this process.

1.2.   Techno-economic Analysis Approach

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. 2013, Dutta et al. 2011, Humbird et al. 2011]. Process flow diagrams and models are based on experimental results from completed and ongoing research at PNNL, NREL, and other research organizations, as well as

information from commercial vendors for mature and similar technologies. The process models are developed in the commercial process flow simulation software tool AspenPlus [Aspentech 2013]. The heat and material balances from the simulation models are used to estimate the capital and operating costs. These are then assembled in a Microsoft Excel$^{©}$ spreadsheet employing a discounted cash flow analysis to estimate the minimum fuel selling price.

This approach is summarized in Figure 2 for the conversion process:
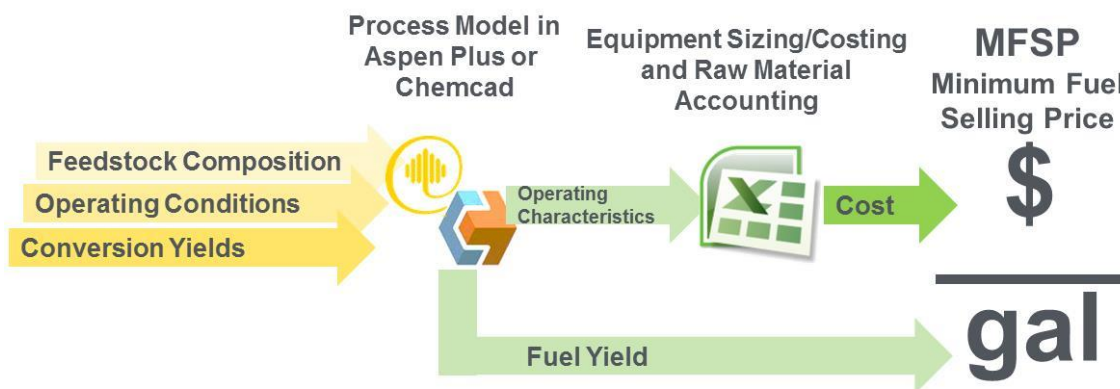
Figure 2 Techno-economic analysis approach

1.3.   **Overall Design Basis Assumptions**

This section briefly describes the general assumptions used in the analysis.

1.3.1. Definition of Nth Plant

A standard reference basis common to the conceptual design reports, known as the "nth" 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 specific assumptions are shown in Table 1. These assumptions are consistent across BETO design cases, thus allowing a standard basis for comparison of different conversion technologies in the context of a well-defined hypothetical plant.

It should be noted that the assumption of 330 operating days per year at full capacity may be optimistic given the potential for seasonal disturbances and maintenance requirements. Sensitivity to this and other assumptions are shown in Section 4.

Table 1 Nth plant assumptions

Assumption Description	Assumed Value
Internal rate of return	10%
Plant financing debt/equity	60% / 40% of total capital investment
Plant life	30 years
Income tax rate	35%
Interest rate for debt financing	8.0% annually
Term for debt financing	10 years
Working capital cost	5.0% of fixed capital investment (excluding land)
Depreciation schedule	7-years MACRS schedule
Construction period	3 years (8% 1st yr, 60% 2nd yr, 32% 3rd yr)
Plant salvage value	No value
Start-up time	6 months
Revenue and costs during start-up	Revenue = 50% of normal Variable costs = 75% of normal Fixed costs = 100% of normal
On-stream factor	90% (330 operating days per year)
Indirect capital costs	60% of total installed capital

1.3.2. General Cost Estimation Basis

All costs in this report are on a 2011 constant dollar basis. This is the current reference year that BETO uses to facilitate comparison of various conversion technologies [DOE 2013]. Indices used to convert capital and operating costs to the 2011 dollars can be found in Appendix E.

Capital costs are estimated from a variety of resources. The heat and material balances generated by the simulation software (Aspen Plus) are used to size the major pieces of equipment. These are input into Aspen Capital Cost Estimator software (reported in 1st quarter 2011 costs) to determine the installed capital cost. In addition, select data from commercial vendors, either as budgetary estimates or from their published literature are used when available.

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 2011 basis using the Chemical Engineering (CE) magazine's published indices:

$$\text{Cost in 2011 \$} = \text{equipment cost in quote year} \times \left(\frac{2011 \text{ index} = 585.7}{\text{quote cost year index}} \right)$$

The scale is adjusted to the match the appropriate scaling term (heat exchanger area for example) by using the following expression:

$$\text{Scaled equipment cost} = \text{cost at original scale} \times \left(\frac{\text{scale up capacity}}{\text{original capacity}}\right)^n$$

Where 'n' is the scale factor, typically, 0.6 to 0.7.

Once the equipment is scaled and adjusted to the common cost year, factors are applied to calculate the total capital investment. Individual installation factors calculated by Aspen Capital Cost Estimator are multiplied to equipment costs, unless installed costs are already available from vendors. The total direct cost is the sum of all the installed equipment costs, plus the costs for buildings, additional piping and site development (calculated as 4%, 4.5% and 10% of purchased equipment, respectively). 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.

Operating costs are estimated by using the results from the Aspen Plus heat and material balances and applying the assumptions shown in Section 3. For the cooling tower, it is assumed that water is available at 90 °F with a 20 °F allowable temperature rise.

2. Process Design and Cost Estimation

This section provides details for converting dewatered whole algae via HTL to a bio-oil, upgrading bio-oil to diesel fuel, HTL aqueous phase treatment, hydrogen generation and utilities. Detailed heat and material balances (derived from the Aspen Plus model) are shown in Appendix A.

2.1.   Basis for Dewatered Algae Feedstock Cost

The 2012 harmonization report [ANL; NREL; PNNL, 2012] for algal lipid extraction and upgrading, and similar ongoing work for AHTL conversion and upgrading establishes baseline resource assessments given current algae productivities. This report builds on the AHTL models developed for the harmonization project, with the aim of identifying gaps and opportunities for improvement to the AHTL process. Since the focus of this report is AHTL conversion and downstream processing, it does not address the ongoing research by others into algae cultivation, harvest and dewatering and the associated costs. Improvements to algae species, cultivation, harvest and dewatering are expected to impact AHTL conversion (and the associated economics). The MYPP [DOE 2013] presents algae feedstock targets associated with the lipid extraction pathway of \$340/ton for cultivation (30 g/m^2/day productivity) and \$90/ton for dewatering to 20 wt% ash free dry weight (AFDW) solids. Thus, a fixed price of \$430/ton for wet algae at 20 wt% solids is used for the out-year 2022 target case. The \$430/ton value as cited includes the assumption of 50% lipid content. Since AHTL treats the whole algal biomass rather than just the extracted lipid portion, highly stressed production schemes to induce lipid accumulation are not necessary in order for AHTL to produce substantial quantities of oil. Hence future work should consider organism and cultivation improvements to increase productivity. Also needed are improvements to harvesting and dewatering methods to reduce costs. Sensitivity to feedstock cost is assessed in Section 4.

Leveraging work from the 2013 AHTL harmonization project, projections were made by NREL for higher productivity cases that might be attained in the future. Following these projections, the basis for the future target case assumed here is an algae farm operating at 30 g/m^2/day and producing a yearly average of 1340 tons per day of algae (dry and ash free basis) delivered to the AHTL plant as 20 wt% solids slurry. This in turn is based on the 10,000 acres of ponds assumed in the harmonization work.

As shown in the 2012 harmonization report, and AHTL harmonization, algae productivity rates vary significantly as a function of location and season. The AHTL harmonization work suggests that on a national scale, there can be as much as a 9-to-1 difference in production rates between summer and winter depending upon the location. However, the specifics will be strain dependent. Some specific locations may allow a smaller variability range down to a 2-to-1 difference. Such a wide seasonal variation in algae production means that for certain locations, part of the conversion plant might have to be idled during the low season or operate at reduced capacity. This work assumes a 5-to-1 fluctuation between summer and winter production and resulting feed rate to the AHTL conversion plant. Diverting a portion of the wet algae during the high season for use in the low season may mitigate this effect. However, storing wet algae for later use requires measures to prevent fermentation, many of which are cost prohibitive. An alternate scheme, assumed in this report, is to dry a portion of the algae during the high season for later use. Approximately 30 wt% (AFDW) of the wet algae produced during the summer months is dried from 80 wt% moisture to 10 wt% moisture. This assumes that the moisture reduction

needed for storage is similar to that for herbaceous feedstocks which require less than 15% moisture (Hess 2009). The dried algal matter is stored until needed for winter operation.

2.2.   Algae HTL

Under the temperature and pressure conditions of HTL, water becomes highly reactive. "Near the critical temperature of water, changes in vapor pressure, liquid density, dielectric constant and solvent power happen quickly with small changes in temperature" [Elliott 2011]. In this environment, algal biomass breaks down into a crude bio-oil containing numerous types of compounds. Some compounds reform into new ones, others are extracted. A few general examples include, carbohydrates forming aromatics, proteins forming amino acids which in turn can form piperidine and pyrrole type compounds, formation of amides, and hydrolysis of triglycerides which can form fatty acids [Illinois 2013]. Sudasinghe et al. [2014] analyzed AHTL oil and its associated aqueous phase that were obtained by gravity separation. They estimated that the liquids contain thousands of compounds. They suggest that oxygenated compounds in the AHTL oil are likely derived from lipid and carbohydrate degradation, while protein degradation forms nitrogen heterocyclic compounds (pyrroles, pyridines, pyrazines, imidazoles and their derivatives). Figure 3 show the structures of a few example compounds identified from water and oil samples by GC-MS. Structures were obtained from the Chem Book [2014]. In general, smaller, more polar compounds report mainly to the aqueous phase and larger less polar compounds report to the oil. However, Sudasinghe et al. [2014] reported a "high degree of commonality" between the two phases.

Pyrazine, methyl-

2-Pyrrolidinone, 1-butyl-

1-Piperidinecarboxaldehyde

3-Ethylamino-4-methylphenol

Hexadecanenitrile

n-Hexadecanoic acid
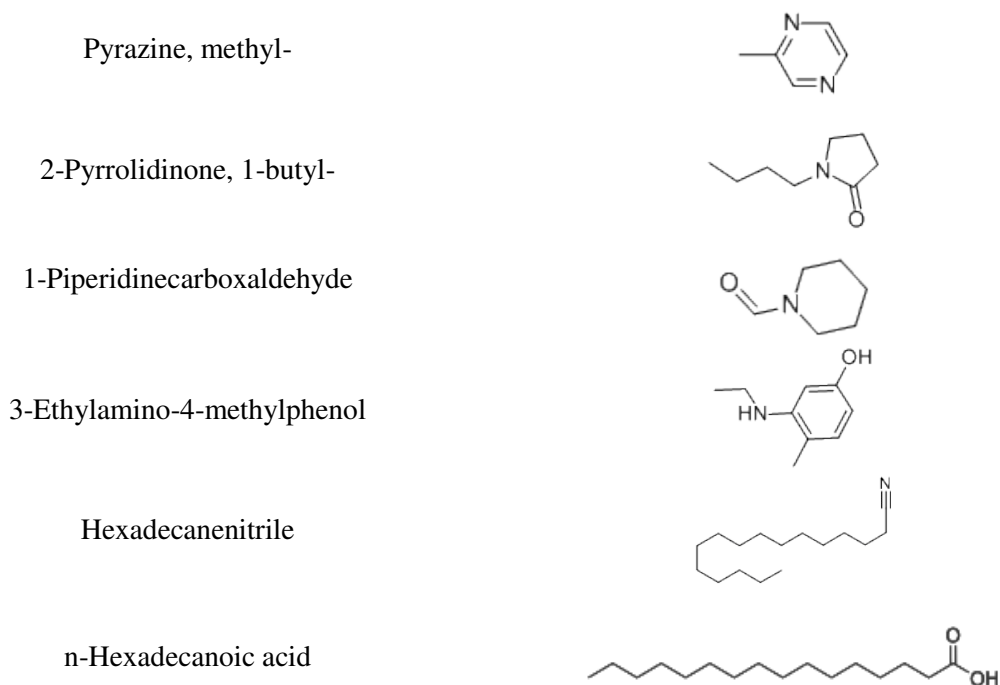
Figure 3 Example AHTL products

The conversion process involves pumping whole algal biomass slurry in water to the HTL reactor at a pressure that allows water to stay in the liquid state at the operating temperature. Lab-scale experiments indicate that algal slurries are not difficult to pump, and that for some strains, solids concentrations as

high as 35 wt% are easily pressurized. Figure 4 depicts the simplified process flow. Whole wet algae slurry is hydrothermally treated in subcritical water, nominally 2,000–3,000 psia and 300–350 °C. A solids content of 20 wt% solid is estimated to be a reasonable trade-off between the capital costs for the HTL system and the costs for dewatering. Higher solids concentrations to HTL reduce the capital cost and make product separation easier but also incur greater dewatering costs. Future work will better quantify these tradeoffs.
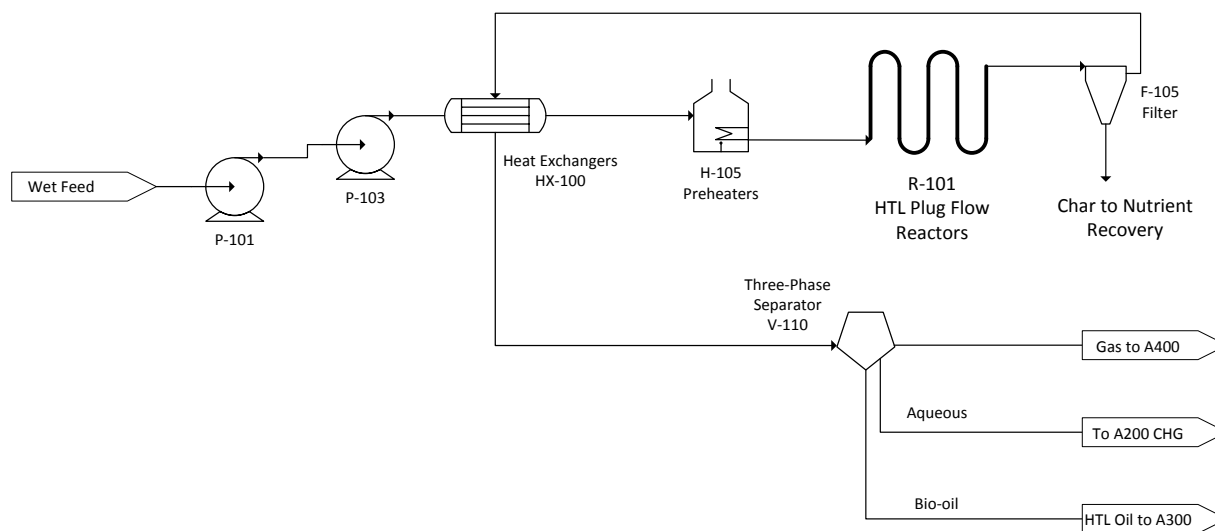
Figure 4 Process flow for Area 100: AHTL

The reaction temperature dictates the reactor pressure (e.g., the reactor pressure is sufficiently high to maintain water in the liquid state at the reaction conditions). The slurry entering the reactor is preheated by exchange with reactor effluent (HX-100). The reactor effluent is primarily composed of the organic bio-oil phase and a separate aqueous phase. Small amounts of solids and gases are also formed. The two liquid phases and the non-condensable gases are cooled and then separated. Algal nitrogen and sulfur partition between each phase to varying degrees. The predominately organic liquid bio-oil phase is sent to catalytic upgrading, and the predominately aqueous phase is sent to water cleanup/catalytic processing for carbon recovery. The non-condensable gases are used in the hydrogen plant. Solids are removed by filtration and contain a significant amount of phosphorus that should be recycled back to the algae ponds.

There are numerous batch HTL studies in the literature. For example, Minowa et al. [1995], Brown et al. [2010], Duan and Savage [2011], Biller and Ross [2011], Jena et al. [2011], Valdez et al. [2011], Yu et al. [2011], Vardon et al. [2011], and Garcia Alba et al. [2012], all studied HTL reactions typically at 30-60 minutes residence times and for various algal types. The reported yields are in the 15–52 wt% range and product recovery is achieved by solvent extraction with a single solvent. Studies at shorter residence times (1-10 minutes) indicated that even higher yields are possible depending upon the strain [Garcia Alba 2012, López Barreiro 2013, Faeth 2013]. For example, López Barreiro et al. [2013] reported yields up to 58% AFDW yield at 375 °C and 5 minutes residence time. In contrast, Li et al. [2014] used very long residences times, up to 90 minutes, and low temperatures (220 - 300 °C) coupled with a multi-step, multi-solvent extraction system. The yield for a high lipid (60 wt%) *Chlorella* was 83%, while the yields for low lipid (14 wt%) *Nannochloropsis* was 55%.

To date, there are two publications reporting AHTL results from continuous reactor systems. Continuous flow reactors produce stable, steady state results that can be used to design commercial systems. Jazwari et al. [2013] published results from a 15-30 L/h plug flow type reactor unit. *Chlorella* and *Spirulina* were processed at solids feed concentrations of 1-10 wt% and reactor temperatures of 250-350 °C. Solvent extraction was used to recover the oil product. Yields were approximately 10-43% AFDW and the oxygen and nitrogen contents were 12-22 wt% and 2.6- 7.9 wt% respectively. Experimental work at PNNL for the National Alliance for Advanced Biofuels and Bioproducts (NAABB) was reported for a 1.5 L/h reactor system processing *Nannochloropsis* sp. at 20-35 wt% feed solids [Elliott 2013]. Gravity phase separation was used to recover the HTL oil, which had a quality range of 5–10 wt% oxygen and 3–5 wt% nitrogen. The yields varied from 38 to 63 wt% (AFDW).

HTL oil yield is a function of residence time, temperature, feed solids concentration and algae characteristics. Figure 5 shows the relationship between solids concentration, lipid and oil yield and is derived from Jazwari et al. [2013], and published [Elliott 2013] and unpublished work from PNNL.
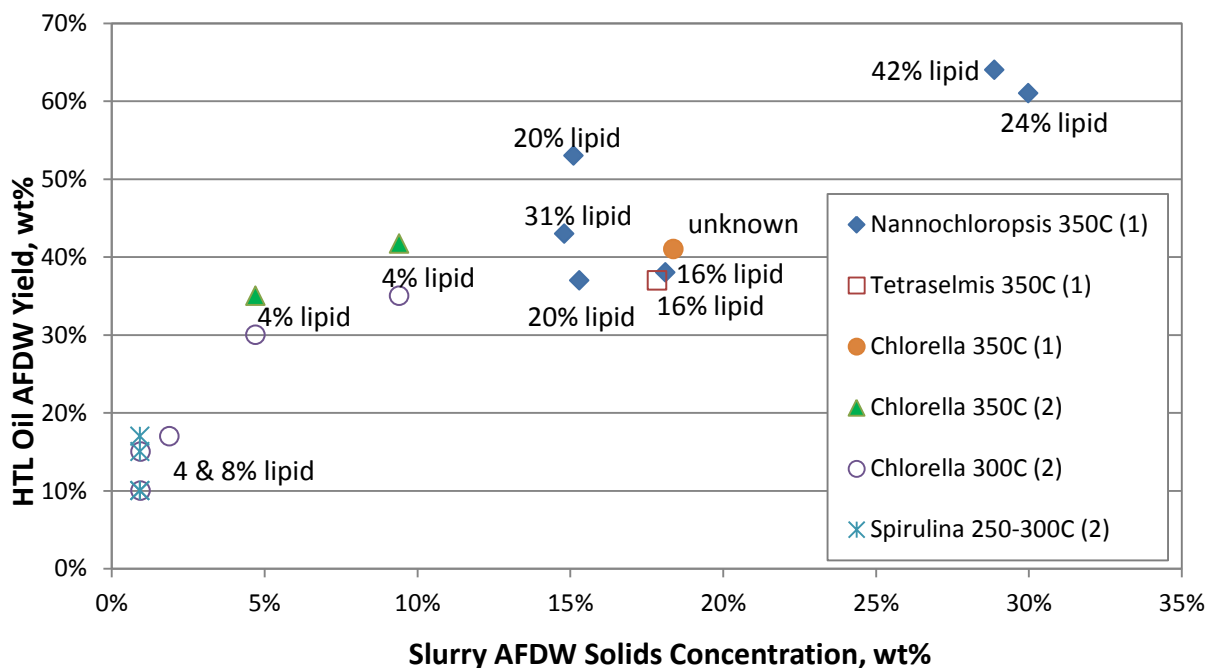
Figure 5 Continuous flow reactor parameter effects on HTL oil yield
(1) PNNL, oil recovery by gravity separation
(2) Jazwari et al. [2013], oil recovery by solvent extraction

Preliminary data from PNNL for both *Nannochloropsis* and *Tetraselmis* indicate that significant oil-type molecules remain in the aqueous phase when processed at 15-20 wt% solids. Approximately 20-30 wt% of the organic mass in the aqueous product is AHTL oil type material that could be recovered with an appropriate separation method. Preliminary data also suggest that salts, including ash components, have a positive effect on oil recovery. Thus simple gravity separation alone is not a sufficient separation technique, and more efficient methods are being explored. Figure 5 also shows that total lipid content affects the yield, likely as a result of producing more compounds with lower affinity for the aqueous phase.

2.2.1. AHTL Process Design Basis

Experimental results from PNNL work with the NAABB for *Nannochloropsis* and from PNNL for *Chlorella* (designated as DOE 1412), and unpublished work for three other algal types are used as the basis for the Aspen models. Detailed results for *Nannochloropsis* and *Chlorella* are reported here. *Nannochloropsis* is a salt water algae and was grown under conditions promoting rapid growth and high biomass productivity rather than extractable lipid content. In general, *Nannochloropsis* has poor productivity when grown over large geographical areas, whereas, *Chlorella* is a fresh water algae with good productivity. Table 2 shows example strain compositions from the experimental work. Further work with other strains is underway, as AHTL is applicable to any of fresh, brackish and saline water algae.

Table 2 Algal biomass elemental composition and ash content

Component	*Nannochloropsis sp.* Wt%	Wt% ash free	*Chlorella* (DOE 1412) Wt%	Wt% ash free	Aspen Design Case Model Wt%
C	51.9	59.5	50.2	54.6	52
H	7.5	8.6	6.8	7.4	7.5
O	22.4	25.7	24.3	26.5	22
N	4.8	5.5	9.8	10.7	4.8
S	0.61	0.7	0.68	0.7	0.61
ash	12.8		8.13		13
P	0.6		1.6		0.6
HHV BTU/lb (Boie)	10,719		10,158		

Table 3 shows the PNNL experimental HTL parameters associated with processing of the strains in Table 2. The experimental setup includes a feed tank, dual syringe feed pumps, a jacketed preheater, a 415 ml continuous stirred tank reactor (CSTR), a 270 ml plug flow reactor (PFR) and a filter. The preheater and filter add another 880 ml of non-optimized volume to the system. Solids are removed by an in-line filter operated at approximately ~20°C below the reactor temperatures. Gaseous products are removed by de-pressuring and the two liquid phases separated by gravity. The operating temperatures correspond to conditions that promote high algal conversion to oil. The operating pressure is sufficiently high to maintain water in the liquid state. The experimental setup can be run in several modes depending upon the need: PFR only, CSTR only or a combination of both. The conceptual AHTL plant modeled here assumes a PFR type reactor. Future work will investigate temperature, residence time and feed concentration affects as these relate to different types of strains.

Table 3 AHTL experimental results and model assumptions

Operating Conditions and Results	*Nannochloropsis*	*Chlorella*	Aspen Design Case Model
Temperature, °F (°C)	667 (353)	658 (348)	660 (349)
Pressure, psia	3020	2930	3035
Feed solids, wt%			
Ash included	34.4%	20.0%	22.3%
Ash free basis	31.5%	18.7%	20.0%
LHSV, vol./h per vol. reactor	2.23 Hybrid PFR-CSTR	2.22 Hybrid PFR-CSTR	4 PFR
Equivalent residence time, minutes	27	27	15
Total dry mass algae, lb. (kg)	12 (5.44)	5.1 (2.3)	Not applicable[3]
Total continuous run time, hours	9.87	7.44	Not applicable[3]
HTL oil yield (dry, ash free algae), wt%	59%	41%	59%
Product yields on dry algae, wt%			
HTL Oil (dry)	56%	38%	51%
Aqueous organic + ash	39%	59%	43%[1]
Gas	5%	1%	4%
Filter solids	1%	2%	2%[1]
HTL dry oil analysis, wt%			
C	77.0%	77.3%	77.0%
H	10.4%	9.4%	10.4%
O	8.0%	6.1%	8.0%
N	4.2%	6.2%	4.2%
S	0.3%	0.65%	0.3%
P	3 ppm	0.03%	Not modeled[2]
Ash	0.14%	0.29%	0.14%
HTL oil moisture, wt%	2.8 wt%	5.6 wt%	5.6 wt%
HTL oil wet density	0.94	0.98	0.94 Aspen est.
Aqueous phase COD	77,200	88,800	63,600 Aspen
Aqueous phase density	1.05	1	1.01 Aspen est.

[1] Experimentally, most of the ash components are solubilized. Until more is known, and for simplicity at this early stage, ash compounds are treated as solids throughout the model.

[2] Phosphorus partitioning is not directly modeled in Aspen because of the small quantity, most of which reports to the solid phase.

[3] Total dry mass and continuous run times are not applicable to the steady-state simulation model

The HTL results from the *Nannochloropsis* run show a higher oil yield than the *Chlorella* run. This is likely caused by the combined impact of higher lipid content and higher solids loading to the HTL reactor combined with compositional differences for the two feeds. Strain specific characteristics, such as total lipid content, fatty acid profile, protein content, and ash constituents all play a role in the resultant oil yield and quality. These effects combine to dictate the quality of the oil HTL oil and the quantity of organic partitioning to the oil phase when simple gravity separation is used for separation and oil recovery.

The higher oil yield is chosen for the design (aka target) case, which is not strain specific More AHTL processing data are needed for algal species with high biomass productivity as opposed to just high lipid producing types. Additionally, there is a need to optimize AHTL process conditions to maximize the oil yield. Improved product separation to efficiently recovered oil and reduce carbon lost to the aqueous phase is needed regardless of the algae type. Examples could include use of high efficiency oil/water separators or the introduction of additives to the AHTL reactor that could facilitate phase separation. Appendix C details the rationale for compounds selected for use in the Aspen model.

2.2.2. AHTL Capital Costs

The capital cost for the HTL reactor system is based on vendor budgetary estimates from the National Advanced Biofuels Consortium (NABC) for wood based HTL systems [Knorr 2013]. The original NABC cost data were scaled to the whole algae HTL rate. Two reactor trains, each containing two parallel HTL reactors is assumed. The HTL reactors are a jacketed serpentine pipe with heating medium in the annular space. This is similar to a double pipe heat exchanger or the serpentine reactors used for low density polyethylene manufacturing [Exxon 2014]. Scaling assumptions and installation factors can be found in Appendix B. The capital costs for the HTL system are shown in Table 4. As will be shown in Section 3, HTL represents the single largest capital cost for the entire conversion plant. Development of kinetic data, corrosion data, and investigating catalytic HTL are means of better defining pathways to reduced costs.

The metallurgy of the NABC cost data (316 stainless) is the same as that used in the algae experimental work. Appropriate metallurgy is a key to safe operation and capital cost; hence corrosion analysis is underway, but not available at the time of this writing.

Table 4 AHTL capital costs

Item	Purchased, million USD	Installed, million USD	Source
Driers	10.0	15.9	Muth 2013
HTL Reactor System: Pumps, heat integration, HTL reactor, knockout drums	36.0	74.8	Knorr 2013
Phase separation	2.36	4.59	Knorr 2013
Reactor hot oil system	4.49	6.44	Knorr 2013
Total	**52.8**	**102**	

2.3.   AHTL Aqueous Phase Treatment

The aqueous product (Table 3) from AHTL contains significant levels of nitrogen and carbon that must be recovered for their nutrient and economic value. The nitrogen content in the aqueous phase precludes the use of anaerobic digestion as a treatment method. Typical C:N molar ratios for anaerobic digestion are in the 27-32:1 range; high nitrogen content causes a build-up of ammonia which is harmful to the organism [Kosseva 2013]. Experimental data from PNNL for the HTL aqueous phase for four different strains have a C:N ratio ranging from 2.6 to 5.2, which are very much out of that given range. Catalytic hydrothermal

gasification (CHG) provides an alternative means for carbon and nitrogen recovery that is not C:N limited.

The CHG reactor catalytically converts all organics to CO_2 and CH_4. The process is similar to HTL in that heat and pressure are used to drive the conversion and water is maintained in the liquid state. However CHG differs from HTL in that employs a catalyst [Elliott 2011, 2012] and produces a gaseous product. The solubility of salts decrease and that of organics increase. Both the change in solubility and change in density affect mass transfer rates. The experimental set up is described by Elliott [2012].

Figure 6 shows the flow diagram for CHG. Since the CHG ruthenium catalyst is sensitive to sulfur, a sulfur scavenger is needed. A nickel guard bed is placed ahead of the CHG reactor (sulfur scrubber) to capture organic sulfur. However, this does not capture sulfates. A possible mitigation method is to add calcium hydroxide to the HTL feed prior to liquefaction to cause the sulfate ions formed during liquefaction to precipitate as solid calcium sulfate. Sulfate removal is under investigation and is not included in this report. Future work will consider more effective means of sulfur capture and/or CHG catalysts less susceptible to poisoning, as this may be necessary for certain algae species and/or cultivation environments.
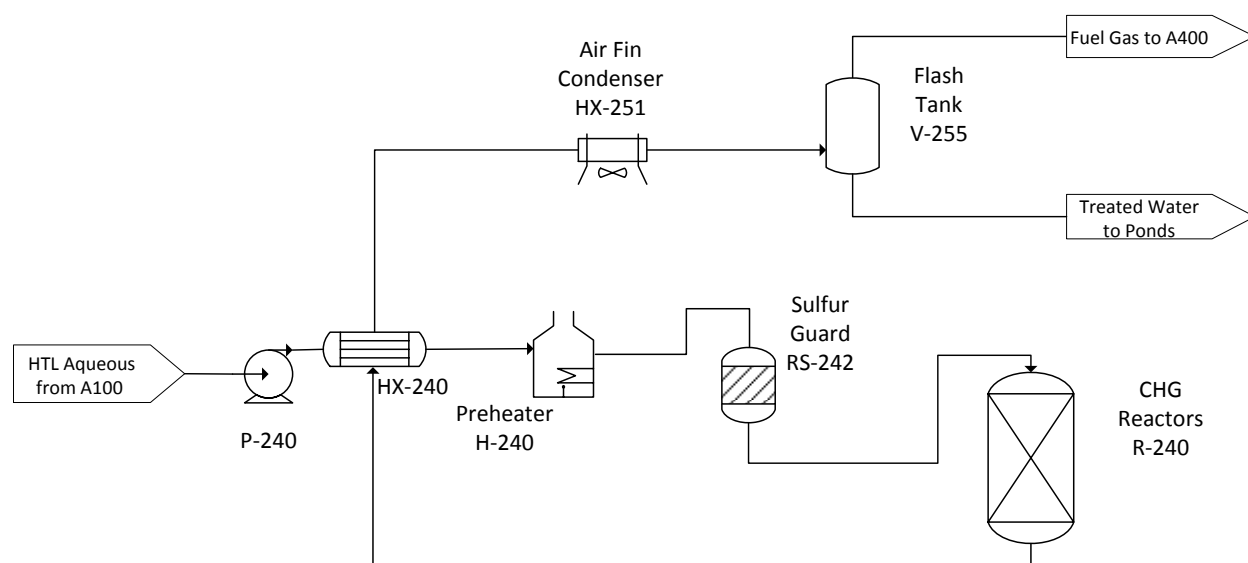
Figure 6 Process flow for Area 200: CHG

In this process, the HTL aqueous phase is pumped to ~3,000 psia, and preheated to 350 °C. The feed to the fixed bed catalyst reactor is preheated using heat recovered from the CHG products stream (HX-240). A fired heater provides trim heat. Organic sulfur is scavenged in a guard bed containing nickel catalyst before being fed to a fixed bed catalytic reactor. Organics in the aqueous phase are mainly converted to CO_2 and CH_4. Treated water is recycled to the algae farm to reduce fresh nutrient demands during cultivation. The produced CHG gas is sent to the hydrogen generation area to generate hydrogen for the upgrading plant. If the AHTL plant is not co-located with the upgrader, part of the offgas from the CHG system can be sent to a boiler to generate steam for process use or power generation. The cost for a hydrocyclone filter is included as a conservative measure. However, this will likely not be necessary if the Area 100 (AHTL) filter operates efficiently.

2.3.1. CHG Process Design Basis

Table 5 shows the results of the continuous flow reactor CHG experiments and the model assumptions. Since CO_2 is soluble in water (especially at high pressure), the produced gas is methane rich, while a significant portion of the CO_2 remains with the condensed treated water. A ninety-nine percent reduction in COD was achieved in the non-optimized experimental system. Further reductions in severity (temperature, pressure, space velocity) may still be achievable. Future work should explore corrosion analysis as well. The Aspen model reflects the experimental set-up in that the HTL aqueous product is cooled prior to downstream processing. Since CHG (and the feed to the hydrotreaters) must be reheated and pumped back to the operating pressure, there is an opportunity for better heat integration between HTL, CHG and possibly the hydrotreaters. Analysis of the cost tradeoffs are beyond the scope this report, and should be considered in the future. Additionally, research is needed to understand the conversion of organics in the aqueous phase to hydrogen, bio-products, and species that can rejoin the predominantly organic phase.

Table 5 CHG experimental results and model assumptions

Component	*Nannochloropsis*	*Chlorella*	Aspen Target Model
Guard Bed	Raney nickel	Raney nickel	Raney nickel
Temperature, °F (°C)	667 (353)	662 (350)	662 (350)
Pressure, psia	2955±40	3063±18	2980
Catalyst	7.8 wt% Ru/C	7.8 wt% Ru/C	7.8% Ru/C
LHSV, vol./hour per vol. catalyst	1.49	2.0	2.0
WHSV, wt./hr per wt. catalyst	2.98	3.99	3.99
% COD conversion	98.8%	99.9%	99.9%
% Carbon to gas[1]	59%	48%	57%
Gas analysis, volume %			
CO_2	28.4%	22%	22%
H_2	2.3%	0%	0%
CH_4	66.2%	76%	71%
C_2+	2.1%	2%	2%
N_2	1.0%	--	--
water	--	--	5.8%
Treated water COD	971	32	Low, recycle treated water to ponds
[1] Note that the remaining converted carbon is dissolved bicarbonate			

2.3.2. CHG Capital Costs

The capital costs for CHG are shown in Table 6. CHG is very similar to AHTL, hence capital costs for the CHG reactor are based on the vendor budgetary estimates from the NABC for wood and corn stover plug flow AHTL reactor [Knorr 2013]. Six CHG reactors in parallel are assumed. Additional details can be found in Appendix B.

Table 6 CHG capital costs

Item or Area	Purchased, million USD	Installed, million USD	Source
Pumps	1.27	1.81	Aspen Capital Cost Estimator
Feed/Product Exchangers	20.2	44.4	Knorr 2013
Fired Heater	0.61	0.74	Knorr 2013
Hydrocyclone	3.56	7.47	Kreb's Engineering Quote
Guard Bed	0.63	1.27	Assumed 5% of CHG reactors
CHG Reactors	12.7	25.3	Knorr 2013
Product Air Fin Cooler	0.37	0.48	Aspen Capital Cost Estimator
Total	**39.3**	**81.4**	

2.4. AHTL Oil Hydrotreating

AHTL oil requires further catalytic processing to remove oxygen, nitrogen and sulfur. Ideally, the AHTL oil would be transported to a centralized upgrader that accepts oil from multiple sites to realize commercial economies of scale. This could be a dedicated system or it could occur at an existing petroleum refinery. However, more work is needed to characterize the processing needs of AHTL oil and the oxygen, nitrogen and sulfur limits that could be tolerated in a conventional plant. Also, distance and scale of the central upgrader must be considered. Therefore, for this preliminary analysis, the hydrotreater and hydrogen plant are co-located with the AHTL unit on the algae farm site. Sensitivity to off-site processing is considered in Section 4.

Typical AHTL oil hydrotreating conditions to date are approximately 350 to 400 °C, 1,000 to 2,000 psig, and 0.2 to 0.3 liquid hourly space velocity. Initial experimental work from the NAABB found that a single hydrotreater (continuous operation) was able to reduce the oxygen content to less than 1% and the nitrogen content to <0.3%. A patent application suggests pressures as low as 500 psia [Marker 2009] for similar type feedstocks.

The AHTL oil hydrotreating process flow is shown in Figure 7. The raw AHTL oil is mixed with hydrogen and preheated. Oxygen is converted to CO_2 and water, nitrogen is converted to ammonia, and sulfur is converted to hydrogen sulfide. Some of the ammonia remains dissolved in the water phase, which in turn is recycled to the algae farm in this configuration that assumes co-location. Ammonia in the gas phase will need to be removed with a water scrubber. The hydrotreater effluent is cooled to

condense the produced water and hydrocarbons. The organic phase is fractionated into four boiling point cuts: C_4 minus, naphtha range, diesel range, and heavy oil range material. The heavy oil is assumed to be cracked in a conventional hydrocracker to produce additional naphtha- and diesel-range products. GC/MS data are available for the whole hydrotreated oil. However, simulated distillation data are used to estimate the volumes of naphtha, diesel and heavy oil boiling range material, as product cut analysis is not yet available.
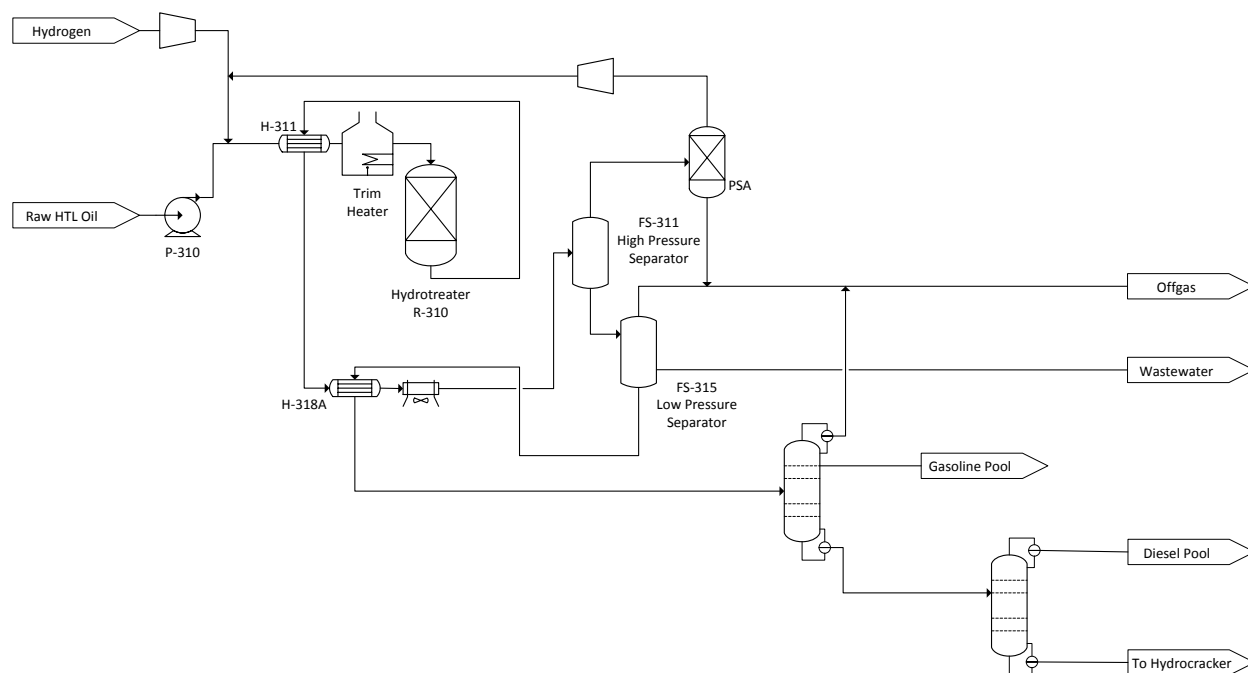
Figure 7 Process flow for hydrotreating

Future work should consider means for reducing the nitrogen, sulfur and oxygen content in the AHTL oil in order to minimize the need for hydrotreating, for example, through oil pretreatment.

2.4.1. AHTL Oil Hydrotreating Design Basis

The design basis for hydrotreating, using PNNL experimental data from flow reactors, is shown in Table 7. Note that the *Nannochloropsis* HTL oil and the *Chlorella* HTL oil were hydrotreated using different scale hydrotreaters and this accounts for the difference in total run time. Elliott et al. [2013] reports 79% to 85% mass yields for hydrotreating HTL oil derived from four different types of *Nannochloropsis*. Recent experimental data from PNNL using HTL oil from *Tetraselmis* show a similar range and less than 1 wt% oxygen in the product. Thus the targeted yield is conservative.

Table 7 Hydrotreating experimental results and model assumptions

Component	*Nannochloropsis*	*Chlorella*	Aspen Target Model
Temperature, °F (°C)	745 (396)	752 (400)	757 (403)
Pressure, psia	1936±7	~1500	1515
Catalyst	CoMo/alumina-F	CoMo/alumina-F	CoMo/alumina
Sulfided?	yes	yes	Purchased presulfided
LHSV, vol./hour per vol. catalyst	0.20	0.20	0.5
WHSV, wt./hr per wt. catalyst	0.23	0.25	0.625
HTL oil feed rate, lb/h (g/h)	0.141 (63.9)	0.011 (4.8)	Commercial scale
Total continuous run time, hours	6.0	20	Not applicable[2]
Chemical H_2 consumption, wt/wt raw HTL bio-oil (wet)	0.0375	0.043	0.043
Products, wt %			
Hydrotreated oil	81%	75%	77%
Aqueous phase	9%	16%	16%
Gas	10%	9%	7%
Product oil, wt% (dry basis)			
C	84.4%	83.4%	86%
H	13.5%	13.5%	14%
O	1.85%	2.2%	<1%
N	0.25%	<0.05	<0.05%
S	<0.005	<0.005	0.0%
Aqueous carbon, wt%	0.75%	0.27%	0.3%
Gas analysis, volume%			
CO_2, CO	6%	12.8%	0%
CH_4	54%	41.3%	45%
C_2+	40%	44.6%	54%
NH_3	Not measured	1.3%	1%
TAN, feed (product)	69 (<0.1)	39.3 (<0.01)[1]	Not calculated
Viscosity@40 °C, cSt,			
feed (product)	475 (4.5)	223 (1.29)	Aspen: (3.07)
Density@40 °C, g/cm^3,			
feed (product)	0.953 (0.768)	0.987 (0.761)	Aspen: 0.925 (0.755)

[1] Two samples below detect, one sample at 0.66
[2] Total continuous run times are not applicable to the steady-state simulation model

The catalyst chosen for this work is commonly used in petroleum hydrodesulfurization. The results indicate that it is active for nitrogen and oxygen removal as well. Further work is needed to optimize the run conditions (temperature, pressure, space velocity and catalyst type) to achieve low nitrogen and oxygen content products while minimizing formation of light compounds.

Chemical hydrogen consumption is the difference between the hydrogen content at the inlet and outlet of the reactor. Typical petroleum refining chemical hydrogen consumption is 450 scf/bbl for a naphtha

desulfurizer and 1200 scf/bbl for a single stage hydrocracker [Parkash 2003]. The hydrogen chemical consumption for AHTL oil shown in Table 7 is approximately equal to 3200 scf/bbl. Thus there is some incentive to improve AHTL operation to reduce the nitrogen and oxygen content in the oil, while minimizing carbon loss. Reduced nitrogen and oxygen will also reduce the size of the exotherm, which may allow higher space velocities.

AHTL oil contains compounds that might cause hydrotreating catalyst deactivation, for example, salts and phosphorus. One possible consideration is to use desalters similar to those used in petroleum refineries, and a simple wash is included in the model. Although petroleum hydrotreater catalyst life is typically several years, a conservative estimate of one year is assumed here. Future work will better quantify feed preparation needs and actual deactivation rates and regeneration methods.

The hydrocracking assumptions are shown in Table 8. No experimental data are yet available. However, as the heavier than diesel fraction is a hydrocarbon, it is likely that it can be processed in a manner similar to conventional petroleum hydrocracking. Some over-cracking (gas production) is assumed and the product is geared towards maximizing the diesel fraction. Experimental demonstration of heavy HTL oil hydrocracking should be conducted in the future.

Table 8 Hydrocracking model assumptions

Process	Basis	Assumptions
Hydrocracking heavier than diesel portion of hydrotreated HTL oil	No experimental data, assumed to be similar to conventional hydrocrackers, with LHSV$\geq$0.5 Temperature: 370 °C Pressure: 1035 psia	H_2 chemical consumption: 0.02 wt/wt heavy oil Product breakdown: Gas (excluding excess H_2); 8 wt% Liquid fuels: 86 wt% Aqueous: 6 wt%

2.4.2. AHTL Oil Hydrotreating Capital Costs

The capital costs shown in Table 9 are based on a review of conventional naphtha, diesel and kerosene hydrotreaters as published in the SRI 2007 Yearbook [SRI 2007a] and from Petroleum Refining Technology and Economics [Gary 2007]. Additional cost details can be found in Appendix B.

Table 9 Hydrotreater capital costs

Item or Area	Purchased, million USD	Installed, million USD	Source
Hydrotreater system (4500 BPSD)	14.4	24.7	SRI 2007a
Hydrocracker system (500 BPSD)	3.8	5.7	SRI 2007b

The costs spanned a broad range from simple naphtha hydrodesulfurization units, to multi-stage hydrocrackers. In addition to the reactor(s), each system at least includes recycle compressors, multi-stage flash systems and distillation. For example, a 6500 bpd feed hydrocracker capital cost (2011$) ranges from $10 million installed (inside battery limits) to $70 million. Costs for a generic hydrocracking system (2000 psia) were chosen as the basis for hydrotreating and hydrocracking. While these costs are

generally applicable to AHTL oil hydrotreating as they employ similar temperatures and pressures, conventional refining space velocities tend to be higher. Hydrotreater reactor cost sensitivity is considered in Section 4.

2.5.   Hydrogen Generation

The hydrogen plant is a conventional natural gas based steam reformer. Most of the off-gas is used to fire the reformer. However, a portion of the off-gas is compressed and mixed with makeup natural gas which is then sent to a hydrodesulfurization (HDS) unit. Figure 8 shows the simplified flow scheme for hydrogen generation by steam reforming of natural gas [SRI International 2007b, Meyers 2004, H_2A 2013] combined with the off-gas streams from CHG, hydrotreating and hydrocracking. Hydrogen for the HDS unit is supplied by the off-gas stream. The gas exiting the HDS unit is then mixed with superheated steam and sent through an adiabatic pre-reformer to convert C_2+ compounds to methane prior to entering the main steam reformer to produce syngas. This reduces the rate of coking in the main reformer. The syngas hydrogen content is increased by high temperature water-gas-shift (WGS). After condensing out the water, the hydrogen is purified by pressure swing adsorption (PSA). Off-gas from the PSA is recycled to the reformer burners.
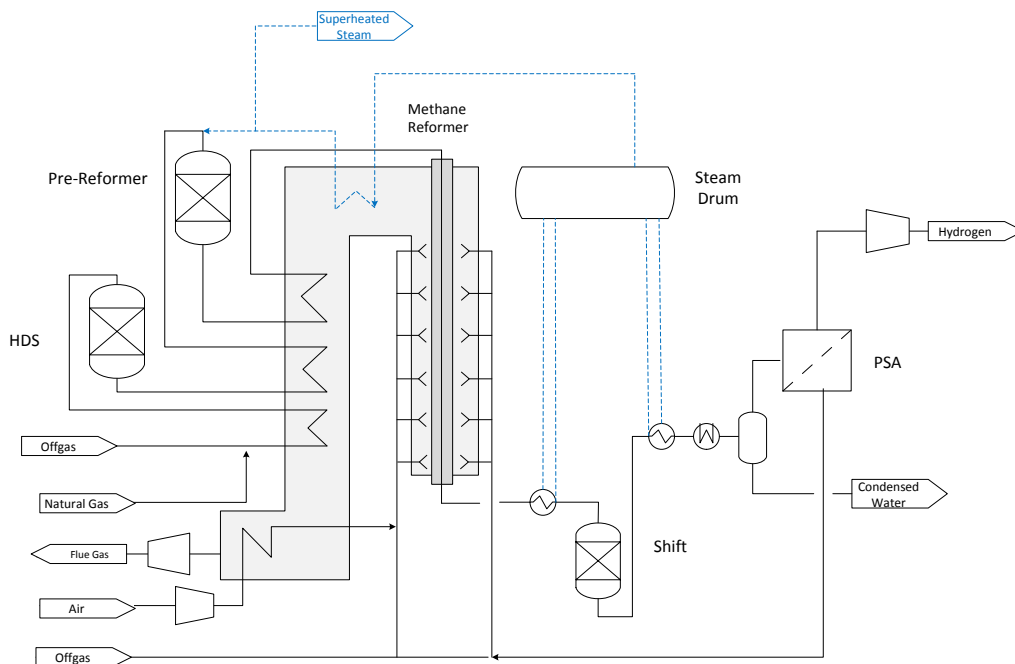
Figure 8 Process flow for hydrogen production

Saturated and superheated steams are generated by recuperating heat from the reformer exhaust and cooling the product from the water gas shift reactor. The generated steam is used in the reformer and also to provide process heat, including the distillation column reboilers.

2.5.1. Hydrogen Generation Design basis

The design assumptions are shown in Table 10. Aspen's Gibbs minimization reactors are used to model the pre-reforming, methane reforming and burner reactions. The reactor methane conversion of 80 mole % matches that reported by SRI [SRI International 2007b].

Table 10 Area 600 design basis

Equipment	Assumptions	
Pre-reformer	Outlet temperature	925 °F (496 °C)
	Outlet pressure	429 psia
	Steam/carbon ratio	3.5
Methane Reformer	Steam pressure	670 psia
	Outlet temperature	1562 °F (850 °C)
	Outlet pressure	399 psia
Burners	Bridge wall temperature	1800 °F (982 °C)
	Pressure	Slightly positive
Shift Reactor	Outlet temperature	568 °F (300 °C)
	Outlet pressure	388 psia
	Approach to equilibrium	98%
PSA	Hydrogen delivery pressure	376 psia
	Hydrogen recovery	90%

2.5.2. Hydrogen Generation Cost Estimation

Capital costs for hydrogen generation are taken from the SRI 2007 Yearbook and scaled to the necessary hydrogen production rate using the SRI scale factor. The equipment includes a sulfur guard bed, pre-reformer, primary reformer with nickel catalyst, high temperature WGS reactor, pressure swing adsorption unit, waste heat recovery producing high pressure steam and all associate outside battery limit equipment. Conventional steam reformer hydrogen plants range in scale from 1 to 100 million scf of hydrogen per day. The hydrogen plant scale needed for the whole algae HTL plant is at the low end: 17 million scf per day. The installed capital cost for this plant is $28.6 million dollars. Additional cost details can be found in Appendix B. The SRI capital costs were crossed checked with results from the (Hydrogen Analysis) H_2A program developed for the DOE Hydrogen Program and were found to be in reasonable agreement. The small size for the hydrogen plant suggests that better economies of scale may be obtained by hydrotreating the HTL oil at a central location.

2.6.   Nutrient Recycle

Water and nutrient recycle from the conversion plant back to the algae farm are important for both economics and life cycle performance. Cleaned water from CHG and produced water from hydrotreating are assumed to be recycled to the farm, as is CO_2. The CO_2 that is recycled partly comes from carbonates in the CHG water stream and, in part, from the hydrogen plant flue gas which is compressed and returned to the pond.

Nitrogen is available as dissolved ammonia in the recycled water streams. Figure 9 shows the expected nitrogen balance as estimated from experimental results. From Figure 9, up to 95% might be recoverable at the conversion plant. It is assumed that 5% will be lost because of volatilization at the farm; hence the net nitrogen recycle is estimated to be 90%. Most of the phosphorus (90%) is bound in the HTL solids and will likely require some type of conversion (such as acid digestion) to make it bio-available. This will require experimental verification. As shown in the figure, a small amount of nitrogen will be lost during phosphorus recovery.

These balances assume the upgrading facilities are co-located. If the upgrading facilities are not co-located with HTL and CHG units, then the nitrogen recycle is reduced from 90% to 63%. The location of the upgrading plant has minimal effect on phosphorus recycle since the most of the phosphorus is associated with the HTL solids.
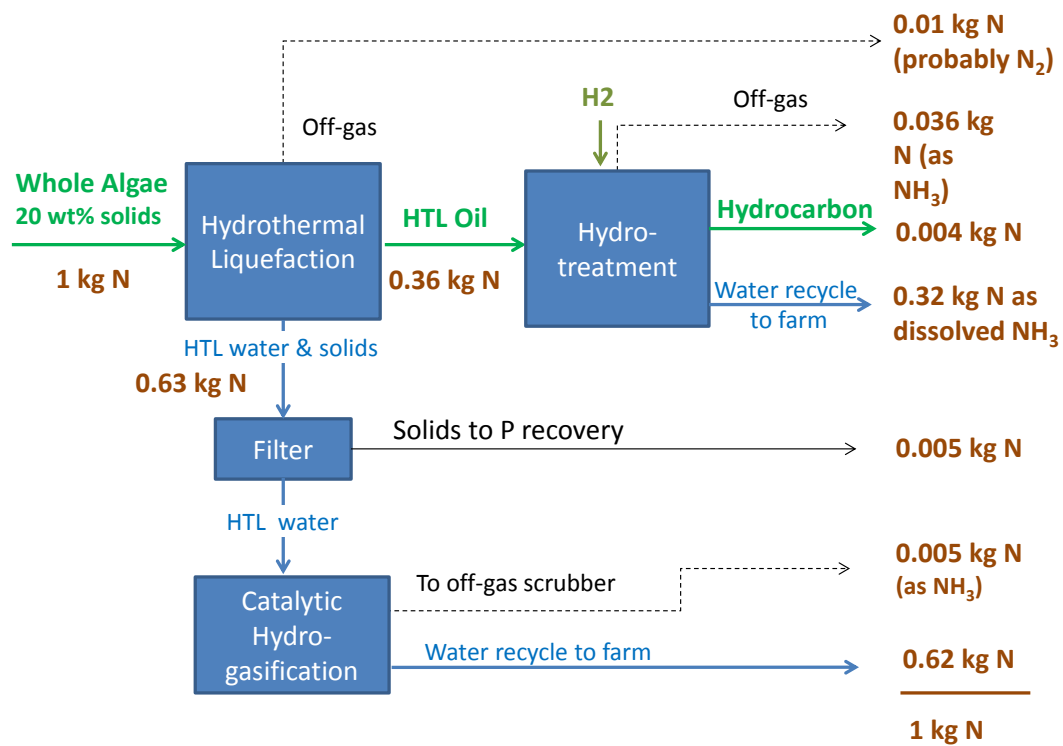
Figure 9 Nitrogen recycle diagram

3. Process Economics

Process economics are the combination of feedstock cost, and capital and operating costs associated with construction and operation of the conversion plant. These costs are combined in a discounted cash flow analysis to estimate the minimum fuel price needed to meet a 10% internal rate of return when the net present value is equal to zero. As explained in Section 1, these are the standard assumptions used by BETO to allow a common basis for comparing one pathway with another. Figure 10 shows the carbon flows for the overall process. Table 11 summarizes the production rates for the conceptual AHTL plant.
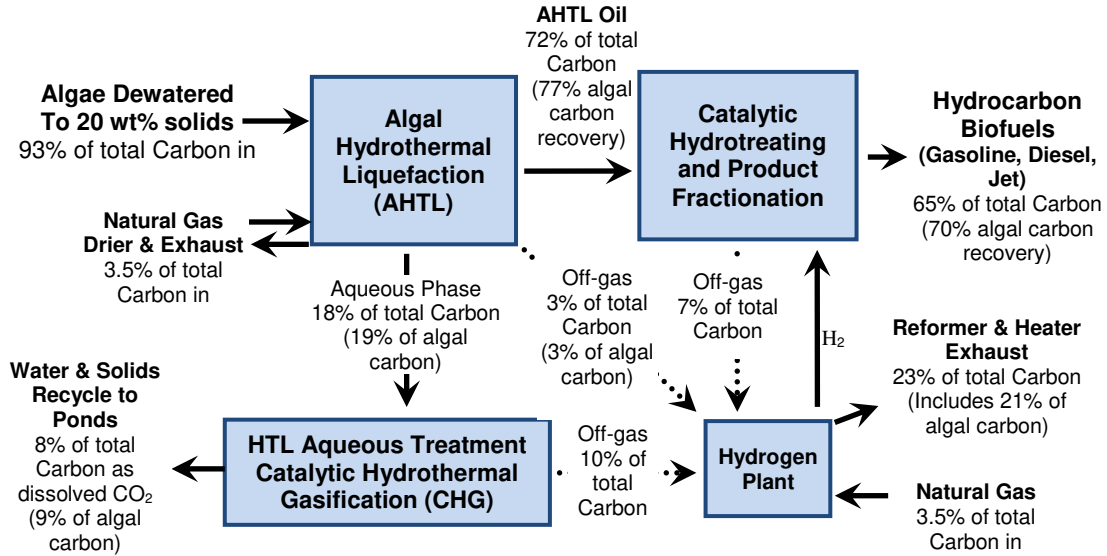
Figure 10 Overall carbon flows

Table 11 Production rates

Feed, Product or Intermediate	Annual average, Million gallons/year	Annual average, Million lbs/year
Dry, ash free algae to fuel production	Not applicable	884
Total flow (algae, ash, water) to HTL	530	4,550
AHTL oil	70	521
Hydrotreated Oil	65	432
Diesel blendstock	54	360
Naphtha (gasoline blendstock)	11	71

3.1. Total Capital Investment

Table 12 summarizes the costs presented in Section 2, including the balance of plant items, such as the tank farm, flare and cooling water system. The HTL reactor section has the single highest capital cost.

Table 12 Total capital investment

	Million US Dollars (2011$)
Dryers (for periods of high algae productivity)	15.9
AHTL oil production	85.9
CHG wastewater treatment	81.4
AHTL oil hydrotreating	24.7
Heavy oil hydrocracking	5.7
Hydrogen plant	28.6
Balance of plant	10.4
Total Installed Cost (TIC)	**252**
Buildings (1% of TIC)	2.5
Site development (9% of TIC)	22.7
Additional piping (4.5% of TIC)	9.6
Total Direct Costs (TDC)	**287**
Indirect Costs	
Prorated expenses (10% TDC)	28.7
Home office & construction fees (20% TDC)	57.5
Field expenses (10% TDC)	28.7
Project contingency (10% TDC)	28.7
Startup and permits (5% TDC)	14.4
Total Indirect	**158**
Fixed Capital Investment (FCI)	**446**
Working Capital	22.2
Land – assumed to be included in the feedstock cost	0
Total Capital Investment (TCI)	**$468**
TCI/annual gallon diesel	**$9**

3.2. Operating Costs

The estimated cost for the CHG catalyst of $60/lb is based on the assumptions listed in Table 13:

Table 13 CHG catalyst cost estimate

Catalyst Component	Value	Catalyst Component	Value
Carbon support	$15-20 $/lb	Ruthenium loading	7.8 wt%
Fabrication costs	50% of materials cost	Ruthenium recovery	95% by burning off support
Ruthenium metal price	$70/troy ounce		

The Platinum Today website [PGM 2013] shows that the price of ruthenium has been steadily dropping since 2008. It is $70 per troy ounce as of August 2013. The calculated catalyst price in 2013 dollars was back cast to 2011 dollars using the indices in Appendix D.

Table 14 lists the assumptions used to calculate the operating cost. The associated cost year is shown in parenthesis. Credits are shown as negative numbers.

Table 14 Variable operating costs

Variable	Value	Source	Total Cost (2011), million USD/year
20 wt% solids algae feedstock, $/dry, ash free ton	$300	assumption	190
Naphtha co-product, $/gallon (2011$)	$3.25	EIA Projection to 2022	-36.2
Hydrotreater Catalyst, $/lb (2007$)	$15.5, 2 year life	SRI 2007	1.02
CHG Catalyst, $/lb (2011$)	$60, 1 year life	Calculated	7.21
Hydrocracking Catalyst, $/lb (2007$)	$15.5, 5 year life	SRI 2007	0.02
Hydrogen Plant Catalysts, $/1000 scf H_2 (2007$)	$3.6, 5 year life	SRI 2007	0.24
Natural Gas, $/1000 scf (1000 btu/scf) (2011$)	5.1	EIA 2011 industrial	6.64
Electricity, ¢/kwh (2011$)	6.89	EIA 2011 industrial	2.97
Water Makeup, $/ metric ton (2001$)	0.22	Dutta 2011	0.09

Fixed costs are shown in Table 15. Salaries are taken from Dutta (2011) and converted to 2011 dollar basis using US Bureau of Labor Statistics labor cost index. The factors for benefits and maintenance, and insurance and taxes are the standard assumptions used for BETO design cases [Dutta 2011].

Table 15 Fixed operating costs

Position Title	Number	Total Cost (2011), million USD/year
Conversion Plant (unburdened)		
Plant Manager	1	0.15
Plant Engineer	1	0.07
Maintenance Super	1	0.06
Lab Manager	1	0.06
Shift Supervisor	5	0.24
Lab Technician	4	0.16
Maintenance Tech	7	0.28
Shift Operators	25	1.20
Yard Employees	4	0.11
Clerks & Secretaries	1	0.04
Subtotal		**2.36**
Overhead & maintenance	90% of labor & supervision	2.12
Maintenance capital	3% TIC	12.85
Insurance and taxes	0.7% FCI	3.12
Total Other Fixed Costs		**20.45**

3.3.   Minimum Fuel Selling Price

The minimum fuel product selling price (MFSP) for diesel blendstock was determined using a discounted cash flow rate of return analysis. The methodology is identical to that used in Jones *et al.* [2014]. The MFSP is the selling price of the fuel that makes the net present value of the process equal to zero with a 10% discounted cash flow rate of return over a 30 year plant life and 40% equity with the remainder debt financed at 8% interest for a 10 year term. This results in a MFSP for the conceptual target plant of $4.77 per gallon of diesel or $4.49 per gasoline gallon equivalent. Section 4 explores the financial and technical assumptions and their impact on the MFSP. The breakdown of costs leading to this MSPF is shown in Table 16. The diesel product is shown in both $/gallon diesel and as the gasoline gallon equivalent.

Table 16 MFSP cost breakdown

	$/gal diesel	$/year	$/gge
Algae feedstock cost	3.51	$190,000,000	3.31
Natural Gas	0.12	$6,600,000	0.12
Catalysts & Chemicals	0.16	$8,500,000	0.15
Waste Disposal	0.00	$0	0.00
Electricity and other utilities	0.06	$3,100,000	0.05
Naphtha Credit	-0.67	-$36,300,000	-0.63
Other Co-product Credits	0.00	$0	0.00
Fixed Costs	0.38	$20,400,000	0.36
Capital Depreciation	0.28	$14,900,000	0.26
Average Income Tax	0.16	$1,800,000	0.15
Average Return on Investment	0.78	$8,600,000	0.73
	4.77		**4.49**

4. Economic and Technical Sensitivities

The design case describes a single operating point for a stand-alone processing plant. This section investigates the production cost sensitivities to technical, financial, and market parameters. These effects include plant size, IRR, feedstock costs, reactor conditions and product yields.

4.1. Sensitivity Discussion

Figure 11 shows the effects of select sensitivities in terms of the $/gallon diesel and percent change.
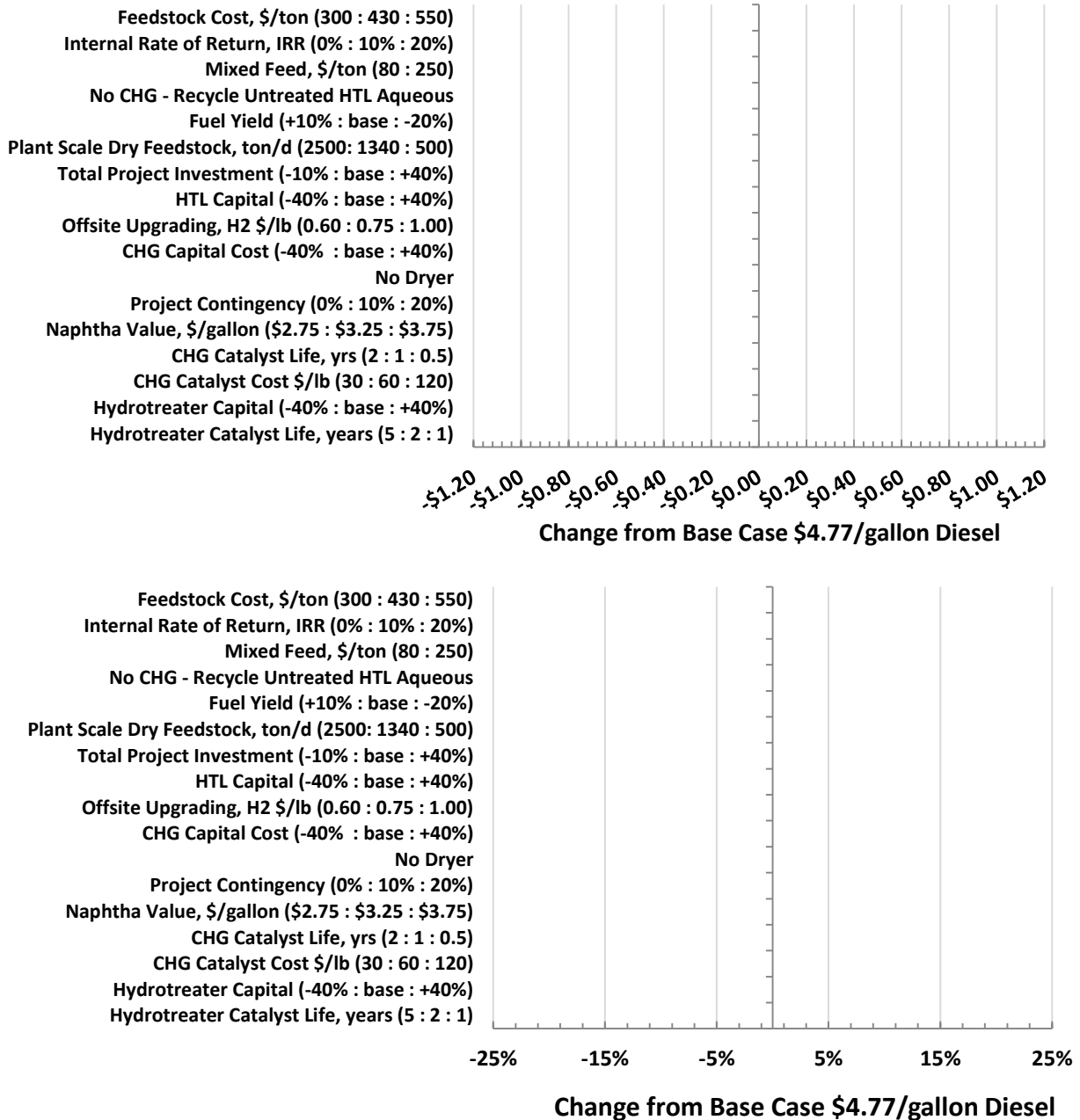
Figure 11 Sensitivity analysis results

As shown in Figure 11, the feedstock cost is the most significant factor and highlights the need for robust cultivation, harvest and dewatering methods and cost models. The next largest effect is the internal rate of return. The zero IRR corresponds to the product cost at the plant gate. The base case 10% IRR is equivalent to a breakeven point and the standard metric for BETO assessment for competing technologies. At 20% IRR, $0.86/gallon is added to the base cost of $4.77/gallon of diesel.

Yield is a key variable. Figure 5 shows AHTL oil yield as a function of algae type, AHTL process conditions, feed solids content and algal lipid content. This suggests that increased AHTL oil recovery can be obtained by improved separation processes. Reduced AHTL oil yields results in lower diesel yield, and more organic material processed in CHG. This in turn reduces the natural gas input to the hydrogen plant and also produces more power. However, Figure 10 shows that these effects do not offset one another, as a 20% reduction in AHTL oil production increases the MSPF to $5.45/gallon of diesel.

Plant scale also has a strong affect. However, achieving larger single plant sizes over the base case likely requires significant improvements in overall productivity, or the ability to co-process algae with other types of biomass. Co-processing algae with other types of biomass, such as wood, is shown by the sensitivity entitled: mixed feedstocks in Figure 11. In this case, the conversion plant is sized to the maximum summer throughput. Supplemental wood is brought in during times of lower productivity to the meet the maximum throughput rate. This eliminates the algae dryer, but adds wood handling equipment costs. The mixed feedstock AHTL oil yield is also reduced somewhat, reflecting lower conversion resulting from processing wood [Knorr 2013]. At a wood price of $80/ton, the diesel MFSP is reduced to $4.17/gallon.

The project investment sensitivity corresponds to the degree of uncertainty in the capital estimate at this level of detail (.i.e.., -10%, +40%). Specific capital cost areas are also shown, using a wider uncertainty range (+40%). The capital costs associated with the AHTL area are the most significant, although CHG capital costs are also quite large. The AHTL conditions for the algae runs are not optimized and there may still be room for temperature and residence time reductions. A possible way to reduce CHG capital is to process only a portion of the AHTL aqueous phase. The extent of organic reduction in the AHTL aqueous phase is dependent upon the level needed to allow recycle back to the algae ponds without a deleterious effect. Garcia Alba et al. [2013a] studied the use of the AHTL aqueous product without pretreatment as a growth medium for the originating algae *(Desmodesmus* sp.). They found that the lack of minor nutrients other than nitrogen and phosphorus, reduced growth rates rather than any potentially toxic organic material. However, a later study [Garcia Alba 2013b] found that continuous recycle could cause the buildup of inhibitory compounds and concluded some degree of treatment is needed. This suggests that reducing the organic level to nearly nil, as assumed in the design case, may not be necessary.

Offsite upgrading refers to leveraging existing infrastructure through hydrotreating at a conventional refinery. This eliminates the capital cost for the hydrotreater, hydrocracker, hydrogen plant and the import of natural gas. Instead, hydrogen would be used at an internal hydrogen transfer price, which is refinery specific. A hydrogen transfer price of $0.75/lb hydrogen is equivalent to the base case MFSP of $4.77/gallon diesel. A better understanding of AHTL oil stability and potential chemical/physical hazards during shipping is a research need for this scenario.

Seasonal variations in algae production are addressed in the next two sensitivities: eliminating the dryer and using mixed feedstocks. Eliminating the dryer and the natural gas needed to supply drying heat results in a savings of over $0.16/gallon of diesel. This is possible in locations where small differences between summer and winter algae production occur. The mixed feed scenario, previously discussed, could be applied in locations where there are large seasonal differences in algae production rates. The price for the wood assumes that it has already been ground to the small size needed for AHTL. The MYPP target cost for such a prepared woody feedstock is $80/ton (AHTL feed is similar to the fast pyrolysis feed cited in the MYPP) for a national average price and corresponds to the base case diesel MFSP.

Catalyst cost and life have smaller individual impact relative to other issues, but taken together make up a $0.20/gallon difference. Efficient sulfur removal is key to CHG catalyst maintenance. Effective AHTL oil preparation, such as water washing to remove salts, will lengthen hydrotreating catalyst life.

4.2. Path Forward to $3/gge Fuel

The projected target case presented here results in an MFSP of $4.77/gallon of diesel ($4.49/gge). Meeting the BETO target of $3/gge fuel will require a combination of improvements. An example of such a combination is upgrading at central location, co-processing with other biomass types and reducing the cost of CHG water treatment. No data are yet available for mixed feed HTL and very little is known regarding the extent of water treatment needed for CHG water recycle to ponds. However, offsite upgrading is already being explored by Sapphire Energy and Phillips 66 [Sapphire 2013].

5. Environmental Sustainability Metrics

In addition to setting technical and economic targets for the conversion pathways included in the MYPP [DOE 2013], BETO has begun the process of setting baselines and targets for environmental sustainability metrics. Sustainability is a cross-cutting element of the BETO program whose overarching goal is to "understand and promote the positive economic, social, and environmental effects and reduce the potential negative impacts of biofuels production activities" [DOE 2013]. To reach this goal, BETO, DOE National Laboratories and others have worked together to develop an initial set of important sustainability metrics for the conversion stage of the biofuel life cycle: greenhouse gas (GHG) emissions, fossil energy consumption, fuel yield, biomass carbon-to-fuel efficiency, water consumption, and wastewater generation.

Shown in Table 17 are the estimated metric values for the conversion plant including upgrading for this conceptual design case. Algae cultivation, harvest and dewatering are excluded, as is fuel end-use. Conversion plant GHG and fossil consumption are shown with and with the use of the natural gas fired algae drier used during the summer. Future work should consider alternate ways to address seasonal variability as a way of eliminating the drier as an emission source.

Table 17 Sustainability metrics for HTL, CHG and upgrading

Sustainability Metric	2022 Projected
Conversion Plant GHGs (g CO_2-e/MJ fuel) – (fossil emission; biogenic emissions)	9.1 (14.0 when including algae drying in summer); 20.5[1]
Conversion Plant Fossil Energy Consumption (MJ fossil energy/MJ fuel)[1]	0.14 (0.22 when including algae drying in summer)
Diesel Fuel Yield (gallon diesel/dry ton ash free algae)	122
Naphtha Fuel Yield (gallon naphtha/dry ton ash free algae)	25
Biomass Carbon-to-Diesel + Naphtha Efficiency (% of algal carbon resulting in liquid fuel product)	70
Conversion Plant Water Consumption (m^3/day; gal/gal diesel)[2]	1126, 1.81
Conversion Plant Wastewater Generation (m^3/day; gal/gal diesel)[3]	None, conversion plant water is recycled to ponds

Table Notes:
1.   This value includes dissolved CO_2 in the CHG water recycle back to the algae ponds (0.5% of total).
2.   Fossil energy consumption does not include power used by the algae farm for cultivating, harvest and dewatering.
3.   Water consumption and wastewater generation include only direct use/emissions and do not include water associated with upstream production of materials and energy used at the plant.

6. Conclusions and Recommendations

AHTL is a promising means of converting algae to liquid transportation fuels. Using whole algae eliminates the need to promote lipid accumulation, and allows use of fast growing species. The diesel yields are higher than those for lipid extraction based routes. AHTL is especially suited for conversion of wet feedstocks, thus, no energy is expended for evaporative algae drying. Finished hydrocarbon fuel can be produced by hydrotreating AHTL oil.

Experimentally derived data for whole algae HTL oil production, hydrodeoxygenation (HDO) and de-nitrification, and wastewater treatment were used to prepare this conceptual design report. All experimental work was conducted using continuous flow reactor systems. The data are from limited testing, but provide a basis for estimating future algal conversion performance targets that define a reasonable path to meeting BETO 2022 goals. Key bottlenecks, uncertainties, and areas for further development are summarized as follows:

- **Feedstock quality and availability**
  - There are known compositional differences between strains of algae, and typically seasonal variations as well. Strains need to be better understood in terms of AHTL processing, particularly for species screened and/or developed for high growth as opposed to lipid production.
  - Mixed feed processing, such as mixed algal species or algae mixed with lignocellulosic biomass should be investigated as a way to eliminate algal productivity seasonal variations and improve process economics.
  - Detailed algal feed characterization is needed to assist in determination of the tradeoffs (if any) between species, lipid content, ash characteristics and final product yield and quality, and the availability of recoverable nutrients.

- **AHTL conversion**
  - Limited continuous flow conversion data are available. Processing a variety of algae grown under different conditions and varying solids loading, temperature, residence time and use of additives would help define the operating envelope.
  - AHTL is a high pressure operation and the capital costs are significant. The economic analysis for this system is based on experiments conducted with a CSTR-PFR hybrid system. It is likely that a PFR, as assumed in the target case would be used commercially. Understanding reaction rates and products from algal components such as, lipids, carbohydrates and, proteins, might help optimize reactor design and improve cost estimates.
  - Corrosion data are needed to inform the choice of metallurgy.
  - AHTL oil and aqueous phase separation needs further work to recover more of the organic material into the AHTL oil phase. This could include optimizing the existing oil/water separator or possibly adding another step such as selective organic extraction of the aqueous phase prior to wastewater treatment.
  - Detailed characterizations of all the AHTL oil, aqueous phase, solids and gaseous products are needed. For example, better understanding of the quality and stability of the AHTL oil will help reveal the underlying HTL reactions and subsequent upgrading requirements.

Currently, ultimate analysis, density, gas analysis and whole oil distillation curves are being collected. Additional analysis by GC/MS, HPLC, and ^{13}C NMR would also be useful. Understanding the speciation of alkanes/alkenes, aromatics, and oxygenates, particularly as a function of processing conditions, will help manage hydrogen usage. Off-gas composition by GC is available from the AHTL and hydrotreating experiments, but this may not be sufficient to assess the need for gas conditioning prior to final use, such as in a hydrogen plant.

- o Characterization methods may need to be developed. Sudasinghe et al. [2013] noted that many analytical methods by themselves are not able to completely characterize AHTL product compounds. For example, chromatography methods lack resolution and selectivity, high molecular weight species go undetected, and highly polar compounds are not well addressed.
- o Little is known about the stability of AHTL oil with time. This will be important when the upgrading facility is not co-located with the ATHL unit and the oil is transported offsite.

- **CHG water treatment for the AHTL aqueous phase**
  - o The CHG tests reported here were limited and of short duration. Process optimization is needed as well as a better understanding of catalyst maintenance and costs.
  - o Effective means of sulfur removal prior to CHG are needed to reduce CHG catalyst deactivation rates.
  - o The extent of treatment needed to allow water recycle to the algae ponds without diminishing algae growth must be better understood.
  - o CHG as it was practiced primarily creates methane and carbon dioxide. Catalysts could be developed to convert the organics in the aqueous phase to other compounds, such as, hydrogen, bio-product chemicals, or fuel precursor species that can rejoin the predominantly organic phase.

- **Upgrading AHTL oil**
  - o Improved catalyst performance needs examination. Hydrotreating catalyst maintenance and stability are unknown, as are regeneration protocols and lifetimes. Longer-term testing with AHTL oil and detailed characterization of catalyst performance and deactivation modes are needed. Pretreatment steps, such as desalting, need to be demonstrated.
  - o Development of HDO and hydrodenitrogenation (HDN) reaction kinetics would assist reactor designs and better inform the choice of co-processing in a petroleum refinery.
  - o Quality characterization of the major distillation fractions, gasoline range, diesel range, and gas oil range for the AHTL oil and the hydrotreated oil needs examination. The jet fuel range should also be characterized, and an understanding of how to produce a jet cut without degrading naphtha and diesel properties would also be useful. Testing for key final fuel qualities, such as flash, octane, cetane, and cold flow properties is desirable.
  - o Hydrocracking yields of the gas oil fraction should be demonstrated.

- **Sustainability, economic and environmental**
  - o Nutrient recycle has been identified by the harmonization work as a key driver in meeting GHG reduction goals in the life cycle assessment. A preliminary assessment of nutrient

partitioning is presented in Section 2; however, cultivation with real recycle should be demonstrated.

- o HTL and CHG are each high pressure, heated processes. Opportunities for integrating them to avoid cooling and reheating and de-pressuring and re-pressing will reduce energy demands.
- o As described earlier, most of the phosphorus (90%) is bound in the AHTL solids and will likely require some type of conversion (such as acid digestion) to make it bio-available. This will require experimental verification.
- o The life cycle analysis conducted for the harmonization work should be extended to the target case. The addition of other sustainability metrics such as energy return on investment would also be useful.
- o Co-product opportunities have the potential to further lower the cost of hydrocarbon production from algal biomass and should be considered where possible. However, it is necessary to ensure that the volumes of co-products produced will not overwhelm market demand.

7. References

ANL; NREL; PNNL. 2012. "Renewable Diesel from Algal Lipids: An Integrated Baseline for Cost, Emissions, and Resource Potential from a Harmonized Model. ANL/ESD/12-4; NREL/TP-5100-55431; PNNL-21437. Argonne, IL: Argonne National Laboratory; Golden, CO: National Renewable Energy Laboratory; Richland, WA: Pacific Northwest National Laboratory.

"Aspentech" 2013 Burlington, MA: Aspen Technology. http://www.aspentech.com/products/aspen-plus.cfm

Biller, P., Ross, A. 2011. "Potential Yields and Properties of Oil from the Hydrothermal Liquefaction of Microalgae with Different Biochemical Content." Bioresource Technology, 102:215-225.

Brown, Tylisha, P. Duan, P. Savage. 2010. "Hydrothermal liquefaction and gasification of *Nannochloropsis* sp." Energy & Fuels, 24:3639-3646.

Chemical Book. 2014. Accessed at http://www.chemicalbook.com/ProductIndex_EN.aspx

Chemical Engineering Magazine Plant Cost Index. Chemical Engineering Magazine. Available from http://www.che.com/pci/.

Davis, Ryan, L. Tao, E. Tan, M. Biddy, G. Beckham, C. Scarlata, J. Jacobson, K. Cafferty, J. Ross, J. Lukas, D. Knorr, P. Schoen. "Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbons: Dilute-Acid and Enzymatic Deconstruction of Biomass to Sugars and Biological Conversion of Sugars to Hydrocarbons." NREL/TP-5100-60223 National Renewable Energy Laboratory, Golden CO. Accessed at http://www.nrel.gov/docs/fy14osti/60223.pdf

DOE (2013). MYPP, *Biomass Multi-year Program Plan - May 2013*, U.S.D.o. Energy, Editor 2013, Bioenergy Technologies Office, http://www1.eere.energy.gov/biomass/pdfs/mypp_may_2013.pdf

Duan, Peigao, P. Savage. 2011. "Hydrothermal liquefaction of microalga with heterogeneous catalysts". Ind. Eng. Chem. Res. 50: 52-61.

Dutta, A., Talmadge, M., Hensley, J., Worley, M., Dudgeon, D., Barton, D., Groenendijk, P., Ferrari, D., Stears, B., Searcy, E., Wright, C., Hess, J.R. (2011). Process design and economics for conversion of lignocellulosic biomass to ethanol: thermochemical pathway by indirect gasification and mixed alcohol synthesis. NREL/TP-5100-51400. National Renewable Energy Laboratory, Golden, CO. Accessed at http://www.nrel.gov/docs/fy11osti/51400.pdf

Elliott DC. 2011. "Hydrothermal Processing." Chapter 7 in Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power, ed. Robert C. Brown, pp. 200-231. Wiley-Blackwell, Oxford, United Kingdom.

Elliott, Douglas, T. Hart, G. Neuenschwander, L. Rotness, M. Olarte, A. Zacher. 2012. "Chemical processing in high-pressure aqueous environments. 9. Process development for catalytic gasification of algae feedstocks." Industrial & Engineering Chemistry Research, 51:10768-10777.

Elliott, Douglas, T. Hart, A. Schmidt, G. Neuenschwander, L. Rotness, M. Olarte, A. Zacher, K. Albrecht, R. Hallen, J. Holladay. 2013. "Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor." Algal Research, 2:445-454.

Energy Information Administration (EIA). 2011 Industrial Natural Gas Prices. Available at http://www.eia.doe.gov/

Exxon 2014. "LDPE tubular process" http://www.exxonmobilchemical.com/Chem-English/productsservices/polymers-ldpe-tubular.aspx

Faeth, Julia, P. Valdez, P. Savage. 2013. "Fast hydrothermal liquefaction of *Nannochoropsis* sp. to produce biocrude." Energy & Fuels 27:1391-1398.

Garcia Alba, L., C. Torri, C. Samor, J. van der Spek, D. Fabbri, S. Kerstn, D. Brilman. 2012. "Hydrothermal treatment (HTT) of microalgae: evaluation for the process as conversion method in an algae biorefinery concept." Energy & Fuels, 26: 642-657.

Garcia Alba, Laura, C, Torri, D. Fabbri, S. Kersten, D. Brilman. 2013a. "Microalgae growth on the aqueous phase from hydrothermal liquefaction of the same microalgae." Chemical Engineering Journal, 228:214-223.

Garcia Alba, Laura, M. Vos, C. Torri, D. Fabbri, S. Kersten, D. Brilman. 2013b. "Recycling nutrients in algae biorefinery." ChemSusChem Communications, 6:1330-1333.

Gary, James, G. Handwerk, M. Kaiser. 2007. Petroluem Refining Technolgy and Economics, CRC Press.

Hess, J. Richard, K. Kenney, L. Park Ovard, E. Searcy, C. Wright. 2009. "Commodity-scale production of an infrastructure-compatible bulk solid from herbaceous Lignocellulosic Biomass." INL/EXT-09-17527, Idaho National Laboratory, Idaho Falls, ID. Accessed at https://inlportal.inl.gov/portal/server.pt?open=512&objID=421&PageID=5806&cached=true&mode=2&userID=1829.

Humbird, David, R. Davis, L. Tao, C. Kinchin, D. Hsu, A. Aden. 2011. "Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover." NREL/TP-5100-47764, National Renewable Energy Laboratory, Golden, CO. Accessed at http://www.nrel.gov/docs/fy11osti/47764.pdf

H2A 2013. DOE EERE Fuel Cell and Hydrogen Program. http://www.hydrogen.energy.gov/h2a_delivery.html

Illinois 2013. UIUC Illini Algae – Hydrothermal Liquefaction, http://algae.illinois.edu/Projects/Hydrothermal.html

Jena, Umakanta, K. Das, J. Kastner. 2011. "Effect of operating conditions of thermochemical liquefaction on biocrude production from *Spirulina platensis*." Bioresource Technology, 102: 6221-6229.

Jazwari, Christopher, P. Biller, A. Ross, A. Montoya, T. Maschmeyer, B. Haynes. 2013. "Pilot plant testing of continuous hydrothermal liquefaction of microalgae." Algal Research, 2:268-277.

Jones, Susanne, P. Meyer, L. Snowden-Swan, A. Padmaperuma, E. Tan A. Dutta, J. Jacobson, K. Cafferty. 2014. "Process design and economics for the conversion of lignocellulosic biomass to hydrocarbon fuels: Fast pyrolysis and hydrotreating bio-oil pathway." PNNL-23053 Pacific Northwest National Laboratory, http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-23053.pdf NREL/TP-5100-61178 National Renewable Energy Laboratory, http://www.nrel.gov/docs/fy14osti/61178.pdf

Kosseva, Maria, and C. Webb. 2013. Food Industry Wastes – Assessment and Recuperation of Commodities. Elsevier Press. Accessed online from Knovel at http://app.knovel.com/hotlink/toc/id:kpFIWARC0E/food-industry-wastes

Knorr, Dan, LJ. Lukas, P.Schoen. 2013. "Production of advanced biofuels via liquefaction: Hydrothermal liquefaction reactor design." Harris Group Incorporated report for the National Advanced Biofuels Consortium. NREL/SR-5100-60462, National Renewable Energy Laboratory, Golden, CO. Accessed at http://www.nrel.gov/docs/fy14osti/60462.pdf

Li, Hao, Z. Liu, Y. Zhang, B. Li, H. Lu, N. Duan, M. Liu, Z, Zhu, B. Si. 2014. "Conversion efficiency and oil quality of low-lipid high-protein and high-lipid-low protein microalgae via hydrothermal liquefaction." Bioresource Technology, 154:322-329.

López Barreiro, Diego, C. Zamalloa, N. Boon, W. Vyverman, F. Ronsse, W. Brilman, W. Prins. 2013. "Influence of strain-specific parameters on hydrothermal liquefaction of microalgae." Bioresource Technology 146:463-471.

Minowa, Tomoaki., S. Yokoyama, M. Kishimoto, T. Okakura. 1995. "Oil production from algal cells of *Dunaliella tertiolecta* by direct thermochemical liquefaction." Fuel, 74(12): 1735-1738.

Meyers RA. 2004. Handbook of Petroleum Refining Processes. 3rd ed. McGraw-Hill, New York.

Muth, David. 2013. Personal correspondence. The cost for a Baker Pullman rotary drum dryer processing 25,000 lb/hr of 80 wt% moisture algae is $905,000 and is fired by 28 million BTUs of natural gas per hour.

Parkash, Surinder, 2003. Refining Processes Handbook. Elsevier Gulf Professional Publishing

PGM 2013. Platinum Today. http://www.platinum.matthey.com/pgm-prices/price-charts/ accessed 1/2/2013.

Sapphire 2013. "Sapphire Energy and Phillips 66 to Advance Commercialization of Algae Crude Oil" accessed at http://www.sapphireenergy.com/press-article/1986963-sapphire-energy-and-phillips-66-to

Sudasinghe, Nilusha, B. Dungan, P. Lammers, K. Albrecht, D. Elliott, R. Hallen, T. Schaub. 2014. "High resolution FT-ICR mass spectral analysis of bio-oil and residual water soluble organics produced by hydrothermal liquefaction of the marine microalga *Nannochloropsis salina*." Fuel 119:47-56.

SRI International. 2007a. "Diesel from High Pressure Hydrocracking." <u>PEP Yearbook International</u>, Vol 1E, SRI International, Menlo Park, California

SRI International. 2007b. "Hydrogen Production from Natural Gas." <u>PEP Yearbook International</u>, Vol 1E, SRI International, Menlo Park, California

Marker, Terry, L. Sabatino, F. Baldiraghi. 2009. "Production of diesel fuel from Renewable Feedstocks Containing Phosphorus" US 2009/0321311 A1, December 31, 2009.

Valdez, Peter, J. Dickinson, P. Savage. 2011. "Characterization of product fractions from hydrothermal liquefaction of *Nannochlorpsis sp*. and the influence of solvents." Energy & Fuels, 25: 3235-3243.

Vardon, Derek, B. Sharma, J. Scott, G. Yu, Z. Wang, L. Schideman. 2011. "Chemical properties of biocrude oil from the hydrothermal liquefaction of *Spirulina* algae, swine manure and digested anaerobic sludge." Bioresource Technology, 102: 8295-8303.

Yu, Guo., Y. Zhang, L. Schideman, T. Funk, Z. Wang. 2011. "Distributions of carbon and nitrogen in the products from hydrothermal liquefaction of low-lipid microalgae." Energy and Environmental Science, 4: 4587-4595.

Appendix A – Heat and Material Balances

AREA 100

Wet Feed — 101 — P-101 — 105 — P-103 — 109 — Heat Exchangers HX-100 — 110 — H-105 Preheaters — 115 — R-101 HTL Plug Flow Reactors — 125 — F-105 Filter — 128

126 — Char to Nutrient Recovery

129 — Three-Phase Separator V-110

131 — Gas to A400

133 — Aqueous — To A200 CHG

135 — Bio-oil — HTL Oil to A300

A100 HYDROTHERMAL LIQUEFACTION
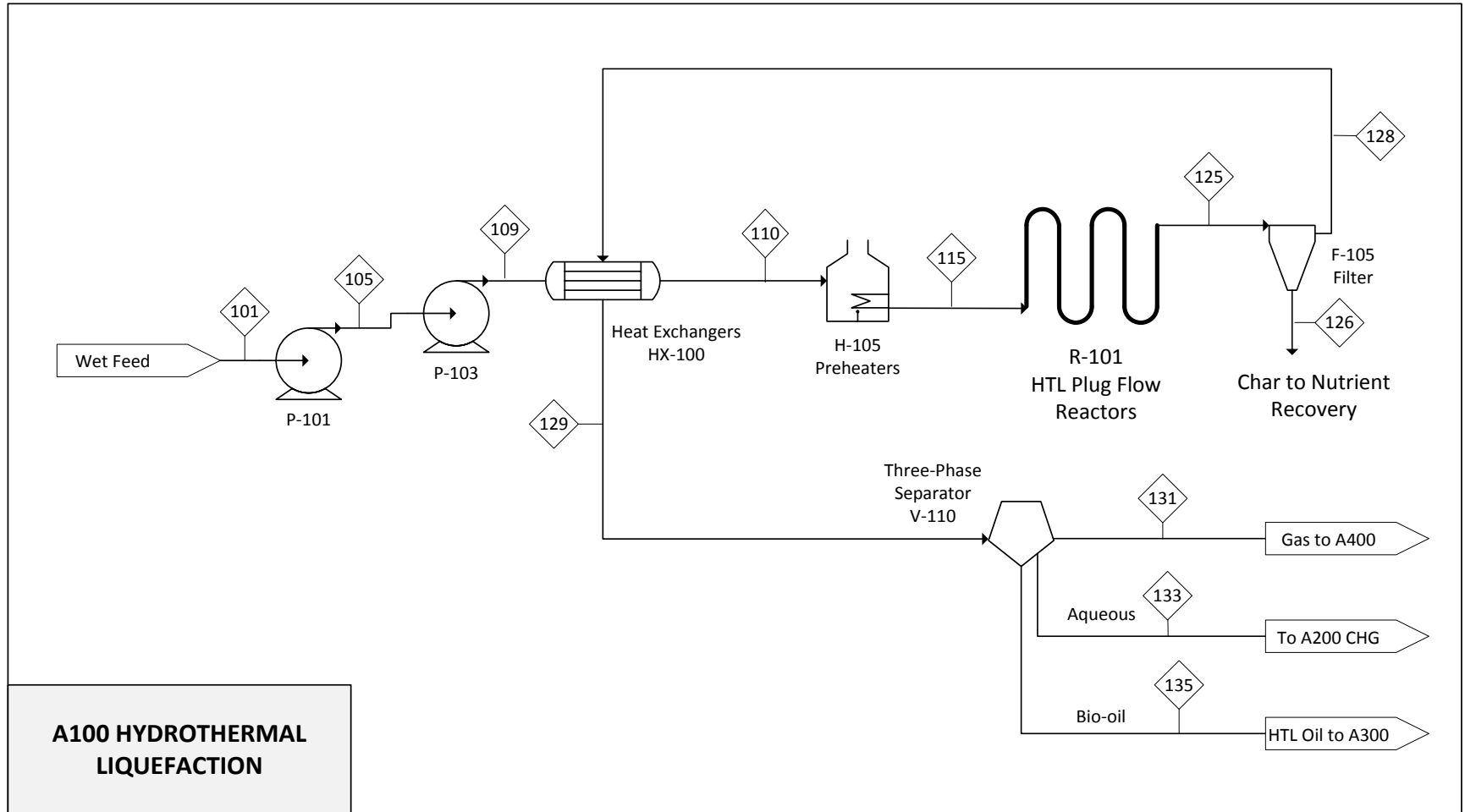
	101	105	109	110	115	125	126	128	129	131	133	135
Total Flow lb/hr	574,476	574,476	574,476	574,476	574,476	574,476	7,423	567,054	567,054	5,580	491,836	69,637
Temperature F	60.0	60.1	64.0	600.0	663.8	651.2		651.0	154.0	140.7	140.7	140.7
Pressure psia	14.7	84.7	3049.7	3044.7	3039.7	3034.7	3029.7	3029.7	3028.7	30.0	30.0	30.0
Vapor Frac	0.00	0.00	0.00	0.00	0.00	0.05		0.05	0.03	1.00	0.00	0.00
Mass Flow lb/hr												
CO2	0	0	0	0	0	12711	0	12711	12711	5122	7589	0
H2O	446432	446432	446432	446432	446432	446432	0	446432	446432	0	442532	3900
NH3	0	0	0	0	0	3460	0	3460	3460	0	3460	0
CH4	0	0	0	0	0	278	0	278	278	278	0	0
C2H6	0	0	0	0	0	180	0	180	180	180	0	0
METHANOL	0	0	0	0	0	5580	0	5580	5580	0	5580	0
ETHANOL	0	0	0	0	0	1116	0	1116	1116	0	1116	0
ACETONE	0	0	0	0	0	1116	0	1116	1116	0	1116	0
FORMACID	0	0	0	0	0	11161	0	11161	11161	0	11161	0
ACEACID	0	0	0	0	0	3348	0	3348	3348	0	3348	0
GLYCEROL	0	0	0	0	0	1116	0	1116	1116	0	1116	0
3-PYRDOL	0	0	0	0	0	1674	0	1674	1674	0	1674	0
1E2PYDIN	0	0	0	0	0	5176	0	5176	5176	0	712	4464
C5H9NS	0	0	0	0	0	1971	0	1971	1971	0	1297	674
ETHYLBEN	0	0	0	0	0	1674	0	1674	1674	0	0	1674
4M-PHYNO	0	0	0	0	0	3348	0	3348	3348	0	0	3348
4EPHYNOL	0	0	0	0	0	3348	0	3348	3348	0	0	3348
INDOLE	0	0	0	0	0	3348	0	3348	3348	0	0	3348
7MINDOLE	0	0	0	0	0	2232	0	2232	2232	0	0	2232
C14AMIDE	0	0	0	0	0	2232	0	2232	2232	0	0	2232
C16AMIDE	0	0	0	0	0	10045	0	10045	10045	0	0	10045
C18AMIDE	0	0	0	0	0	4464	0	4464	4464	0	0	4464
C16:1FA	0	0	0	0	0	8929	0	8929	8929	0	0	8929
C16:0FA	0	0	0	0	0	6696	0	6696	6696	0	0	6696
C18FACID	0	0	0	0	0	1116	0	1116	1116	0	0	1116
NAPHATH	0	0	0	0	0	3348	0	3348	3348	0	0	3348
CHOLESOL	0	0	0	0	0	1116	0	1116	1116	0	0	1116
AROAMINE	0	0	0	0	0	5353	0	5353	5353	0	0	5353
C30DICAD	0	0	0	0	0	3348	0	3348	3348	0	0	3348
ALGAE	128044	128044	128044	128044	128044	0	0	0	0	0	0	0
ASH	0	0	0	0	0	16436	6574	9862	9862	0	9862	0
SOLIDS	0	0	0	0	0	2121	848	1272	1272	0	1272	0
Enthalpy, 10^6Btu/hr	-3234.30	-3234.10	-3228.60	-2948.90	-2900.80	-2912.30	-1.71	-2910.60	-3190.30	-20.38	-3114.80	-75.00

AREA 200

A200 CATALYTIC HYDROTHERMAL GASIFICATION
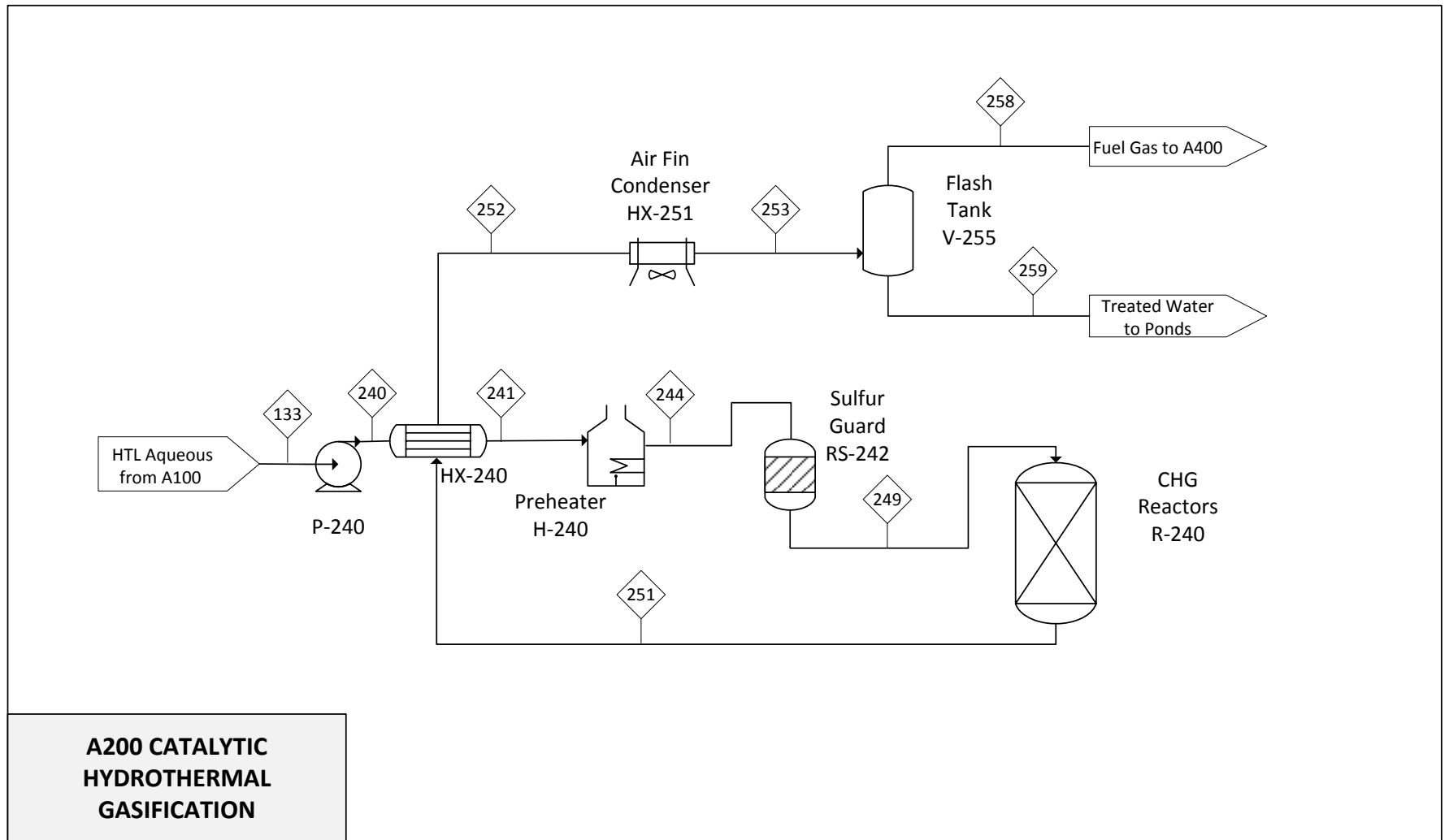
	133	240	241	244	249	251	252	253	258	259
Total Flow lb/hr	491,836	491,836	491,836	491,836	491,498	491,498	491,498	491,498	13,374	478,124
Temperature F	140.7	147.1	620.0	665.6	660.2	653.6	230.5	140.0	140.0	140.0
Pressure psia	30.0	3089.7	3084.7	3083.7	3078.7	3068.7	3067.7	3065.7	50.0	50.0
Vapor Frac	0.00	0.00	0.00	0.00	0.00	0.19	0.03	0.04	1.00	0.00
Mass Flow lb/hr										
H2	0	0	0	0	0	1	1	1	1	0
CO2	7,589	7,589	7,589	7,589	7,589	25,075	25,075	25,075	5,509	237
H2O	442,532	442,532	442,532	442,532	442,532	443,968	443,968	443,968	618	431,819
NH3	3,460	3,460	3,460	3,460	3,460	4,059	4,059	4,059	0	0
CH4	0	0	0	0	0	6,735	6,735	6,735	6,722	13
C2H6	0	0	0	0	0	143	143	143	142	0
C3H8	0	0	0	0	0	383	383	383	382	1
SULFUR	0	0	0	0	0	0	0	0	0	0
NH4+	0	0	0	0	0	0	0	0	0	4,299
H3O+	0	0	0	0	0	0	0	0	0	3,822
HCO3-	0	0	0	0	0	0	0	0	0	26,800
METHANOL	5,580	5,580	5,580	5,580	5,580	0	0	0	0	0
ETHANOL	1,116	1,116	1,116	1,116	1,116	0	0	0	0	0
ACETONE	1,116	1,116	1,116	1,116	1,116	0	0	0	0	0
FORMACID	11,161	11,161	11,161	11,161	11,161	0	0	0	0	0
ACEACID	3,348	3,348	3,348	3,348	3,348	0	0	0	0	0
GLYCEROL	1,116	1,116	1,116	1,116	1,116	0	0	0	0	0
3-PYRDOL	1,674	1,674	1,674	1,674	1,674	0	0	0	0	0
1E2PYDIN	712	712	712	712	712	0	0	0	0	0
C5H9NS	1,297	1,297	1,297	1,297	0	0	0	0	0	0
C5H11N	0	0	0	0	959	0	0	0	0	0
ALGAE	0	0	0	0	0	0	0	0	0	0
SOLUBLE ASH	9,862	9,862	9,862	9,862	9,862	9,862	9,862	9,862	0	9,862
SOLUBLE SOLIDS	1,272	1,272	1,272	1,272	1,272	1,272	1,272	1,272	0	1,272
Enthalpy, 10^6Btu/hr	-3114.80	-3108.20	-2867.50	-2834.30	-2837.90	-2837.90	-3078.60	-3121.20	-38.41	-3091.20

AREA 300

Process flow diagram — A310 HYDROTREATING

Hydrogen From A400 — 330 — Makeup Compressor C-311 — 331A

Recycle Compressor C-310 — 327 — 326

328 — 307 — H-311 — 308 — 311

319

PSA V-300

HTL Oil From A100 — 135 — P-310 — 304 — 312

HP Flash V-311

325 — 339 — Offgas to A350

313 — 318 — 323

HX-320 — Hydrotreater R-310 — E-310 — 321

LP Flash V-315 — 332 — 320 — To Water Recycle

316 — 316A — 317 — 322

Feed/Product HX-318A — Air Fin Condenser H-316 — 324

Lights Column T-310

335 — To Gasoline Pool

334 — Naphtha Column T-320 — 337 — To Diesel Pool

336 — Diesel Column T-330 — 338 — To A350 Hydrocracker

A310 HYDROTREATING

42

	135	304	307	308	311	312	313	316	316A	317	318	319	320	321	322	323	324	325	326	327	328	330	331A	332	334	335	336	337	338	339
Total Flow lb/hr	69,637	69,637	78,692	78,692	78,692	78,692	78,692	78,692	78,692	78,692	78,692	11,237	11,711	67,455	55,359	386	55,359	5,835	5,402	9,055	9,055	3,654	3,654	775	54,585	7,125	47,460	41,497	5,963	6,996
Temperature F	140.7	123.8	171.4	345.0	755.5	593.8	581.5	270.0	232.1	140.0	110.0	110.0	116.6	110.0	116.6	116.6	220.0	110.0	179.2	243.5	140.0	281.1	130.3	485.7	228.9	546.5	508.9	717.2	717.2	111.3
Pressure psia	30.0	1530.0	1530.0	1525.0	1515.0	1514.5	725.0	724.5	724.4	722.4	717.4	717.4	55.0	717.4	55.0	55.0	54.0	20.0	707.4	707.4	1530.0	423.5	710.0	48.0	50.0	25.0	25.0	18.7	18.7	20.0
Vapor Frac	0.00	0.00	0.89	0.92	1.00	0.96	0.98	0.90	0.88	0.82	0.80	1.00	0.00	0.00	0.00	1.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00	1.00
Mass Flow lb/hr																														
H2	0	0	9,055	9,055	6,037	6,037	6,037	6,037	6,037	6,037	6,037	6,002	0	35	1	34	1	600	5,402	9,055	9,055	3,654	3,654	1	0	0	0	0	0	635
H2O	3,900	3,900	3,900	3,900	8,349	8,349	8,349	8,349	8,349	8,349	8,349	262	8,056	8,086	18	12	18	262	0	0	0	0	0	18	0	0	0	0	0	293
NH3	0	0	0	0	2,868	2,868	2,868	2,868	2,868	2,868	2,868	759	2,014	2,109	36	59	36	759	0	0	0	0	0	25	11	11	0	0	0	843
CH4	0	0	0	0	1,368	1,368	1,368	1,368	1,368	1,368	1,368	1,320	0	48	7	41	7	1,320	0	0	0	0	0	7	0	0	0	0	0	1,368
C2H6	0	0	0	0	1,754	1,754	1,754	1,754	1,754	1,754	1,754	1,542	0	212	100	112	100	1,542	0	0	0	0	0	100	0	0	0	0	0	1,754
C3H8	0	0	0	0	990	990	990	990	990	990	990	707	0	283	208	75	208	707	0	0	0	0	0	208	0	0	0	0	0	989
N-C4H10	0	0	0	0	522	522	522	522	522	522	522	247	2	275	253	20	253	247	0	0	0	0	0	188	65	65	0	0	0	455
N-PENTAN	0	0	0	0	407	407	407	407	407	407	407	104	1	303	293	9	293	104	0	0	0	0	0	73	220	220	0	0	0	186
HEXANE	0	0	0	0	245	245	245	245	245	245	245	29	0	216	213	2	213	29	0	0	0	0	0	22	192	192	0	0	0	53
1E2PYDIN	4,464	4,464	4,464	4,464	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C5H9NS	674	674	674	674	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ETHYLBEN	1,674	1,674	1,674	1,674	1,224	1,224	1,224	1,224	1,224	1,224	1,224	17	2	1,207	1,204	1	1,204	17	0	0	0	0	0	1	1,203	1,203	0	0	0	19
4M-PHYNO	3,348	3,348	3,348	3,348	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4EPHYNOL	3,348	3,348	3,348	3,348	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
INDOLE	3,348	3,348	3,348	3,348	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
7MINDOLE	2,232	2,232	2,232	2,232	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C14AMIDE	2,232	2,232	2,232	2,232	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C16AMIDE	10,045	10,045	10,045	10,045	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C18AMIDE	4,464	4,464	4,464	4,464	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C16:1FA	8,929	8,929	8,929	8,929	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C16:0FA	6,696	6,696	6,696	6,696	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C18FACID	1,116	1,116	1,116	1,116	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NAPATH	3,348	3,348	3,348	3,348	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CHOLESOL	1,116	1,116	1,116	1,116	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
AROAMINE	5,353	5,353	5,353	5,353	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C30DICAD	3,348	3,348	3,348	3,348	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2MBUTAN	0	0	0	0	245	245	245	245	245	245	245	75	1	170	163	6	163	75	0	0	0	0	0	53	109	109	0	0	0	135
2MPENTA	0	0	0	0	245	245	245	245	245	245	245	37	0	207	204	3	204	37	0	0	0	0	0	27	177	177	0	0	0	68
2MHEXAN	0	0	0	0	245	245	245	245	245	245	245	17	0	228	226	1	226	17	0	0	0	0	0	12	214	214	0	0	0	30
HEPTANE	0	0	0	0	245	245	245	245	245	245	245	12	0	232	231	1	231	12	0	0	0	0	0	8	223	223	0	0	0	21
CC6-METH	0	0	0	0	612	612	612	612	612	612	612	29	1	583	580	2	580	29	0	0	0	0	0	14	566	566	0	0	0	45
PIPERDIN	0	0	0	0	245	245	245	245	245	245	245	1	38	244	205	1	205	1	0	0	0	0	0	0	205	205	0	0	0	2
TOLUENE	0	0	0	0	612	612	612	612	612	612	612	19	0	593	591	2	591	19	0	0	0	0	0	6	585	585	0	0	0	27
3MHEPTA	0	0	0	0	612	612	612	612	612	612	612	17	0	595	593	1	593	17	0	0	0	0	0	6	587	587	0	0	0	25
OCTANE	0	0	0	0	612	612	612	612	612	612	612	13	0	599	598	1	598	13	0	0	0	0	0	3	595	595	0	0	0	17
ETHCYC6	0	0	0	0	245	245	245	245	245	245	245	4	0	240	240	0	240	4	0	0	0	0	0	1	239	239	0	0	0	5
O-XYLENE	0	0	0	0	612	612	612	612	612	612	612	6	1	606	604	1	604	6	0	0	0	0	0	0	604	604	0	0	0	7
C9H20	0	0	0	0	245	245	245	245	245	245	245	2	0	243	242	0	242	2	0	0	0	0	0	0	242	242	0	0	0	2
PROCYC6	0	0	0	0	245	245	245	245	245	245	245	2	0	243	243	0	243	2	0	0	0	0	0	0	243	242	0	0	0	2
C3BENZ	0	0	0	0	612	612	612	612	612	612	612	4	0	608	607	0	607	4	0	0	0	0	0	0	607	607	0	0	0	4
C10H22	0	0	0	0	122	122	122	122	122	122	122	0	0	122	122	0	122	0	0	0	0	0	0	0	122	116	6	6	0	0
C4BENZ	0	0	0	0	734	734	734	734	734	734	734	2	0	732	732	0	732	2	0	0	0	0	0	0	732	114	618	618	0	2
C11H24	0	0	0	0	1,224	1,224	1,224	1,224	1,224	1,224	1,224	2	0	1,222	1,222	0	1,222	2	0	0	0	0	0	0	1,222	8	1,214	1,214	0	2
C10H12	0	0	0	0	1,224	1,224	1,224	1,224	1,224	1,224	1,224	2	1	1,222	1,221	0	1,221	2	0	0	0	0	0	0	1,221	1	1,220	1,220	0	2
C12H26	0	0	0	0	1,224	1,224	1,224	1,224	1,224	1,224	1,224	1	0	1,223	1,223	0	1,223	1	0	0	0	0	0	0	1,223	0	1,223	1,223	0	1
1234NA	0	0	0	0	612	612	612	612	612	612	612	1	0	611	611	0	611	1	0	0	0	0	0	0	611	0	611	611	0	1
C6BENZ	0	0	0	0	1,224	1,224	1,224	1,224	1,224	1,224	1,224	1	0	1,223	1,223	0	1,223	1	0	0	0	0	0	0	1,223	0	1,223	1,223	0	1
12346N	0	0	0	0	1,224	1,224	1,224	1,224	1,224	1,224	1,224	1	0	1,223	1,223	0	1,223	1	0	0	0	0	0	0	1,223	0	1,223	1,223	0	1
C7BENZ	0	0	0	0	1,224	1,224	1,224	1,224	1,224	1,224	1,224	0	0	1,224	1,223	0	1,223	0	0	0	0	0	0	0	1,223	0	1,223	1,223	0	0
C8BENZ	0	0	0	0	1,224	1,224	1,224	1,224	1,224	1,224	1,224	0	0	1,224	1,224	0	1,224	0	0	0	0	0	0	0	1,224	0	1,224	1,224	0	0
C10H16O4	0	0	0	0	1,102	1,102	1,102	1,102	1,102	1,102	1,102	0	148	1,102	953	0	953	0	0	0	0	0	0	0	953	0	953	953	0	0
C15H32	0	0	0	0	3,672	3,672	3,672	3,672	3,672	3,672	3,672	0	0	3,672	3,672	0	3,672	0	0	0	0	0	0	0	3,672	0	3,672	3,672	0	0
C16H34	0	0	0	0	11,016	11,016	11,016	11,016	11,016	11,016	11,016	0	0	11,015	11,016	0	11,016	0	0	0	0	0	0	0	11,016	0	11,016	11,016	0	0
C17H36	0	0	0	0	4,896	4,896	4,896	4,896	4,896	4,896	4,896	0	0	4,896	4,896	0	4,896	0	0	0	0	0	0	0	4,896	0	4,896	4,896	0	0
C18H38	0	0	0	0	2,448	2,448	2,448	2,448	2,448	2,448	2,448	0	0	2,448	2,448	0	2,448	0	0	0	0	0	0	0	2,448	0	2,448	2,447	1	0
C19H40	0	0	0	0	2,448	2,448	2,448	2,448	2,448	2,448	2,448	0	0	2,448	2,448	0	2,448	0	0	0	0	0	0	0	2,448	0	2,448	2,448	0	0
C21H44	0	0	0	0	2,448	2,448	2,448	2,448	2,448	2,448	2,448	0	0	2,448	2,448	0	2,448	0	0	0	0	0	0	0	2,448	0	2,448	158	2,290	0
C23H48	0	0	0	0	2,448	2,448	2,448	2,448	2,448	2,448	2,448	0	0	2,448	2,448	0	2,448	0	0	0	0	0	0	0	2,448	0	2,448	4	2,444	0
C30H62	0	0	0	0	122	122	122	122	122	122	122	0	0	122	122	0	122	0	0	0	0	0	0	0	122	0	122	0	122	0
PHYTANE	0	0	0	0	6,120	6,120	6,120	6,120	6,120	6,120	6,120	0	0	6,120	6,120	0	6,120	0	0	0	0	0	0	0	6,120	0	6,120	6,118	1	0
C24H38O4	0	0	0	0	490	490	490	490	490	490	490	0	0	490	490	0	490	0	0	0	0	0	0	0	490	0	490	24	465	0
C26H42O4	0	0	0	0	612	612	612	612	612	612	612	0	0	612	612	0	612	0	0	0	0	0	0	0	612	0	612	0	612	0
N2H8SO4	0	0	0	0	773	773	773	773	773	773	773	110	0	773	773	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N2H8CO3	0	0	0	0	669	669	669	669	669	669	669	0	669	669	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Enthalpy, 10⁶Btu/hr	-75.00	-75.18	-68.37	-55.14	-55.90	-69.13	-69.13	-94.11	-97.12	-105.15	-107.67	-7.37	-63.9	-104.76	-40.93	-0.46	-37.91	-7.97	0.67	3.28	5.45	0.81	2.62	-0.83	-27.68	-3.26	-23.52	-21.01	-2.91	-9.26

Off-Gas From A310

To Ammonia Scrubber

339

366

377

378

Make-up Compressor C-350

380

376

368

385

351

352

353

355

362

365

Hydrogen From A400

H-351

Trim Heater H-352

Make-up Compressor C-350

Hydrocracker R-350

338

361

Heavy Oil From A310

370

P-350

371

374

372

V-375

381

V-351

T-350 Reboiler HX-380

HX-381

Air Fin Condenser H-381

383

386

To Gasoline Pool

Naphtha Splitter T-350

A350 HYDROCRACKING

389

To Diesel Pool

	338	339	351	352	353	355	361	362	365	366	368	370	371	372	374	376	377	378	380	381	383	385	386	389
Total Flow lb/hr	5,963	6,996	132	132	6,902	6,902	5,963	6,902	6,902	7,370	160	6,902	6,902	6,902	6,902	1,008	807	202	807	5,894	5,734	13	1,805	3,916
Temperature F	717.2	111.3	140.0	262.0	583.3	700.0	726.4	741.2	844.6	112.8	140.4	710.2	507.5	140.0	270.0	140.0	140.0	140.0	147.9	140.0	140.4	140.0	140.0	427.5
Pressure psia	18.7	20.0	423.5	1039.7	1034.7	1029.7	1034.7	1009.7	1009.7	20.0	30.0	1008.7	1008.2	1005.7	1007.7	1005.7	1005.7	1005.7	1039.7	1005.7	30.0	20.0	20.0	24.0
Vapor Frac	0.00	1.00	1.00	1.00	0.90	0.92	0.00	0.93	1.00	1.00	1.00	1.00	0.92	0.78	0.80	1.00	1.00	1.00	1.00	0.00	0.00	1.00	0.00	0.00
Mass Flow lb/hr																								
H2	0	635	132	132	372	372	0	372	305	700	5	305	305	305	305	300	240	60	240	5	0	0	0	0
CO2	0	0	0	0	422	422	0	422	656	228	115	656	656	656	656	528	422	106	422	128	13	7	5	0
H2O	0	293	0	0	0	0	0	0	0	293	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH3	0	843	0	0	0	0	0	0	0	843	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CH4	0	1,368	0	0	112	112	0	112	150	1,406	10	150	150	150	150	140	112	28	112	10	1	0	0	0
C2H6	0	1,754	0	0	0	0	0	0	0	1,754	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C3H8	0	989	0	0	0	0	0	0	0	989	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-C4H10	0	455	0	0	0	0	0	0	0	455	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-PENTAN	0	186	0	0	0	0	0	0	0	186	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HEXANE	0	53	0	0	3	3	0	3	70	58	3	70	70	70	70	4	3	1	3	66	63	1	62	0
ETHYLBEN	0	19	0	0	0	0	0	0	0	19	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2MBUTAN	0	135	0	0	0	0	0	0	0	135	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2MPENTA	0	68	0	0	0	0	0	0	0	68	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2MHEXAN	0	30	0	0	0	0	0	0	0	30	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HEPTANE	0	21	0	0	14	14	0	14	706	40	13	706	706	706	706	17	14	3	14	689	676	2	674	0
CC6-METH	0	45	0	0	0	0	0	0	0	45	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PIPERDIN	0	2	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
TOLUENE	0	27	0	0	0	0	0	0	0	27	0	0	0	0	0	0	0	0	0	0	0	0	0	0
3MHEPTA	0	25	0	0	0	0	0	0	0	25	0	0	0	0	0	0	0	0	0	0	0	0	0	0
OCTANE	0	17	0	0	4	4	0	4	494	22	4	494	494	494	494	5	4	1	4	489	486	1	484	1
ETHCYC6	0	5	0	0	0	0	0	0	0	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0
O-XYLENE	0	7	0	0	0	0	0	0	0	7	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C9H20	0	2	0	0	2	2	0	2	550	5	2	550	550	550	550	2	2	0	2	548	546	0	360	186
PROCYC6	0	2	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C3BENZ	0	4	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C10H22	0	0	0	0	1	1	0	1	710	1	1	710	710	710	710	1	1	0	1	709	708	0	7	701
C4BENZ	0	2	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C11H24	0	2	0	0	1	1	0	1	1,017	2	0	1,017	1,017	1,017	1,017	1	1	0	1	1,016	1,016	0	0	1,015
C10H12	0	2	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C12H26	0	1	0	0	0	0	0	0	796	1	0	796	796	796	796	0	0	0	0	796	796	0	0	796
1234NA	0	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C6BENZ	0	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
12346N	0	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C13H28	0	0	0	0	0	0	0	0	561	0	0	561	561	561	561	0	0	0	0	561	561	0	0	561
C7BENZ	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C14H30	0	0	0	0	0	0	0	0	280	0	0	280	280	280	280	0	0	0	0	280	280	0	0	280
C15H32	0	0	0	0	0	0	0	0	196	0	0	196	196	196	196	0	0	0	0	196	196	0	0	196
C16H34	0	0	0	0	0	0	0	0	116	0	0	116	116	116	116	0	0	0	0	116	116	0	0	116
C17H36	0	0	0	0	0	0	0	0	26	0	0	26	26	26	26	0	0	0	0	26	26	0	0	26
C18H38	1	0	0	0	1	1	1	1	6	0	0	6	6	6	6	0	0	0	0	6	6	0	0	6
C19H40	27	0	0	0	27	27	27	27	30	0	0	30	30	30	30	0	0	0	0	30	30	0	0	30
C20H42	0	0	0	0	0	0	0	0	1	0	0	1	1	1	1	0	0	0	0	1	1	0	0	1
C21H44	2,290	0	0	0	2,290	2,290	2,290	2,290	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C23H48	2,444	0	0	0	2,444	2,444	2,444	2,444	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C30H62	122	0	0	0	122	122	122	122	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PHYTANE	1	0	0	0	1	1	1	1	1	0	0	1	1	1	1	0	0	0	0	1	1	0	0	1
C24H38O4	465	0	0	0	465	465	465	465	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C26H42O4	612	0	0	0	612	612	612	612	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CYCHEX	0	0	0	0	8	8	0	8	232	10	7	232	232	232	232	10	8	2	8	221	214	1	213	0
Enthalpy, 10^6 Btu/h	-2.9	-9.3	0.0	0.1	-4.6	-3.8	-2.9	-3.5	-3.5	-10.2	-0.5	-4.3	-5.6	-7.8	-7.1	-2.3	-1.8	-0.5	-1.8	-5.5	-5.0	0.0	-1.6	-2.6

A300 PRODUCT COOLING
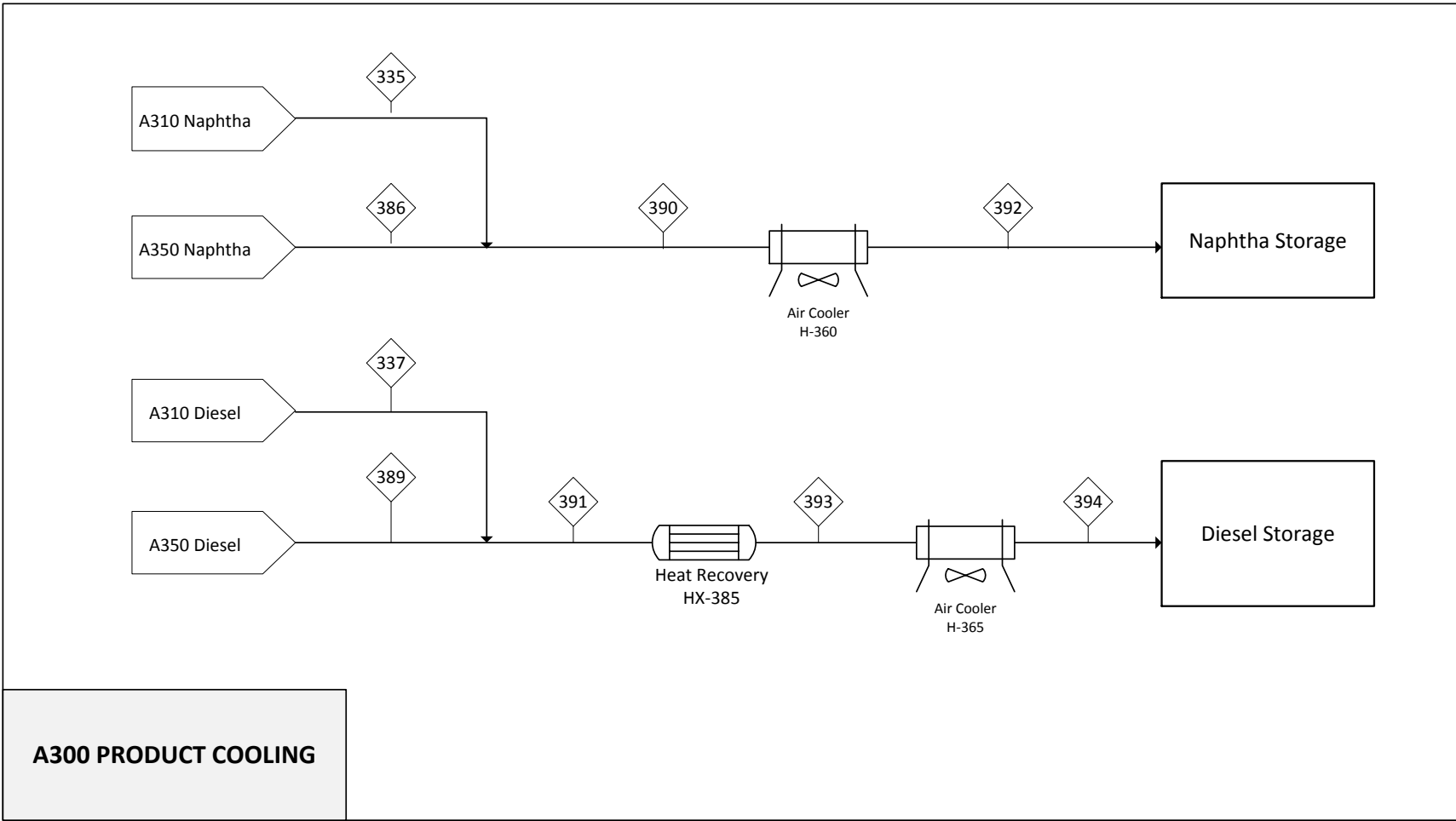
	335A	337A	386	389	390	391	392	393	394
Total Flow lb/hr	7,125	41,497	1,805	3,916	8,930	45,412	8,930	45,412	45,412
Temperature F	228.9	508.9	140.0	427.5	209.2	495.9	140.0	300.0	140.0
Pressure psia	25.0	18.7	20.0	24.0	20.0	18.7	19.0	17.7	16.7
Vapor Frac	0.00	0.00	0.00	0.00	0.01	0.05	0.00	0.00	0.00
Mass Flow lb/hr									
CO2	0	0	5	0	5	0	5	0	0
NH3	11	0	0	0	11	0	11	0	0
N-C4H10	65	0	0	0	65	0	65	0	0
N-PENTAN	220	0	0	0	220	0	220	0	0
HEXANE	192	0	62	0	254	0	254	0	0
ETHYLBEN	1,203	0	0	0	1,203	0	1,203	0	0
2MBUTAN	109	0	0	0	109	0	109	0	0
2MPENTA	177	0	0	0	177	0	177	0	0
2MHEXAN	214	0	0	0	214	0	214	0	0
HEPTANE	223	0	674	0	897	0	897	0	0
CC6-METH	566	0	0	0	566	0	566	0	0
PIPERDIN	205	0	0	0	205	0	205	0	0
TOLUENE	585	0	0	0	585	0	585	0	0
3MHEPTA	587	0	0	0	587	0	587	0	0
OCTANE	595	0	484	1	1,080	1	1,080	1	1
ETHCYC6	239	0	0	0	239	0	239	0	0
O-XYLENE	604	0	0	0	604	0	604	0	0
C9H20	242	0	360	186	602	186	602	186	186
PROCYC6	242	0	0	0	242	0	242	0	0
C3BENZ	607	1	0	0	607	1	607	1	1
C10H22	116	6	7	701	123	707	123	707	707
C4BENZ	114	618	0	0	114	618	114	618	618
C11H24	8	1,214	0	1,015	8	2,230	8	2,230	2,230
C10H12	1	1,220	0	0	1	1,220	1	1,220	1,220
C12H26	0	1,223	0	796	0	2,019	0	2,019	2,019
1234NA	0	611	0	0	0	611	0	611	611
C6BENZ	0	1,223	0	0	0	1,223	0	1,223	1,223
12346N	0	1,223	0	0	0	1,223	0	1,223	1,223
C13H28	0	0	0	561	0	561	0	561	561
C7BENZ	0	1,223	0	0	0	1,223	0	1,223	1,223
C8BENZ	0	1,224	0	0	0	1,224	0	1,224	1,224
C10H16O4	0	953	0	0	0	953	0	953	953
C14H30	0	0	0	280	0	280	0	280	280
C15H32	0	3,672	0	196	0	3,868	0	3,868	3,868
C16H34	0	11,016	0	116	0	11,132	0	11,132	11,132
C17H36	0	4,896	0	26	0	4,922	0	4,922	4,922
C18H38	0	2,447	0	6	0	2,453	0	2,453	2,453
C19H40	0	2,421	0	30	0	2,450	0	2,450	2,450
C20H42	0	0	0	1	0	1	0	1	1
C21H44	0	158	0	0	0	158	0	158	158
C23H48	0	4	0	0	0	4	0	4	4
C30H62	0	0	0	0	0	0	0	0	0
PHYTANE	0	6,118	0	1	0	6,120	0	6,120	6,120
C24H38O4	0	24	0	0	0	24	0	24	24
CYCHEX	0	0	213	0	213	0	213	0	0
Enthalpy, 10^6Btu/hr	-3.3	-21.0	-1.6	-2.6	-4.9	-23.7	-5.2	-29.9	-33.9

47

AREA 400

Pre-Reformer

Steam Reformer

Sulfur Removal

Steam Drum

315

414

413

410

330 — Hydrogen To A310

351 — Hydrogen To A350

425

PSA

131

A100 Offgas

367 — A350 Offgas from NH₃ Scrubber

434

421

402

468 — Flue Gas

460 — Air

461

462

416

417

418

419

Water Gas Shift

429 — Condensate to BFW makeup

436

427

Natural Gas

A200 Offgas

431 — Fuel Gas to H-105

438 — Fuel Gas to H-240

432 — Fuel Gas to H-352

A400 HYDROGEN PLANT

	131	258	367	401	402	410	411	413	414	416	417	418	419	420	421	425	426	427	429	431	432	434	436	438	460	461	462	468
Total Flow lb/hr	5,580	13,374	6,898	3,048	467	58,423	58,423	58,423	58,423	58,423	58,423	58,423	58,423	58,423	32,268	3,786	26,155	28,482	26,632	4,639	30	12,002	477	3,210	120,164	120,164	120,164	154,609
Temperature F	140.7	140.0	108.2	60.0	60.0	547.1	900.0	943.6	1050.0	1562.0	428.0	568.6	270.0	140.0	140.0	140.0	140.0	140.0	140.9	140.0	140.0	298.9	140.3	140.0	90.0	175.4	400.0	322.0
Pressure psia	30.0	50.0	19.8	450.0	450.0	450.0	449.5	429.5	429.0	399.0	398.5	388.5	388.0	386.0	386.0	376.0	386.0	20.0	19.8	50.0	50.0	450.0	19.8	50.0	14.7	21.2	20.7	16.0
Vapor Frac	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.74	0.66	1.00	1.00	0.00	1.00	0.00	0.99	0.99	1.00	0.00	0.99	1.00	1.00	1.00	1.00
Mass Flow lb/hr																												
H2	0	1	700	0	0	700	700	683	683	3,606	3,606	4,207	4,207	4,207	4,207	3,786	0	421	0	0	0	700	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	137	137	8,920	8,920	575	575	575	575	0	0	575	0	0	0	0	0	0	0	0	0	0
N2	0	0	0	17	3	17	17	37	37	38	38	38	38	38	38	0	0	38	0	0	0	0	0	0	88,980	88,980	88,980	89,020
O2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	27,263	27,263	27,263	4,541
AR	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1,518	1,518	1,518	1,518
CO2	5,122	5,509	228	34	5	5,383	5,383	7,049	7,049	12,649	12,649	25,760	25,760	25,760	25,734	0	26	25,734	26	1,911	12	5,349	0	1,322	59	59	59	42,167
H2O	0	618	639	0	0	43,536	43,536	42,084	42,084	31,850	31,850	26,483	26,483	26,483	355	0	26,129	355	26,605	214	1	162	477	148	2,345	2,345	2,345	17,361
NH3	0	0	28	28	0	28	28	4	4	3	3	3	3	3	3	0	0	3	0	0	0	28	0	0	0	0	0	3
CH4	278	6,722	1,406	2,997	459	4,681	4,681	8,429	8,429	1,357	1,357	1,357	1,357	1,357	1,357	0	0	1,357	0	2,331	15	1,684	0	1,613	0	0	0	0
C2H6	180	142	1,754	0	0	1,934	1,934	0	0	0	0	0	0	0	0	0	0	0	0	49	0	1,934	0	34	0	0	0	0
C3H8	0	382	989	0	0	989	989	0	0	0	0	0	0	0	0	0	0	0	0	133	1	989	0	92	0	0	0	0
N-C4H10	0	0	454	0	0	454	454	0	0	0	0	0	0	0	0	0	0	0	0	0	0	454	0	0	0	0	0	0
N-PENTAN	0	0	185	0	0	185	185	0	0	0	0	0	0	0	0	0	0	0	0	0	0	185	0	0	0	0	0	0
HEXANE	0	0	58	0	0	58	58	0	0	0	0	0	0	0	0	0	0	0	0	0	0	58	0	0	0	0	0	0
ETHYLBEN	0	0	19	0	0	19	19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	19	0	0	0	0	0	0
2MBUTAN	0	0	135	0	0	135	135	0	0	0	0	0	0	0	0	0	0	0	0	0	0	135	0	0	0	0	0	0
2MPENTA	0	0	68	0	0	68	68	0	0	0	0	0	0	0	0	0	0	0	0	0	0	68	0	0	0	0	0	0
2MHEXAN	0	0	30	0	0	30	30	0	0	0	0	0	0	0	0	0	0	0	0	0	0	30	0	0	0	0	0	0
HEPTANE	0	0	40	0	0	40	40	0	0	0	0	0	0	0	0	0	0	0	0	0	0	40	0	0	0	0	0	0
CC6-METH	0	0	45	0	0	45	45	0	0	0	0	0	0	0	0	0	0	0	0	0	0	45	0	0	0	0	0	0
PIPERDIN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
TOLUENE	0	0	27	0	0	27	27	0	0	0	0	0	0	0	0	0	0	0	0	0	0	27	0	0	0	0	0	0
3MHEPTA	0	0	25	0	0	25	25	0	0	0	0	0	0	0	0	0	0	0	0	0	0	25	0	0	0	0	0	0
OCTANE	0	0	22	0	0	22	22	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22	0	0	0	0	0	0
ETHCYC6	0	0	5	0	0	5	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5	0	0	0	0	0	0
O-XYLENE	0	0	7	0	0	7	7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	7	0	0	0	0	0	0
C9H20	0	0	5	0	0	5	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5	0	0	0	0	0	0
PROCYC6	0	0	2	0	0	2	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0
C3BENZ	0	0	4	0	0	4	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0
C10H22	0	0	1	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0
C4BENZ	0	0	2	0	0	2	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0
C11H24	0	0	2	0	0	2	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0
C10H12	0	0	2	0	0	2	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0
C12H26	0	0	1	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0
1234NA	0	0	1	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0
C6BENZ	0	0	1	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0
12346N	0	0	1	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0
CYCHEX	0	0	10	0	0	10	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	10	0	0	0	0	0	0
Enthalpy, 10⁶Btu/hr	-20.4	-38.4	-11.3	-6.2	-0.9	-273.2	-261.3	-261.3	-257.6	-197.6	-239.3	-239.3	-269.3	-281.7	-103.4	0.8	-178.3	-104.2	-181.6	-13.4	-0.1	-27.8	-3.3	-9.2	-13.4	-10.9	-4.2	-252.4

AREAS 600 & 700

A600 STEAM SYSTEM
A700 COOLING WATER
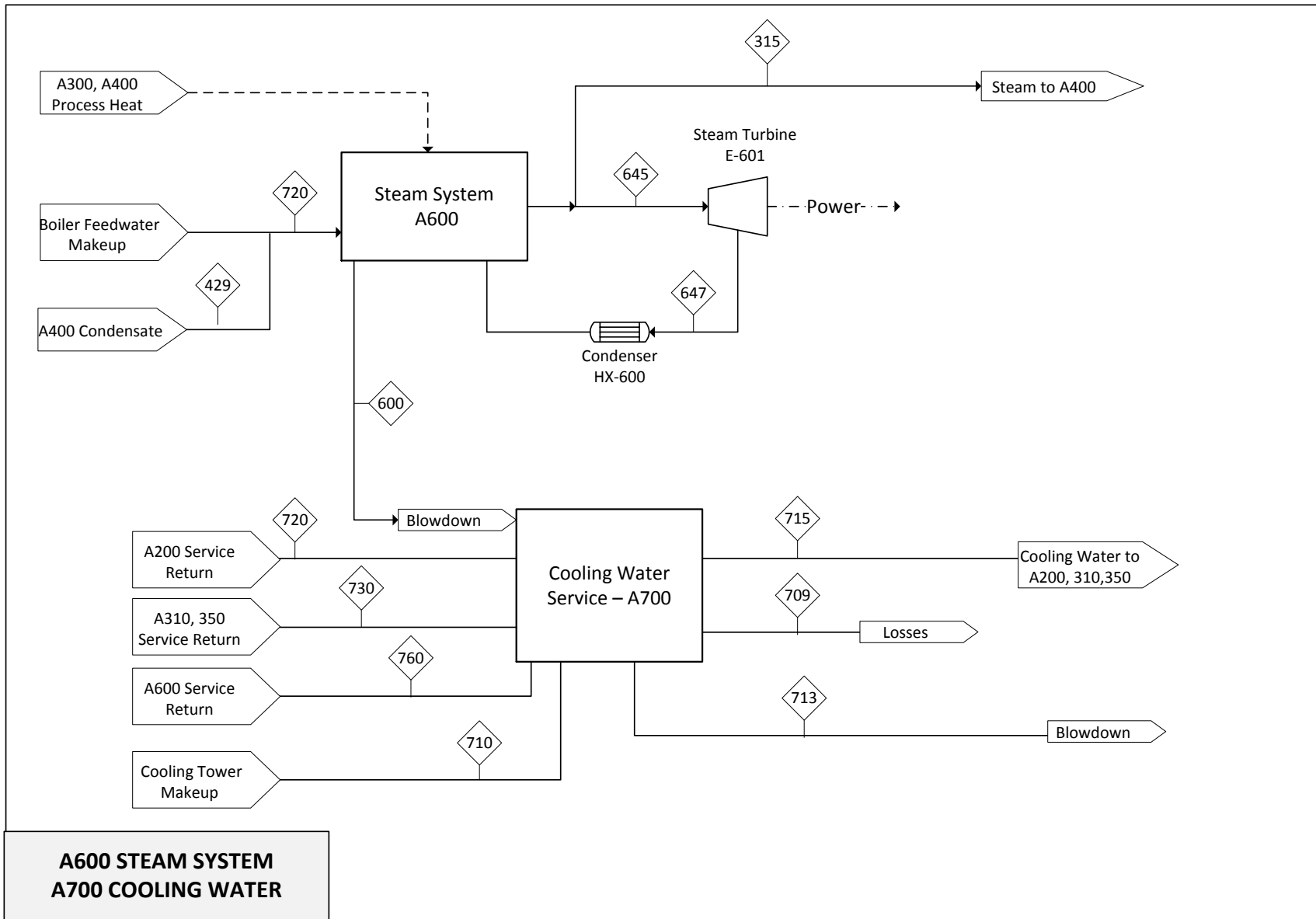
	600	618	635	644	645	647	648
Total Flow lb/hr	1,910	45,282	1	43,373	50,194	50,194	50,194
Temperature F	111.7	60.0	60.0	700.0	700.0	147.6	147.6
Pressure psia	14.7	14.7	22.0	659.2	659.2	3.5	3.5
Vapor Frac	0.00	0.00	0.00	1.00	1.00	0.90	0.00
Mass Flow lb/hr							
H2O	1,910	45,282	1	43,373	50,194	50,194	50,194
Enthalpy, 10^6Btu/hr	-13.0	-309.6	0.0	-239.4	-277.0	-293.2	-338.8
POWER, E-601 kW	-4754.93						

	709	710	713	715	720	730	760
Total Flow lb/hr	2,453,590	56,846	10,751	2,501,600	45,816	126,108	2,329,670
Temperature F	89.9	60.0	89.3	89.3	110.0	110.0	110.0
Pressure psia	14.7	14.7	14.7	74.7	59.7	59.7	59.7
Vapor Frac	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass Flow lb/hr							
H2O	2,453,590	56,846	10,751	2,501,600	45,816	126,108	2,329,670
Enthalpy, 10^6Btu/hr	-16,880.0	-393.0	-74.0	-17,210.0	-314.1	-864.5	-15,970.0

RECYCLE TO PONDS

To A400

367

NH$_3$ Scrubber
T-390

366

Offgas From
A350

259

From A200

To Ponds

320

From A310

WATER RECYCLE TO PONDS
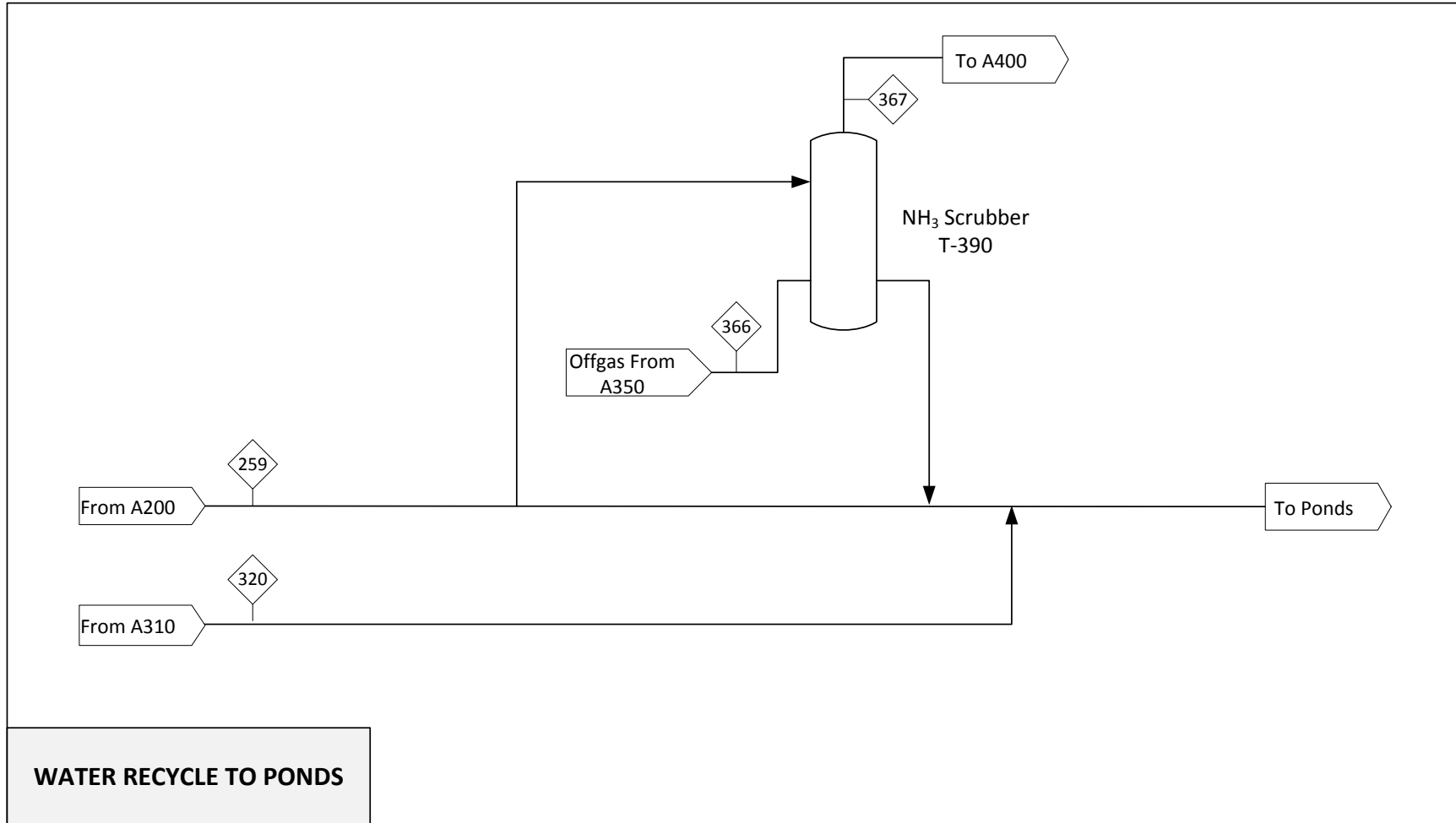
	366	367	320	259
Total Flow lb/hr	7,370	6,898	11,711	478,124
Temperature F	112.8	108.2	116.6	140.0
Pressure psia	20.0	19.8	55.0	50.0
Vapor Frac	1.00	1.00	0.00	0
Mass Flow lb/hr				
H2	700	700	0	0
CO2	228	228	0	237
H2O	293	639	8,056	431,819
NH3	843	28	2,014	0
CH4	1,406	1,406	0	13
C2H6	1,754	1,754	0	0
C3H8	989	989	0	1
N-C4H10	455	454	2	0
N-PENTAN	186	185	1	0
HEXANE	58	58	0	0
ETHYLBEN	19	19	2	0
2MBUTAN	135	135	1	0
2MPENTA	68	68	0	0
2MHEXAN	30	30	0	0
HEPTANE	40	40	0	0
CC6-METH	45	45	1	0
PIPERDIN	2	0	38	0
TOLUENE	27	27	0	0
3MHEPTA	25	25	0	0
OCTANE	22	22	0	0
ETHCYC6	5	5	0	0
O-XYLENE	7	7	1	0
C9H20	5	5	0	0
PROCYC6	2	2	0	0
C3BENZ	4	4	0	0
C10H22	1	1	0	0
C4BENZ	2	2	0	0
C11H24	2	2	0	0
C10H12	2	2	1	0
C12H26	1	1	0	0
1234NA	1	1	0	0
C6BENZ	1	1	0	0
12346N	1	1	0	0
C7BENZ	0	0	0	0
C8BENZ	0	0	0	0
C10H16O4	0	0	148	0
N2H8SO4	0	0	773	0
N2H8CO3	0	0	669	0
CYCHEX	10	10	0	0
NH4+	0	0	0	4,299
H3O+	0	0	0	3,822
HCO3-	0	0	0	26,800
SOLUBLE ASH	0	0	0	9,862
SOLUBLE SOLIDS	0	0	0	1,272
Enthalpy, 10^6Btu/	-10.2	-11.3	-63.9	-3091.20

Appendix B – Equipment Cost Details

Equipment Number	# Req'd	# Spares	Equipment Name	Scaling Stream	Original Equipment Stream Flow	New Flows	stream flow units	Size Ratio	Original Equip Cost (per unit)	Base Year	BASIS: installed (i) or bare (b)	Total Original Equip Cost (Req'd & Spare) in Base Year	Scaling Exponent	Scaled Cost in Base Year	Install Factor	Installed Cost in Base Year	Installed Cost in 2011$	Scaled Uninstalled Cost in 2011$	Ref
A100			HTL Oil																
DR-101	12	0	Algae Dryer	D100	5,556	5,675	lb/h	1.02	$905,000	2013	b	$10,860,000	0.8	11,045,044	1.6	17,672,070	15,936,153	$9,960,096	1
P101	1	1	Booster Pump	50% S100	367,437	111,608	lb/h	0.30	$379,600	2007	b	$759,200	0.8	292,661	2.3	673,121	750,375	$326,250	2
HTL System	2	0	Equipment Included:	S100	306,198	287,238	lb/h	0.94	$18,743,378	2011	b	$37,486,757	0.77	35,686,319	2.1	74,084,799	74,084,799	$35,686,319	2
			Static mixer																
			Feed pump																
			Heat integration																
			HTL Reactor																
			K/O Drums																
Phase Separation	1	0	Solids filter, Oil/w ater separator		1,219,765	574,475	lb/h	0.47	$3,945,523	2011	b	$3,945,523	0.68	2,364,510	1.9	4,594,244	4,594,244	$2,364,510	2
Hot Oil System	1	0	Hot oil system including Dow therm		306,198	287,238	lb/h	0.94	$4,670,532	2011	b	$4,670,532	0.6	4,494,793	1.4	6,441,038	6,441,038	$4,494,793	2
			A100 TOTAL														101,806,610	52,831,969	
A200			CHG HTL Water Treatment System																
P240	1	0	Feed Pump	S232 scaled	201,905	480,702	lb/h	2.38	$611,300	1Q 2011	b	$611,300	0.8	1,223,594	1.4	1,713,032	1,754,982	$1,253,558	3
P240a	1	0	Booster Pump	S232 scaled	201,905	480,702	lb/h	2.38	$8,900	1Q 2011	b	$8,900	0.8	17,814	3.2	57,006	58,402	$18,251	3
H240	4	0	Feed/Product Exchanger	AREA	7,720	7,779	ft2	1.01	$5,013,647	2011	b	$20,054,588	0.7	20,162,070	2.2	44,356,553	44,356,553	$20,162,070	2
H241	1	0	Fired Heater	Heat DUTY	115	33	MMBTU	0.29	$1,372,262	2011	b	$1,372,262	0.65	609,561	1.21	737,569	737,569	$609,561	2
SP240A	1	0	Hydrocyclone	S232 scaled	968,859	480,702	lb/h	0.50	$5,000,000	2009	b	$5,000,000	0.65	3,170,443	2.1	6,657,931	7,471,834	$3,558,016	4
RS-241	1	0	Guard Bed=10% CHG reactor	S232 scaled										632,661		1,265,322	1,265,322	632,661	2
R-240	6	0	CHG Reactor (90% of equiv HTL reactor cost)	S232 scaled	76,235	80,117	lb/h	1.05	$2,041,875	2011	b	$12,251,250	0.65	12,653,221	2.0	25,306,441	25,306,441	$12,653,221	2
H251	1	0	Product Air Fin Cooler	S232 scaled	201,905	480,702	lb/h	2.38	$204,100	1Q 2011	b	$204,100	0.65	358,688	1.31	469,881	481,388	$367,472	3
			A200 TOTAL														$81,432,492	$39,254,810	
A300			HTL Oil Upgrading and Product Separation																
A310			HTL Oil Hydrotreating & Separations																
R-301a	1	0	Hydrotreater Reactor, vessels, columns	S224	6,524	5,051	bpd fd	0.77	$27,000,000	2007	i	$15,625,000	0.75	12,895,660	1.51	12,895,660	14,375,692	$9,520,325	5
K-310	1	0	Hydrogen Compressor	S327	17.1	17.1	mmscfd H2	1.00	$1,385,600	1Q 2011	b	$1,385,600	0.8	1,385,600	1.1	1,524,160	1,561,484	$1,419,531	3
PSA-310	1	0	PSA for Hydrogen Recycle	S326	10	17.1	mmscfd H2	1.71	$1,750,000	2004	b	$1,750,000	0.8	2,688,634	2.47	6,640,927	8,756,396	$3,545,099	6
			A310 Total							Subtotal							$24,693,571	$14,484,956	
A350			Hydrocracking and Separations																
R-350	1	0	Hydrocracker Unit + auxiliaries	S338	2,200	497	bpd fd	0.23	$25,000,000	2007	i	$15,625,000	0.75	5,119,835	1.51	5,119,835	5,707,437	$3,779,760	5
			A350 Total							Subtotal							$5,707,437	$3,779,760	
			A300 TOTAL														$30,401,008	$18,264,716	
A400			Hydrogen Plant - OSBL																
	1	0	Stm Reformer system w / associated OSBL		24.5	17	mmscfd H2	0.70	$32,765,625	May 2007	i	$32,765,625	0.65	25,940,996	1.92	25,940,996	28,570,216	$14,880,321	7
			A400 TOTAL							Subtotal							$28,570,216	$14,880,321	
A600			Power Generation - OSBL																
K-	1	0	Steam Turbine	DAF Algae	46,666	111,608	lb/hr	2.39	$1,493,900	2010	b	$1,493,900	0.85	3,134,810	1.08	3,385,595	3,600,115	$3,333,439	10
			A600 TOTAL														$3,600,115	$3,333,439	
											Subtotal						$3,600,115	$3,333,439	
A700			OSBL - including cooling water system																
M-701	1	0	Cooling Tow er System	circ rate	35,631,668	2,501,594	lb/hr	0.07	2,000,000	2009	b	$2,000,000	0.6	406,311	2.95	1,198,617	1,345,143	$455,981	8
P-702	1	0	Cooling Water Pump	circ rate	35,631,668	2,501,594	lb/hr	0.07	445,700	2009	b	$445,700	0.6	90,546	2.95	267,112	299,765	$101,615	8
																			8
	1	0	Plant Air Compressor	dry algae rate	2,000	1,215	mtpd	0.61	$32,376	2002	b	$32,376	0.34	27,329	2.95	80,622	119,364	$40,462	9
	1	0	Hydraulic Truck Dump w ith Scale	dry algae rate	2,000	1,215	mtpd	0.61	$80,000	1998	b	$80,000	0.6	59,322	2.95	175,000	263,151	$89,204	9
	1	0	Firew ater Pump	dry algae rate	2,000	1,215	mtpd	0.61	$18,400	1997	b	$18,400	0.79	12,411	2.95	36,613	55,483	$18,808	9
	1	0	Instrument Air Dryer	dry algae rate	2,000	1,215	mtpd	0.61	$8,349	2002	b	$8,349	0.6	6,191	2.95	18,263	27,040	$9,166	9
	1	0	Plant Air Receiver	dry algae rate	2,000	1,215	mtpd	0.61	$7,003	2002	b	$7,003	0.72	4,891	2.95	14,430	21,364	$7,242	9
	1	0	Firew ater Storage Tank	dry algae rate	2,000	1,215	mtpd	0.61	$166,100	1997	b	$166,100	0.51	128,818	2.95	380,012	575,869	$195,210	9
TK-230	1	0	HTL oil intermediate Storage - 3 day	S224	1,056,846	4,227,367	gallons	4.00	470,000	1Q 2005	b	$470,000	0.65	1,157,273	2.95	3,413,955	4,278,950	$1,450,492	8
	1	0	Product Storage - 3 day	S392	558,000	101,400	gallons	0.18	320,384	1Q 2005	b	$320,384	0.65	105,751	2.95	311,965	391,007	$132,545	8
	1	0	Product Storage - 3 day	S393	558,000	491,869	gallons	0.88	320,384	1Q 2005	b	$320,384	0.65	295,163	2.95	870,729	1,091,346	$369,948	8
			A700 TOTAL														$6,823,574	$2,870,672	

REFRENCES	
1	Muth 2013
2	Knorr 2013
3	Aspen Capital Cost Estimator, 7.3.2
4	Kreb's Engineering Quote from February 2009
5	SRI 2007a
6	Ron Pasadan Quote from 2004
7	SRI 2007b
8	Aspen Icarus Project Manager 2006
9	Phillips, S. et al. NREL/TP-510-41168, April 2007
10	Aspen Capital Cost Estimator, 7.3.1

Total Equipment Cost $252,634,014 $131,435,926

Appendix C – Compound Selection

HTL Liquid Products Composition

HTL organic products are a complex mixture of hundreds of compounds. The number and type of compounds used in the Aspen model to represent HTL oil and the associated aqueous phase must reasonably match key properties of such as CHONS, density, heating value, GC/MS data, expected HTL oil distillation range, and aqueous solubility. The compounds chosen for the Aspen model are shown in Table C-1. Note, that this list does not imply that these compounds occur in the given percentages in actual HTL oil, rather each compound represents a group of compounds that taken together exhibit the bulk properties of the oil. Carbon dioxide and ammonia in the aqueous phase actually form their ionic species in various amounts and types, including NH_4^+, NH_2COO^-, HCO_3^-, CO_3^{2-}. For simplification purposes, ion formation is not simulated in this model.

Table C-1 Compounds used to model HTL liquid products

HTL OIL	Heat & Mat'l Balance Names	Wt%	C	H	O	N	S	CAS
1-ethyl-2-pyrrolidinone	1E2PYDIN	6.79117%	6	11	1	1		2687-91-4
N-methylthiopyrrolidone	C5H9NS	1.02567%	5	9		1	1	10441-57-3
Ethylbenzene	ETHYLBEN	2.54669%	8	10				100-41-4
Phenol, 4-methyl-	4M-PHYNO	5.09338%	7	8	1			106-44-5
Phenol, 4-ethyl-	4EPHYNOL	5.09338%	8	10	1			123-07-9
Indole	INDOLE	5.09338%	8	7		1		120-72-9
1H-Indole, 7-methyl-	7MINDOLE	3.39559%	9	9		1		933-67-5
Myristamide (C14 amide)	C14AMIDE	3.39559%	14	29	1	1		638-58-4
Palmitamide (C16 mide)	C16AMIDE	15.28014%	16	33	1	1		629-54-9
Stearamide (C18 amide)	C18AMIDE	6.79117%	18	37	1	1		124-26-5
Palmitoleic acid (C16:1FA)	C16:1FA	13.58234%	16	30	2			373-49-9
Palmitic acid (Hexadecanoic acid)	C16:0FA	10.18676%	16	32	2			57-10-3
Oleic acid	C18FACID	1.69779%	18	34	2			112-80-1
Naphthalene	NAPHATH	5.09338%	10	8				91-20-3
Fused rings (cholesterol)	CHOLESOL	1.69779%	27	46	1			57-88-5
Aromatic amines	AROAMINE	8.14241%	18	16		2		74-31-7
1,2-benzenedicarboxylic acid)	C30DICAD	5.09338%	30	50	4			3648-20-2
		100%						
HTL Aqueous Phase Organics		**Wt%**	**C**	**H**	**O**	**N**	**S**	**CAS**
Methanol	METHANOL	14.61988%	1	4	1			67-56-1
Ethanol	ETHANOL	2.92398%	2	6	1			64-17-5
Acetone	ACETONE	2.92398%	3	6	1			67-64-1
Formic acid	FORMACID	29.23977%	1	2	2			64-18-6
Acetic acid	ACEACID	8.77193%	2	4	2			64-19-7
Glycerol	GLYCEROL	2.92398%	3	8	3			56-81-5
Carbon dioxide	CO2	19.88304%	1		2			124-38-9
Ammonia	NH3	9.06433%		3		1		7664-41-7
3-pyridinol	3-PYRDOL	4.38596%	5	5	1	1		109-00-2
1-ethyl-2-pyrrolidinone	1E2PYDIN	1.86564%	6	11	1	1		2687-91-4
N-methylthiopyrrolidone	C5H9NS	3.39752%	5	9		1	1	10441-57-3
		100.000%						

Hydrotreated Oil Model Compounds

Similar to HTL oil, hydrotreated oil contains numerous compounds and a limited number is used for modeling purposes. Tables C-2 shows the mixture of compounds used to represent the hydrotreated oil in the models. Note, that this list does not imply that these compounds occur in the given percentages in actual hydrotreated oil, rather each compound represents a group of compounds that taken together exhibit the bulk properties.

Table C-2 Compounds used to model hydrotreated product

Compound	Heat & Mat'l Balance Names	C	H	O	N	Wt%	CAS
Butane, 2-methyl-	2MBUTAN	5	12	0		0.0077	78-78-4
Pentane	N-PENTAN	5	12	0		0.0077	109-66-0
Pentane, 2-methyl-	2MPENTA	6	14	0		0.0310	107-83-5
Hexane	HEXANE	6	14	0		0.0155	110-54-3
Hexane, 2-methyl-	2MHEXAN	7	16	0		0.0310	591-76-4
Heptane	HEPTANE	7	16	0		0.0155	142-82-5
Cyclohexane, methyl-	CC6-METH	7	14	0		0.0155	108-87-2
Piperidine	PIPERDIN	5	11	0	1	0.0077	110-89-4
Toluene	TOLUENE	7	8	0		0.0155	108-88-3
Heptane, 3-methyl-	3MHEPTA	8	18	0		0.0155	589-81-1
Octane	OCTANE	8	18	0		0.0155	111-65-9
Cyclohexane, ethyl-	ETHCYC6	8	16	0		0.0155	1678-91-7
Ethylbenzene	ETHYLBEN	8	10	0		0.0310	100-41-4
o-Xylene	O-XYLENE	8	10	0		0.0155	95-47-6
Nonane	C9H20	9	20	0		0.0155	111-84-2
Cyclohexane, propyl-	PROCYC6	9	18	0		0.0310	1678-92-8
Benzene, propyl-	C3BENZ	9	12	0		0.0155	103-65-1
Nonane, 4-methyl-	4MNONAN	10	22	0		0.0155	17301-94-9
Decane	C10H22	10	22	0		0.0464	124-18-5
Benzene, butyl-	C4BENZ	10	14	0		0.0155	104-51-8
Undecane	C11H24	11	24	0		0.0310	1120-21-4
1-Phenyl-1-butene	C10H12	10	12	0		0.0155	824-90-8
Dodecane	C12H26	12	26	0		0.0310	112-40-3
Naphthalene, 1,2,3,4-tetrahydro-	1234NA	10	12	0		0.0155	119-64-2
Benzene, hexyl-	C6BENZ	12	18	0		0.0155	1077-16-3
Naphthalene, 1,2,3,4-tetrahydro-6-methyl-	12346N	11	14	0		0.0155	1680-51-9
Benzene, heptyl-	C7BENZ	13	20	0		0.0155	1078-71-3
Benzene, octyl-	C8BENZ	14	22	0		0.0310	2189-60-8
1,4-Cyclohexanedicarboxylic acid, dimethyl ester	C10H16O4	10	16	4		0.0155	94-60-0
Pentadecane	C15H32	15	32	0		0.0155	629-62-9
Hexadecane	C16H34	16	34	0		0.1238	544-76-3
Heptadecane	C17H36	17	36	0		0.0464	629-78-7
Octadecane	C18H38	18	38	0		0.0310	593-45-3
Nonadecane	C19H40	19	40	0		0.0310	629-92-5
Eicosane	C20H42	20	42	0		0.0774	638-36-8
Heneicosane	C21H44	21	44	0		0.0310	629-94-7
Tricosane	C18H38	23	48	0		0.0155	638-67-5
1,2-Benzenedicarboxylic acid, diisooctyl ester	C24H38O4	24	38	4		0.0310	27554-26-3
heptyl undecyl phthalate	C26H42O4	26	42	4		0.0310	65185-88-8
Triacontane	C30H62	30	62	0		0.0015	638-68-6
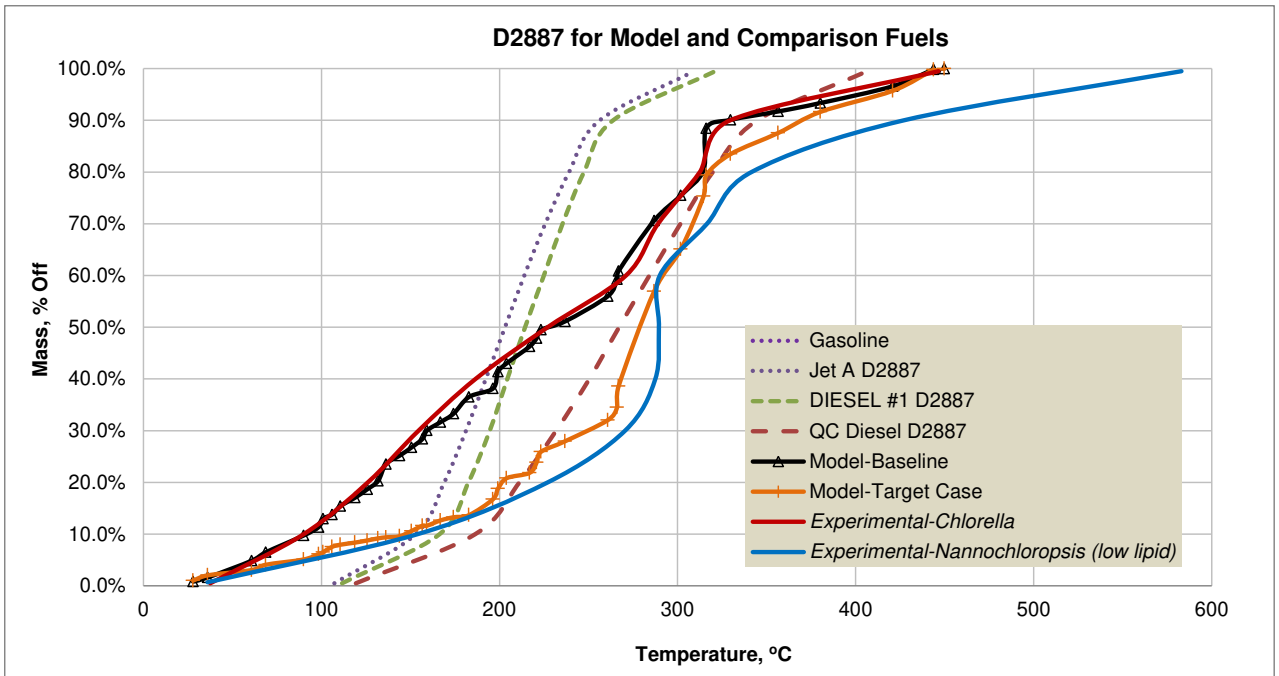
Figure C-1 Hydrotreated HTL oil distillation curve by ASTM D2887

Table C-3 shows the experimentally derived distillation curves that were used to help select the final fuel compounds based on their boiling points.

Table C-3 Hydrotreated HTL oil distillation data

Sample	*Chlorella*			*Nannochloropsis*
	HT61573-6-4	HT61573-6-5	HT61573-6-6	HT-190
Recovered mass%	°C	°C	°C	°C
0.5	37.5	37.5	37.5	36
10	90.0	90.0	89.0	154
20	124.5	126.0	126.0	227
30	151.5	154.5	154.5	271
40	182.0	186.5	188.0	288
50	221.5	227.0	231.0	290
60	266.5	271.0	272.0	290
70	288.5	289.0	290.0	317
80	309.5	312.5	317.0	342
90	321.5	329.5	340.5	427
99.5	434.5	446.5	458.0	583

Appendix D – Indices

Table D-1 Labor indices
Source: Bureau of Labor Statistics
Series ID: CEU3232500008 Chemicals
Average Hourly Earnings of Production Workers
Current indices @ http://data.bls.gov/cgi-bin/srgate

YEAR	INDEX	YEAR	INDEX
2002	17.97	2007	19.55
2003	18.50	2008	19.50
2004	19.17	2009	20.30
2005	19.67	2010	21.07
2006	19.60	2011	21.46

Table D-2 Capital cost indices
Chemical Engineering Magazine, CEI annual index
2012 and 2013 regressed from previous year data (DOE 2013)

YEAR	INDEX	YEAR	INDEX
1990	357.6	2002	395.6
1991	361.3	2003	402.0
1992	358.2	2004	444.2
1993	359.2	2005	468.2
1994	368.1	2006	499.6
1995	381.1	2007	525.4
1996	381.7	2008	575.4
1997	386.5	2009	521.9
1998	389.5	2010	550.8
1999	390.6	2011	585.7
2000	394.1	*2012*	*617.6*
2001	394.3	*2013*	*649.5*
2000	394.1		

Table D-3 Inorganic chemical indices
Source: SRI International Chemical Economics Handbook, Economic Environment of the Chemical
Industry, September 2006 (2012 and 2013 regressed from previous year data (DOE 2013)
Current indices @https://www.sriconsulting.com/CEH/Private/EECI/EECI.pdf

YEAR	INDEX	YEAR	INDEX
1990	123.6	2002	157.3
1991	125.6	2003	164.6
1992	125.9	2004	172.8
1993	128.2	2005	187.3
1994	132.1	2006	196.8
1995	139.5	2007	203.3
1996	142.1	2008	228.2
1997	147.1	2009	224.7
1998	148.7	2010	233.7
1999	149.7	2011	249.3
2000	156.7	*2012*	
2001	158.4	*2013*	