

THESIS

TECHNO-ECONOMIC ANALYSIS OF ASH REMOVAL IN ALGAL BIOMASS

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ABSTRACT

TECHNO-ECONOMIC ANALYSIS OF ASH REMOVAL IN ALGAL BIOMASS

Large-scale microalgae cultivation for biodiesel production is expected to be performed utilizing open air growth infrastructure which will inherently introduce ash into the system. High ash content biomass represents a significant challenge for the production of biofuel as it increases processing capital and operational costs. This study directly assesses the economic viability of pretreatment processes focused on the removal of ash from biomass grown with an algal turf scrubber (ATS) unit. An engineering process model of biofuel production was developed based on an ATS growth architecture followed by an ash removal process and conversion of the biomass to fuels through hydrothermal liquefaction. The model was validated with literature for the growth and conversion processes and validated with experimental data for the de-ashing process. A total of 14 different scenarios were investigated based on two different ash removal techniques, water wash and alkaline extraction treatment operated at various temperatures and alkaline levels. The engineering process model was integrated with techno-economic modeling to investigate the impact of ash on the required biomass and fuel selling price for economic viability. Capital costs associated with the conversion of biomass to biofuel were found to double as ash content increased from 0% to 70%, correlating to a 21% increase in fuel selling price. Integrating an ash removal step resulted in reduced conversion capital costs. However, only the water wash at 25°C scenario was found to reduce the overall fuel selling price. Operational expenses associated with required waste water treatment, chemical cost associated with the alkaline extraction de-ashing technology, and heating of the microalgae

slurry during the de-ashing process were found to significantly increase the overall fuel selling price of the microalgae biofuel.

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1 INTRODUCTION

As the global consumption of energy continues to rise, the world continues to look for new sources of energy. Renewable sources of energy are in high demand due to awareness of environmental sustainability. One of the promising next generation renewable fuels is microalgae biofuel. Some inherent advantages of microalgae when compared to other alternative fuel feedstocks include: high yield potential, no land quality requirement, and utilization of waste water or other poor water quality sources. Large-scale microalgae cultivation necessary for commercial biodiesel production is expected to be performed utilizing open air growth infrastructure, and possibilities include open raceway ponds (ORP) or algal turf scrubbers (ATS). These systems represent inexpensive and simple growth platforms in comparison to closed photobioreactor systems.

ATS growth platforms are defined by a physical matrix on which native microalgae grow, and primary biomass types include filamentous algae, diatoms, and cyanobacteria. The most common application of ATS systems were designed to remediate waterways affected by high nutrient agricultural runoff [1]. Several characteristics of interest inherent to microalgae grown in an ATS system are high microalgae growth rates and minimal energy requirements for harvesting and dewatering in comparison to traditional ORPs [2]. The main barriers for biofuel production from the biomass harvested from the ATS system is the high ash content and low lipid content inherent to the microalgae polyculture. The accumulation of biogenic and non-biogenic ash in biomass harvested from the ATS systems result from the open air growth infrastructure, integration with water streams containing high total dissolved and suspended solids, and growth of diatoms. Ash contents of microalgae from ORPs can vary from scenarios

below 3 wt.% ash [3] up to and above 60 wt.% ash [4]. Ash contents of 50 wt.% and higher are not uncommon for microalgae biomass cultivated in an ATS system [5]. High ash contents represent a significant challenge for the often energy intensive and costly downstream conversion economics of a microalgae biorefinery. In downstream conversion technologies, ash is a largely inert substance that increases the size requirements of the conversion equipment needed for the steady state processing of the biomass. The removal of ash from microalgae biomass prior to conversion represents a plausible route for significant capital cost savings through the decrease in the size requirements of downstream conversion equipment.

Large-scale algal cultivation is expected to be done in open systems located in arid locations. Ash content has the potential to significantly impact the composition of harvested biomass. Some open air growth infrastructure such as ATSs inherently have a high ash content [1, 5, 6]. Many of the techno-economic [3, 7, 8] and life cycle analysis [9-11] in literature utilize data that assumes low ash content. Further, a vast number of sustainability assessments either completely ignore or do not report ash content [12-16]. This low ash content condition inherently suggests that ash removal will be necessary for high ash content biomass. Current sustainability models cannot adequately model the potential impacts of processing high ash biomass. Consequently, the effect of ash content, especially high ash content, on the production of microalgae and estimated biofuel selling price has not been quantified. In conjunction, the further effects of ash removal technologies on the production of microalgae biofuel utilizing high ash content microalgae has not been investigated through the metrics of economic viability and economic impact.

This study evaluates the effects of ash content and ash removal technologies such as simple water washing and a more intensive pre-processing step (alkaline extraction) on the

economics of microalgae biofuel. Water washing has been explored as a means to remove non-biogenic ash, while alkaline extraction targets biogenic ash removal, specifically the silica inherent to diatoms [17]. The model covers the entire value chain of an algal biorefinery and includes microalgae cultivated in an ATS system, a preprocessing ash removal step using yields described in Aston et al. [17], conversion to fuel through hydrothermal liquefaction (HTL), followed by catalytic upgrading. Multiple scenarios are evaluated based on different alkaline operating conditions.

The techno-economic model focuses on two system boundaries with the first limited to growth, harvest, and de-ashing and the second extending the boundary to include conversion and upgrading to fuel. The results for these two boundaries are biomass selling cost and minimum fuel selling price (MFSP), respectively. The model was further utilized to evaluate the energetics of the system in order to assess sustainability metrics. Results from the analysis are used to illustrate the importance of understanding the impact of ash content and ash removal technologies on the microalgae-to-biofuel process.

2 MATERIALS AND METHODS

The methods for this work are divided into three main efforts 1) development and validation of an engineering process model, 2) techno-economic modeling, and 3) an energy assessment. The baseline process model includes sub-process models of biomass acquisition, optional de-ashing through either water washing or alkaline extraction, and conversion to biofuel through hydrothermal liquefaction followed by catalytic upgrading of the fuel, Figure 1. The model was constructed in a modular fashion to support the evaluation of multiple system configurations. Biomass acquisition and HTL conversion sub-process models were based on the work of Hoffman et al. [2] and Jones et al. [7], respectively. Ash removal sub-process models were validated with experimental data presented in Aston et al. [17]. Multiple scenarios were evaluated based on the experimental data and the various production pathways including a no de-ashing scenario. Two system boundaries were defined, the first is limited to biomass procurement and de-ashing (de-ashing system boundary) and a second that expands the first to include downstream processing and upgrading (biofuel system boundary). The first boundary is used to understand the impact of de-ashing on de-ashing biomass selling price and the second focused on the impact of de-ashing on biofuel selling price.

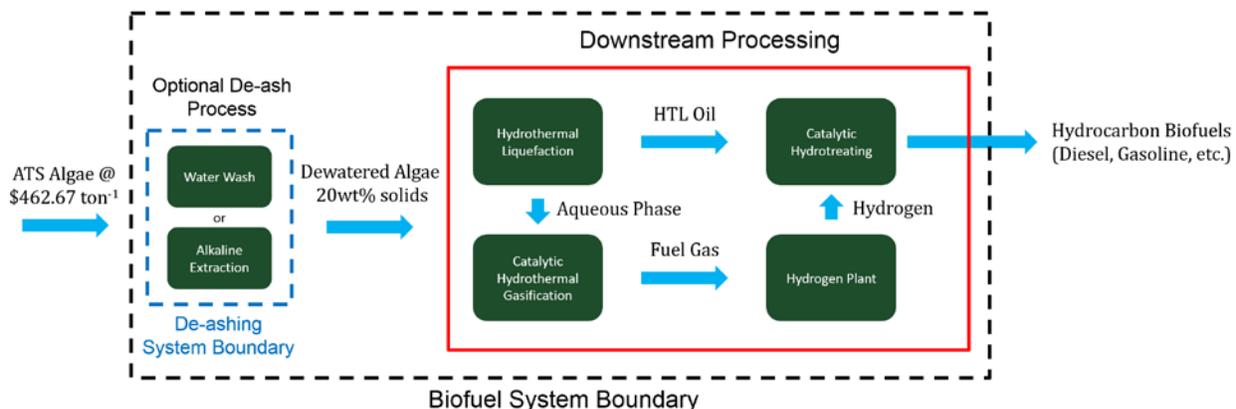


Figure 1. Process flow and system boundaries utilized in TEA models for the production of fuel from ATS algae.

2.1 Engineering Process Modeling

The engineering process model is developed based on sub-process modeling and focuses on energy and mass balances, Figure A1. Each sub-process model is validated and integrated into the engineering process model. Modularity supports the evaluation of multiple production pathways and different system boundaries. A total of 14 scenarios were evaluated including a baseline no de-ash pathway.

2.1.1 Algae Cultivation and Acquisition

Microalgae biomass was modeled as purchased at a rate of 1340 tons per day [2, 7] from an ATS growth system at a price of \$462.67 per ton of ash free dry weight (AFDW) microalgae [2]. The microalgae is harvested at the ATS at 20 wt% solids with the ash content of 65%.

2.1.2 Algae Cultivation and Acquisition De-ashing Processes

Two different de-ashing technologies were considered following procurement of biomass, a simple water wash and an alkaline ash extraction. The effects of various combinations of temperatures (25°C, 50°C, and 80°C) and alkaline concentrations (0.0%, 0.5%, 1.0%, 1.5%, and 2.0% NaOH) on ash removal and algae biomass recovery, reported previously [17], were

used as inputs for the de-ashing sub-process model, as shown in Table 1. Ash removal was performed at 5 wt% solids content with a 4 hour residence time [17]. Required labor costs for the de-ashing technologies were based on values from Jones [7] and Peters [18]. Capital and operational costs for the different de-ashing technologies were based on values from Brown [19]. The water wash or alkaline extraction is performed in twelve 400,000 gallon steel tanks with each tank and its associated piping costing \$257,000. The microalgae slurry is then concentrated to 20% solids in preparation for conversion with the excess water being removed via belt filter presses [20] and, in the case of alkaline extraction, sent to a waste water treatment facility. In the no de-ash scenario algae biomass proceeds directly to conversion after purchase without ash removal.

Table 1. Experimental results from de-ashing processes focused on ash removal and organic recovery.

	Ash Removal	Organic Recovery
No Treatment	0% ± 0.2%	100% ± 1.7%
Water Wash, 25°C	38% ± 0.5%	100% ± 0.9%
0.5% NaOH, 25°C	52.7% ± 0.5%	94.6% ± 1.5%
1.0% NaOH, 25°C	57.2% ± 0.5%	93.8% ± 2.3%
1.5% NaOH, 25°C	73.2% ± 3.6%	68.3% ± 2.7%
Water Wash, 50°C	43.7% ± 0.4%	99.2% ± 1.8%
0.5% NaOH, 50°C	56.1% ± 1.2%	95.2% ± 1.4%
1.0% NaOH, 50°C	60.6% ± 0.6%	92.7% ± 1.8
1.5% NaOH, 50°C	74.1% ± 2.1%	65.2% ± 3.5%
Water Wash, 80°C	45.9% ± 0.2%	97.3% ± 1.2%
0.5% NaOH, 80°C	58.3% ± 1.1%	94.9% ± 1.6%
1.0% NaOH, 80°C	60.6% ± 0.5%	91.5% ± 1.9%
1.5% NaOH, 80°C	72.5% ± 2.3%	69.3% ± 1.9
2.0% NaOH, 80°C	84% ± 0.5%	72.4% ± 1.5

2.1.3 Downstream Processing

Concentrated algae slurry (20 wt% solids) from the water wash, alkaline extraction, or no de-ash process was delivered to a HTL conversion reactor followed by catalytic upgrading to biofuel, as shown in Figure 1. Due to the pressure and temperature conditions used by HTL (21.0 MPa and 351°C assumed for this work) water becomes highly reactive and the algae biomass slurry breaks down into biocrude, aqueous, and gaseous streams. HTL conversion of microalgae to biocrude was assumed to be 59% efficient (AFDW) based on work done by Pacific Northwest National Laboratory [7]. HTL biocrude requires further catalytic processing and hydrotreating to remove oxygen, nitrogen and sulfur and produce drop-in fuels. Hydrotreating to renewable diesel was assumed to have an efficiency of 83% with 84% of the final product being diesel and the remaining 16% being naphtha [7]. Ash content and changes in ash content were assumed to not increase or hinder the performance of the HTL and other downstream systems. Catalytic Hydrothermal Gasification (CHG) was included to remove soluble carbon from the aqueous HTL byproduct and recirculate nitrogen back to algae cultivation. The CHG reactor catalytically converts all organics to CO₂ and CH₄, while preserving dissolved nitrogen content and is similar to HTL in that high pressures and temperatures drive the conversion. A pressure and temperature of 21.3 MPa and 352°C were assumed in this work. Processed gas from the HTL and CHG units are utilized to generate hydrogen at a natural gas-based steam reformer type hydrogen plant that provides the hydrogen required for the hydrotreating of the HTL biocrude into renewable diesel. Catalytic upgrading of HTL biocrude was performed using hydrotreating and hydrocracking [7]. Concentrated aqueous phase and biochar co-products of the biofuel production process were assumed to be removed with no costs or benefits. A list of downstream processing assumptions made can be found in Table A1 of Appendix A. Estimates of the capital and operational costs of

the downstream processing system were made based on the work of Jones et al. [7]. Modeling of the downstream processing was validated by harmonizing inputs with Jones et al. [7] and comparing results. Using the same biomass assumptions a fuel selling price of $\$4.66 \cdot \text{GGE}^{-1}$ was obtained which is within 4% of the reported value in Jones et al., which was deemed acceptable for making general cost comparisons of the impact of ash reduction on MFSP.

Effects of ash content and biomass losses from the de-ashing process on downstream capital costs were accounted for utilizing scaling factors based on changes in mass throughput. Scaling assumptions, installation factors and capital costs can be found in Table A2 of Appendix A.

2.2 Techno-economic Assumptions

The economic viability of all of the scenarios presented was performed based on a system boundary as outlined in Figure 1. Economic evaluation focused on understanding the impact of including a de-ashing step on the cost of biomass at 20% solids and end cost of fuel. The costs of the production were divided into capitals costs, operational costs, and taxes. The techno-economic assumptions made were held constant throughout all scenarios tested to ensure that a direct comparison of the costs and benefits of each de-ashing scenario could be directly compared. The model was created utilizing assumptions for the standard reference of the “Nth” plan design [21]. Economic inputs and assumptions used in the construction of this model are shown in Table 2. These assumptions were chosen so that this work would be consistent with previous studies allowing a basis for comparison [2, 3, 7, 22]. Additional assumptions used in alkaline extraction scenarios include a NaOH purchase price of $\$0.125 \cdot \text{lb}^{-1}$ [23] and waste water treatment fees of $\$2.00 \cdot \text{ton}^{-1}$ [24]. A discounted cash flow rate of return analysis was used to

determine required biomass cost or MFSP necessary for an internal rate of return of 10% over the 30 year life of the operation.

Table 2. Discounted Flow Rate of Return Assumptions

Assumption description	Assumed value
Internal rate of return	10%
Plant life	30 years
Plant financing debt/equity	60% / 40% of total capital investment
Interest rate for debt	8.0%
Term for debt financing	10 years
Working capital cost	5.0% of fixed capital investment (excluding land)
Construction period	3 years (8% 1 st yr. 60% 2 nd yr. 32% 3 rd year)
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
Indirect capital costs	60% of total installed capital
Working days annually	330 days·year ⁻¹
Operating hours per day	24 hour·day ⁻¹
Shift supervisor/operator salary	\$48,067·year ⁻¹
Benefits and general overhead	90% of total salaries
Repair & Maintenance	3% of fixed capital investment annually
Insurance and taxes	0.7% of fixed capital investment annually
Electricity	\$0.0736·kWh ⁻¹

2.3 Energy Assessment Modeling

The engineering process model was leveraged to evaluate the energetics of the different production pathways. The performance was assessed through a net energy ratio (NER). NER is defined here as the ratio of energy used to create a product over the energy contained within the product. A NER of less than one is desirable. Energy flows into and out of the engineering system model serve as the primary inputs by which energy consumption (e.g. natural gas, electricity), energy production, and the net energy ratio of the processes were determined.

3 RESULTS AND DISCUSSION

Results focus on the impact of different de-ashing processes (water wash or alkaline extraction) on biomass selling price, biofuel selling price, and system energetic results. A total of 14 scenarios were simulated based on the different de-ashing scenarios as well as a no de-ashing scenario. Results obtained detail the tradeoffs of implementing an ash reduction technology and the capital cost reduction of the downstream technology due to throughput reduction by ash removal.

3.1 Effects of Ash Content on Fuel Selling Prices

To understand the need for and value of adding a de-ashing technology into a microalgae to biofuel production facility, a TEA was performed to understand the effect that biomass ash content has on downstream capital costs, operational costs and the corresponding impact on selling price of the derived biofuel. The downstream HTL model based on the work of Jones et al. was scaled based on flow rate. Ash contents from 0% up to 70% were tested and as expected the total dollars per gallon of gas equivalent ($\$ \cdot \text{GGE}^{-1}$) was found to increase with rising ash content, Figure 2. Downstream capital cost was found to increase from $\$0.97 \cdot \text{GGE}^{-1}$ to $\$2.00 \cdot \text{GGE}^{-1}$ as the ash content increases from 0% to 70% corresponding to a 21% increase in total fuel selling price.

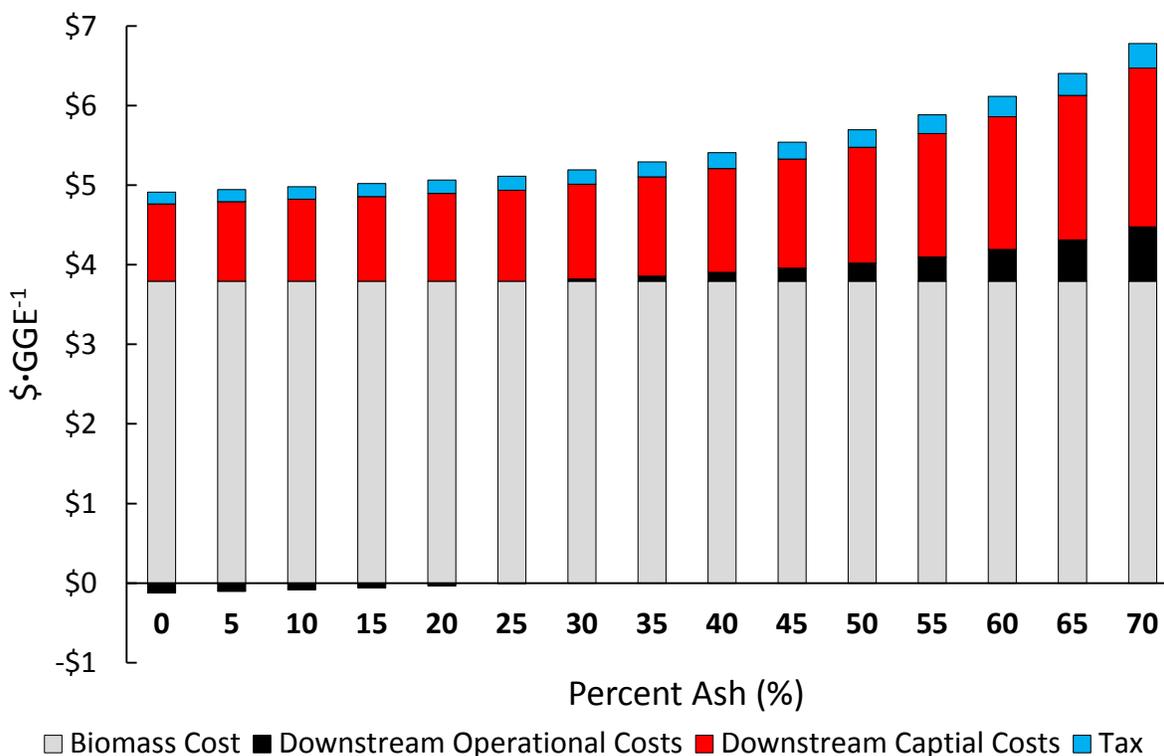


Figure 2. The effect of increasing microalgae ash content on fuel selling price based on a downstream conversion through HTL. The baseline model assumes an ash content of 65%

Biofuel selling price increases with increasing ash content primarily due to rising downstream capital costs. Consistent with previous studies, the total fuel price is dominated by biomass cost which does not change with increasing ash content [2, 7]. To understand the impact of ash on MFSP, the amount of biomass processed through conversion is held constant on an ash-free dry weight basis, while the total biomass (dry weight basis) is allowed to fluctuate with varying ash content. Because ash is inert, the total fuel yield remains constant, while the total amount of material increases with increasing ash. To illustrate, 3.33 tons of 70% ash biomass must be processed to achieve an identical fuel yield as 1 ton of 0% ash biomass. For this work, the biomass purchase price is fixed on an ash free basis and thus represents a constant cost in the analysis. As ash increases it is assumed the cost for transport is minimal based on production and

processing facilities being co-located. The major change across the different ash scenarios is the increase in capital cost. At the baseline of 65% ash, the biomass is comprised of 1340 tons·d⁻¹ that can be converted and 2489 tons·d⁻¹ of ash that is inert. For a HTL conversion process, the capital associated with this process is economically intensive based on the pressures and temperatures required for processing. The increase in capital does not represent an increase in yield but rather is required for processing.

Operational costs were also found to increase slightly with ash content. Negative operational expense values were achieved at lower ash contents as the selling price of a naphtha co-product was subtracted from the overall operational expenses. At low ash contents the selling price of this co-product was greater than the downstream operational expenses thus the total downstream operational costs are negative. In terms of operational costs, increasing ash does have an impact but primarily due to the water that accompanies the ash. For example in a 20% solids scenario every kg of ash that is added to the system is accompanied by 4 kg of water. The large fraction of water in the stream dominates the operational energetics of the HTL process. This total mass does not have an impact on the yield and represents a parasitic load on the conversion system. These results highlight the importance of minimizing ash content and the corresponding impact on the biofuel selling price.

3.2 Biomass Costs

The developed model was used to evaluate the cost to deliver biomass (at 20% solids) to the conversion facility for each de-ashing scenario. The system boundary includes the procurement of biomass at 20% solids, integration of a de-ashing step, and dewatering reduced ash biomass to 20% solids, de-ashing system boundary in Figure 1. The impact of de-ashing on total microalgae biomass selling price in ash free dry weight (AFDW) \$·ton⁻¹ and final ash

content were determined and compared to no de-ash, Figure 3. All de-ashing scenarios were found to increase the total biomass selling price, as expected. The increase in cost is attributed to two factors, 1) costs associated with biomass processing and 2) loss of biomass in the process. For the water wash scenarios, heating of the microalgae slurry to 50°C or 80°C was found to have minimal effect on ash content but significantly increased biomass cost due to heating costs. Compared to the water wash at 25°C (ash content of 54.8% and a biomass selling price of \$511.64·Ton⁻¹ (AFDW)), ash content for the water wash at 50°C and 80°C scenarios slightly decreased to 51.3% and 50.8% while biomass selling prices increased to \$547.58·Ton⁻¹ (AFDW) and \$596.98·Ton⁻¹ (AFDW), respectively, See Table A3 of Appendix A. The results show increasing temperature has minimal value in the water wash de-ashing step.

An alternative de-ashing technology is based on alkaline extraction as it is capable of removing biogenic ash. The purchase cost of the chemical sodium hydroxide used for de-ashing in alkaline extraction scenarios and the required treatment of the post-extraction water were largely responsible for all increases in biomass selling price for these scenarios. This is best illustrated by the 1.5% NaOH at 25°C scenario which increases the biomass selling price by 161.6% compared to the no de-ashing pathway while reducing ash content from 65% to 42.2%. The predominate increase in cost from the baseline of \$462.67·ton⁻¹ (AFDW) to \$1,210.16·ton⁻¹ (AFDW) is from a NaOH cost of \$317.62·ton⁻¹ (AFDW) and a waste water treatment cost of \$144.39·Ton⁻¹ (AFDW). These results indicate that the minimization of the de-ashing chemical costs and waste water treatment costs are crucial for alkaline extraction to be a financially competitive method for ash reduction in microalgae biomass.

Other significant sources increasing the biomass selling price include biomass loss and heating costs during the de-ashing process. Biomass loss is predominantly a function of NaOH

concentration as in almost every case increasing the percent NaOH added was found to increase biomass loss. An example of the effect of NaOH addition on biomass loss and the incurred cost was seen when comparing alkaline extractions performed at 0.5% NaOH, 1.0% NaOH, and 1.5% NaOH at 25°C. In all three cases there was an increase in biomass selling price associated with biomass loss, $\$32.47 \cdot \text{ton}^{-1}$ (AFDW) for the 0.5% NaOH scenario, $\$36.68 \cdot \text{ton}^{-1}$ (AFDW) for the 1.0% NaOH scenario, and $\$223.11 \cdot \text{ton}^{-1}$ (AFDW) for the 1.5% NaOH scenario with the biomass loss being 5.4%, 6.2%, and 31.7%, respectively. Biomass loss represents a significant impact on biomass selling price at high NaOH concentrations. Costs associated with heating the microalgae slurry were also found to have a significant effect on biomass selling price. An example of this is comparing the 1% NaOH at ambient temperature (25°C) with a biomass selling price of $\$800.50 \cdot \text{Ton}^{-1}$ (AFDW) to the 1% NaOH cases at 50°C and 80°C scenarios with biomass selling prices of $\$844.82 \cdot \text{Ton}^{-1}$ (AFDW) and $\$897.24 \cdot \text{Ton}^{-1}$ (AFDW), respectively. The difference in ash content between all three scenarios was less than 2% thus the addition of heat represents a non-practical step in the alkaline extraction process.

These results indicate that if possible, de-ashing processes should seek to minimize the use of chemicals unless these costs can be recuperated by the impact of decreases in ash content when processing the microalgae into final products. All of the scenarios represent an increase in biomass cost as energy and materials being utilized result in a cost increase for AFDW algae. All the scenarios do decrease the ash content that will impact the capital and operational costs for downstream processing. These results are integrated with downstream processing modeling to understand if the increase in biomass cost is offset by capital and operational savings from a reduced ash biomass.

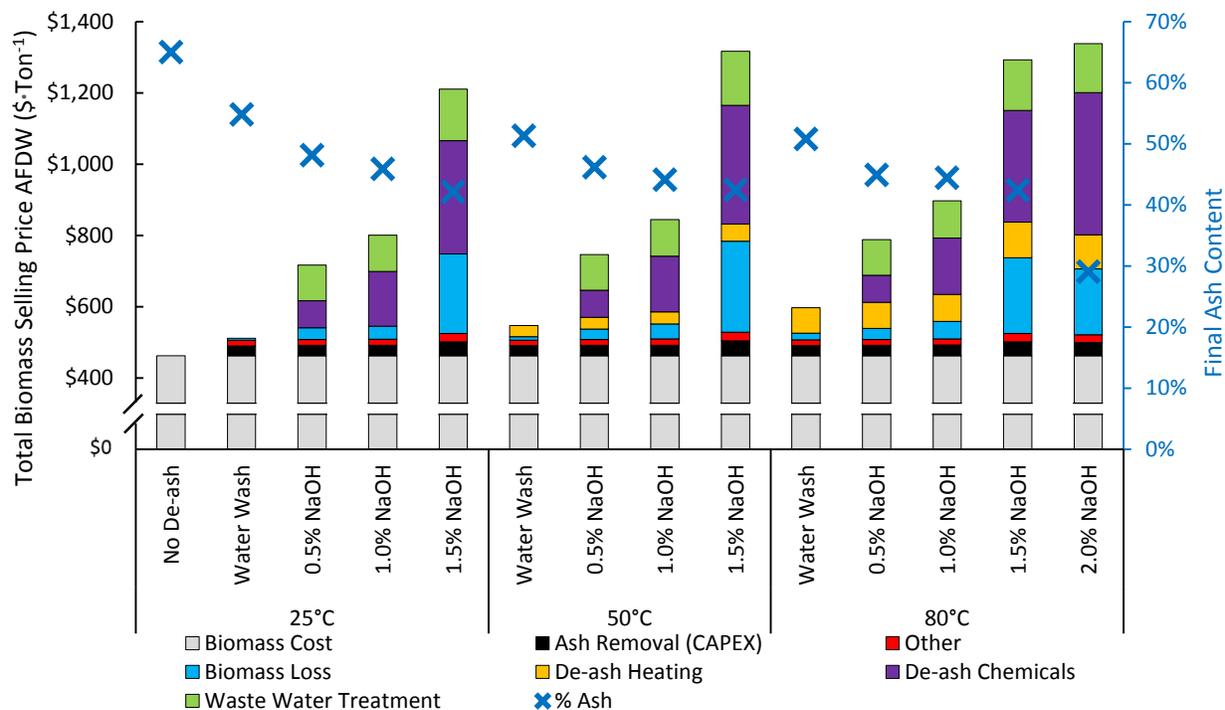


Figure 3. Economic results for the various de-ashing scenarios considered based on a biomass system boundary.

3.3 Biofuel Production Costs

To more holistically understand the impact of de-ashing on biofuel production costs, the system boundary was expanded to include downstream processing through HTL and catalytic upgrading of the biocrude to fuels. The results designate a MFSP based on capital and operating expenditures for microalgae acquisition, de-ashing, downstream processing, and tax over the 30 year life of the plant, Figure 4.

All scenarios were found to increase the $\$ \cdot \text{GGE}^{-1}$ fuel selling price of the renewable diesel except the water wash at 25°C scenario in which the $\$ \cdot \text{GGE}^{-1}$ price dropped from $\$6.40 \cdot \text{GGE}^{-1}$ for the no de-ash case to $\$6.23 \cdot \text{GGE}^{-1}$. To better understand the current hurdles associated with the de-ashing scenarios that were tested, three scenarios (no de-ashing, water wash at 25°C, and 1% NaOH at 25°C) are described in depth to quantify the operational and

capital costs associated with each stage of the renewable diesel production process. Table 3 describes the ash content before and after ash removal, the resulting impact on HTL throughput, and the CAPEX for ash removal and conversion. Capital expenses associated with the implementation of the de-ashing system, \$52-54 million, were found to be largely similar in value across the different scenarios though the scenarios that had more ash removal and biomass loss were found to be on the low end of that spectrum. This was due to reduced belt filter press, piping, and pump requirements. The most significant decrease in capital expenses were, as predicted, in the downstream processing. A decrease in capital expenses was found to be associated with all of the de-ashing scenarios, as less total solids is processed through HTL conversion. For example, HTL throughput was reduced by 39.3% as a result of 1% NaOH at 25°C conditions compared to no de-ashing and thus reduced conversion associated CAPEX by nearly 27%. Increasing NaOH concentration was inversely correlated with capital expenses, as NaOH addition increased, the capital expenses of the conversion system decreased. This is a direct outcome of reduced ash. Biomass with less ash results in less material to process without a decrease in overall fuel yield. Each ash removal scenario resulted in a reduction in conversion CAPEX greater than ash removal capital costs, such that total CAPEX (ash removal + conversion) was less than the no de-ash case. The difference in total CAPEX was greatest for scenarios employing alkaline extraction. A detailed breakdown of capital expenses for some of the key scenarios that were modeled can be found in Table A2 of Appendix A.

Table 3. Ash content, HTL throughput and capital expenditures (CAPEX)

	% Ash in Biomass		HTL Throughput		CAPEX (Millions of \$)		
	Before De-ash	After De-ash	Dry Weight (Tons/day)	AFDW (Tons/day)	Ash Removal	Conversion	Total
No De-ash	65.0%	NA	3829	1340	\$0.00	\$432.40	\$432.40
Water Wash, 25°C	65.0%	54.8%	2966	1340	\$54.09	\$368.71	\$422.80
1.0% NaOH, 25°C	65.0%	45.9%	2323	1257	\$53.28	\$315.56	\$368.85

*all costs reported in 2014\$

Operating expenses associated with ash removal and downstream conversion are presented in Table 4. Operating costs represent annual expenses incurred including electricity, chemical, wastewater treatment, and labor. Total operating costs show the combined impact of each treatment through conversion to fuels.

Table 4. Annual operational expenditures (OPEX) reported in Millions of \$.

	Biomass Cost	Ash Removal				Conversion	Total
		Biomass Loss	NaOH	Water Treatment	Other		
No De-ash	\$204.59	NA	NA	NA	\$0.00	\$28.13	\$232.72
Water Wash, 25°C	\$204.59	\$0.00	\$0.00	\$0.00	\$0.85	\$20.37	\$225.81
1.0% NaOH, 25°C	\$191.91	\$12.68	\$63.17	\$41.37	\$0.85	\$14.19	\$324.18

*all costs reported in 2014\$

The primary operational cost of the renewable diesel production process was the initial biomass cost of \$462.67·ton⁻¹ (AFDW) microalgae, which corresponds to a total operational cost of \$204.6 million dollars each year for the plant modeled, Table 4. It is therefore important to maximize fuel yield in order to minimize the fuel selling price. While each scenario begins with the same quantity of biomass, the amount processed through conversion varies based on biomass lost during the de-ashing step. For each 1% loss in biomass, 507,660 gallons year⁻¹ of fuel is lost,

contributing to a $\$0.06 \text{ GGE}^{-1}$ increase in MFSP. For example, the organic losses in the 1.0% NaOH, 25°C scenario corresponded to $\$12.7$ million in associated operating costs. This highlights the importance of maximizing organic recovery in the de-ashing step. For instance organic losses in the 1.5% NaOH at 25°C scenario are 25.5% greater than those observed in the 1.0% NaOH at 25°C scenario leading to an increase of $\$3.43 \text{ GGE}^{-1}$. Given the high feedstock costs, it is imperative that losses throughout the process be minimized. Scenarios with low organic recovery will not be economically viable.

Some of the de-ashing scenarios explored did successfully significantly reduce ash content which in turn decreased the capital costs for downstream processing. However, achieving this result required significant operational expenditures in the de-ashing processes. For the alkaline extraction scenarios it was found that de-ashing chemicals (NaOH) and waste water treatment costs play a large factor in the overall operational expenditures of the renewable diesel production process. For example, the 1% NaOH, 25°C treatment increased annual OPEX by over $\$100$ million. This is again caused by the high costs of NaOH ($\$63 \text{ million year}^{-1}$) and waste water treatment requirements ($\$41 \text{ million year}^{-1}$). There is a decrease in operational costs of $\$14 \text{ million year}^{-1}$ associated with the conversion costs as a result of the total biomass throughput reduction due to ash reduction, though it was far exceeded by the increase in cost associated with the addition of chemical costs and waste water treatment required by chemical extraction. These results indicate a similar conclusion as the results from the biomass cost analysis, capital savings in the downstream processing from a reduction in ash must be balanced with increases in costs in the de-ashing process to attain economic viability. For the NaOH de-ashing scenarios the input costs outweigh the corresponding savings associated with a lower ash biomass. A possible future area of research and solution for reducing NaOH and waste water

treatment costs is NaOH recovery which had been demonstrated with efficiencies of up to 80% [25-27]. Recovery of the NaOH would require capital infrastructure and operational costs which would need to be balanced by the value of the recovered NaOH for the system to be viable.

For the water wash scenarios, there was a decrease in operational costs associated with the downstream processing of the microalgae into biofuel caused by ash reduction and throughput reduction. An example being, the total operational cost per year of the water wash at 25°C scenario was \$226 million per year compared to that of the no de-ash scenario which was \$233 million per year.

By combining the operational and capital expenses into a TEA covering the 30 year lifespan of the microalgae biofuel plant the total effect of the addition of the various de-ashing scenarios can be assessed on a \$·GGE⁻¹ basis. A breakdown of these costs are presented in Table 5 for key scenarios and Figure 4 for all 14 modeled scenarios.

Table 5. Minimum fuel selling price

Minimum Fuel Selling Price (\$/GGE)									
	Biomass Cost	De-ash Cost					Conversion	Tax	Total Cost
		CAPEX	OPEX						
			Biomass Loss	NaOH	Water Treatment	Other			
No De-ash	\$3.79	NA	NA	NA	NA	NA	\$2.33	\$0.28	\$6.40
Water Wash, 25°C	\$3.79	\$0.23	\$0.00	\$0.00	\$0.00	\$0.02	\$1.92	\$0.27	\$6.23
1.0% NaOH, 25°C	\$3.79	\$0.24	\$0.25	\$1.25	\$0.82	\$0.02	\$1.69	\$0.25	\$8.31

*all costs reported in 2014\$

These fuel selling prices were comprised of a biomass purchase cost, de-ashing cost, downstream cost, and tax. Cost associated with taxes were found to remain relatively constant around \$0.26·GGE⁻¹ with a slight variance depending on the scenario. Biomass purchase price

into the de-ashing process was held constant so that the effects of the different de-ashing scenarios could be compared. The MFSP for no de-ash HTL based conversion of ATS biomass to fuels assuming 65% ash is \$6.40 GGE⁻¹. Only the water washing at 25°C scenario reduced costs compared to no ash removal, with a MFSP of \$6.23 GGE⁻¹. Despite the reduced CAPEX costs, increases in annual OPEX costs associated with alkaline treatment increased the final MFSP for all other scenarios. For example, the 1% NaOH, 25°C treatment increased MFSP by nearly \$2 GGE⁻¹ compared to no de-ash treatment. De-ashing costs which were primarily driven by operational expenses were found to play a major role in the alkaline extraction scenarios due to NaOH and waste water treatment costs. Downstream conversion costs were found to decrease with improved ash removal, as expected. A significant find that was noted is the increased biomass loss associated with increased NaOH concentration. While both ash removal and biomass losses were found to decrease downstream capital costs, biomass loss does so at the expense of revenue due to lower overall fuel yields and therefore should be minimized to decrease fuel selling price. An optimized caustic loading will increase the likelihood of economic feasibility by maximizing organic retention and minimizing chemical costs.

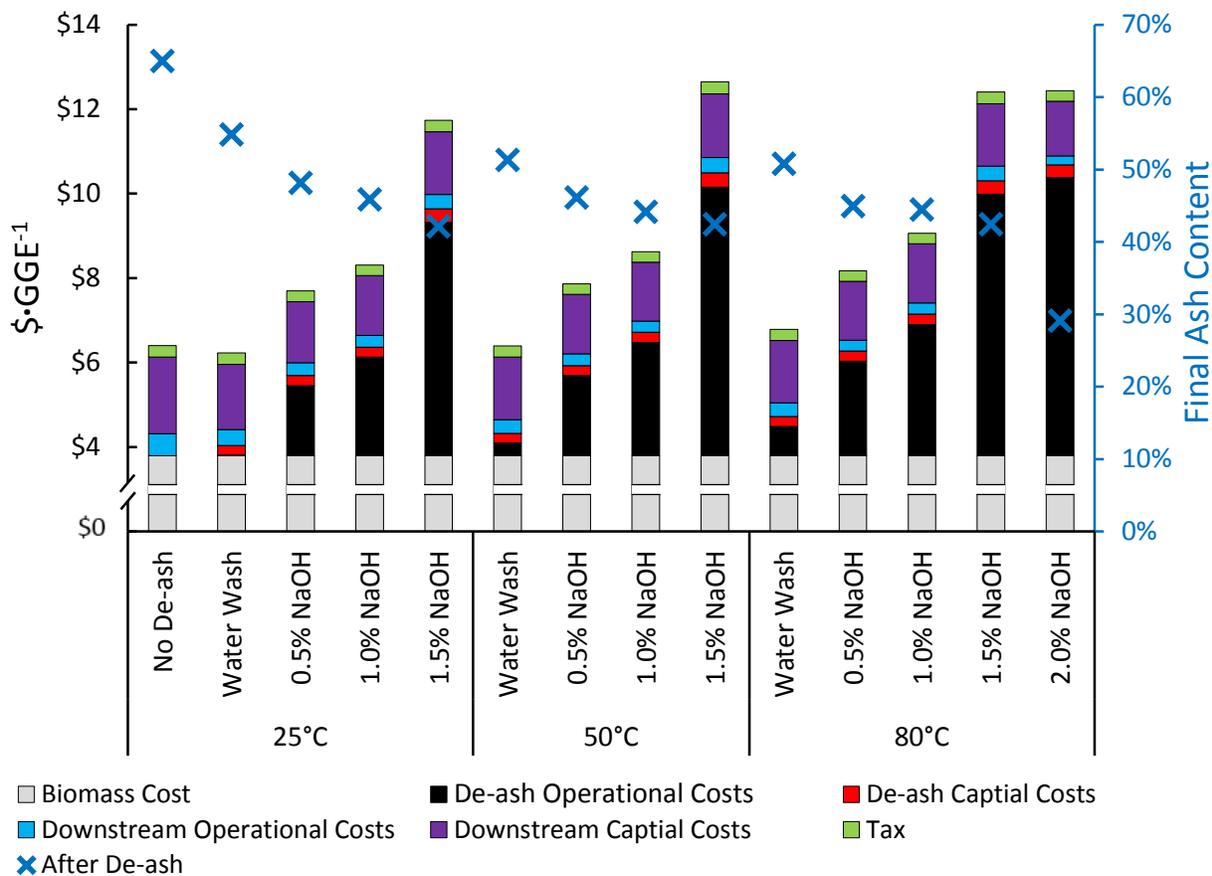


Figure 4. Comparative breakdown of fuel selling prices ($\$ \cdot \text{GGE}^{-1}$) for the various scenarios.

3.4 Energy Assessment

Sustainability metrics are an important aspect in determining effective approaches for biofuel production. Turf scrubbers have great potential for remediating excess nutrients in waterways, and downstream processing should be consistent with this. An energy assessment module was incorporated with the engineering process model. Energy and mass outputs from the engineering system model serve as the primary inputs to the work by which energy consumption (e.g. natural gas, and electricity) were determined for the water wash and 1.0 wt% NaOH, 25°C scenarios, as shown in Table A4 of Appendix A.

Energy consumption for the ash removal processes was approximately 1,400 kW annually for the 25°C approaches. However, this accounted for less than 1% of the total energy consumption in combined ash removal and HTL conversion to fuels. HTL conversion and associated unit operations of 65% ash biomass required over 145,000 kW annually. Total energy consumption of ash removal and HTL conversion was reduced in all of the ash removal scenarios due to a reduction in tonnages in HTL. Water washing reduced the total energy consumption of the process by 20%, whereas the 1% NaOH, 25°C approach reduced energy consumption by 36%.

The energy use of the different processes was evaluated based on a NER defined here as the energy required to produce the fuel over the energy embodied in the fuel product. The engineering process model was leveraged with life cycle energy modeling to understand the net energy usage of the biofuel production scenarios. For some of the key experimental scenarios, a breakdown of the energy consumption of the biofuel production process can be found in Table A4 of Appendix A. Net energy results were determined for all of the experimental scenarios, Figure 5. From these results it was determined that at low temperature the addition of the de-ashing technologies had a positive effect and reduced the NER as compared to the no de-ash scenario for all de-ashing scenarios modeled. Increasing the temperature or increasing the NaOH concentration at which the de-ashing process was performed was found to increase the NER with one of the highest temperature and NaOH concentration scenarios tested, 1.5% NaOH at 80°C, being above desirable limits with a value of 1.02. The energy requirements at increased ash removal temperatures were shown to have no great effect on ash removal and are shown here to be a detriment to efficient energy use. Overall, the NER results highlight the importance of minimizing energy inputs to the de-ashing process.

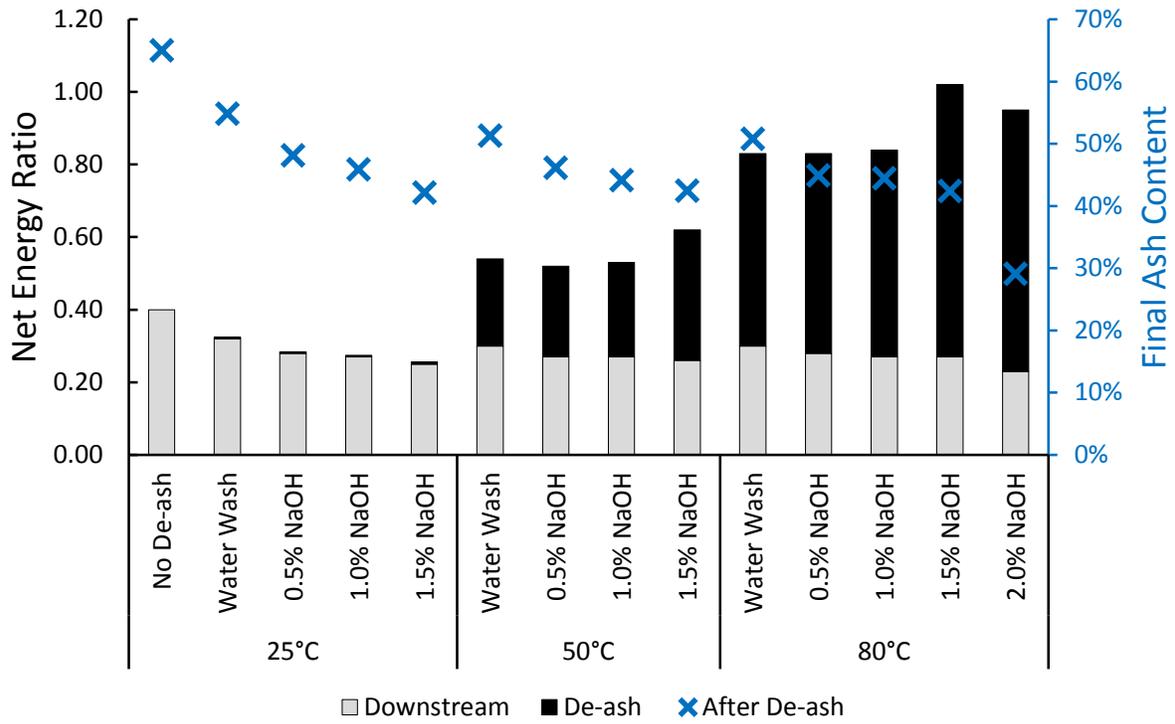


Figure 5. Effect of No De-ash and De-ash scenarios on Net Energy Ratio defined here as energy in to the process over energy in the product.

4 CONCLUSION

High ash contents of microalgae represent a significant challenge for microalgae biofuel production utilizing open growth systems and or waste stream nutrient sources. This work evaluated the economic impact of high ash content algae and the effect of integrating a de-ashing process after harvest and prior to downstream processing on the minimum fuel selling price. A modular engineering process model was built and coupled with techno-economic modeling to estimate the impact of ash reduction on biofuel costs through the HTL conversion approach. Downstream capital costs were found to double as the ash content increased from 0% to 70%, correlating to a 21% increase in fuel selling price. Modeling work was integrated with two de-ashing technologies, water wash and alkaline extraction, to evaluate the potential economic viability. In all scenarios downstream capital costs were found to be reduced by the addition of an ash removal technology into the microalgae biofuel production process. Only the water wash at 25°C scenario was found to reduce the overall fuel selling price. All alkaline ash removal processes were found to increase the biomass selling price of microalgae and the final fuel selling price. The purchase of NaOH and waste water treatment were found to be key factors in the increase of annually-incurred operational expenses. The additional CAPEX incurred by adding an ash removal module to the conversion process was countered with a significant reduction in CAPEX for the HTL conversion process, as expected. While this cost trade-off was not sufficient in countering the increase in OPEX associated with alkaline treatment, advances in chemical reuse and water recycle would optimize this processes in order to reduce overall conversion costs.

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APPENDIX A

Table A1. Downstream Processing Modeling Assumptions

Assumption Description	Assumed Value
HTL	
Temperature (°C)	351
Pressure (MPa)	21.0
Product yields on dry algae, wt%	
HTL Oil	59.0%
Aqueous organics	4.3%
Gas	36.7%
CHG	
Temperature (°C)	352
Pressure (MPa)	21.3
Conversion of Organics to Fuel Gas, wt%	25.0%
Hydrotreating	
Temperature (°C)	402
Pressure (MPa)	10.5
Conversion of HTL oil to products, wt%	
Diesel	63.1%
Naphtha	10.8%
Heavy Oil	9.1%
Offgas	10.6%
Filter	6.4%
Hydrocracking	
Temperature (°C)	395
Pressure (MPa)	7.1
Conversion of heavy oil to products, wt%	
Diesel	65.7%
Naphtha	30.3%
Offgas	0.1%
Filter	3.9%

Table A2. Installation Costs

Installation (Capital) Costs							
Project Year	2014						
Equipment Title	# of Units		Quote Source	Install Factor	Installed Cost in Project Year (Millions of \$)		
	De-ash	No De-ash			Water Wash	1% NaOH	No De-ash
De-ash							
Tanks	12	1	<i>Thane Brown (2005)</i>	1.14	\$2.73	\$2.73	\$0.23
Heat Exchangers	12	0	<i>Thane Brown (2005)</i>	1.6	\$2.38	\$2.06	\$0.00
Belt Filter Press	1	0	<i>Davis (2016)</i>	1.8	\$28.56	\$28.31	\$0.00
Piping	1	1	<i>Thane Brown (2005)</i>	1.7	\$15.36	\$15.13	\$0.16
Pumps	5	0	<i>Jones 2014</i>	2.3	\$5.07	\$5.07	\$0.00
De-ashing Total					\$54.09	\$53.28	\$0.39
HTL							
Booster Pump	5	5	<i>Jones 2014</i>	2.3	\$1.36	\$1.12	\$1.67
Static Mixer	1	1	<i>Jones 2014</i>	2.1	\$132.97	\$110.14	\$161.84
Solids Filter, Separator	1	1	<i>Jones 2014</i>	1.9	\$7.44	\$6.30	\$8.85
Feed Heater Hot Oil System	1	1	<i>Jones 2014</i>	1.4	\$9.80	\$8.46	\$11.42
HTL Total					\$151.57	\$126.02	\$183.78
CHG							
Pump	1	1	<i>Jones 2014</i>	1.4	\$3.50	\$2.85	\$4.34
Booster Pump	1	1	<i>Jones 2014</i>	3.2	\$0.12	\$0.09	\$0.14
HEX - Feed x Product	1	1	<i>Jones 2014</i>	2.2	\$80.90	\$67.56	\$97.70
Feed Heater	1	1	<i>Jones 2014</i>	1.21	\$1.29	\$1.09	\$1.53
Hydrocyclone	1	1	<i>Jones 2014</i>	2.1	\$13.04	\$11.03	\$15.54
Sulfur Guard Bed	1	1	<i>Jones 2014</i>	2	\$2.21	\$1.87	\$2.63
CHG Reactor	1	1	<i>Jones 2014</i>	2	\$44.16	\$37.36	\$52.62
Air Fin Cooler	1	1	<i>Jones 2014</i>	1.31	\$0.84	\$0.71	\$1.00
CHG TOTAL					\$146.05	\$122.55	\$175.50
Hydrotreating							
Hydrotreater Reactor, vessels, columns	1	1	<i>Jones 2014</i>	1.51	\$14.21	\$13.54	\$14.21
Hydrogen Compressor	1	1	<i>Jones 2014</i>	1.1	\$1.52	\$1.44	\$1.52
Hydrogen PSA for recycle	1	1	<i>Jones 2014</i>	2.47	\$8.52	\$8.10	\$8.52
Hydrotreating Total					\$24.25	\$23.09	\$24.25

Installation (Capital) Costs: Continued							
Project Year	2014						
Equipment Title	# of Units		Quote Source	Instal l Facto r	Installed Cost in Project Year (Millions of \$)		
	De-ash	No De-ash			Water Wash	1% NaOH	No De-ash
Hydrocracking							
Hydrocracker Unit + auxiliaries	1	1	<i>Jones 2014</i>	1.51	\$5.10	\$4.86	\$5.10
Hydrocracking Total					\$5.10	\$4.86	\$5.10
Hydrogen plant							
Hydrogen Plant	1	1	<i>Jones 2014</i>	1.92	\$34.18	\$32.79	\$34.18
Hydrogen Plant Total					\$34.18	\$32.79	\$34.18
Fuel Storage							
Diesel Tank	1	1	<i>Thane Brown (2005)</i>	1.45	\$0.52	\$0.50	\$0.52
Gasoline Tank	1	1	<i>Thane Brown (2005)</i>	1.45	\$0.25	\$0.24	\$0.25
Fuel Storage Total					\$0.76	\$0.74	\$0.76
Steam Turbine							
Steam Turbine	1	1	<i>Jones 2014</i>	1.08	\$6.79	\$5.52	\$8.44
Steam Turbine Total					\$6.79	\$5.52	\$8.44
					Water Wash	1% NaOH	No De-ash
Total Installed Cost (Millions of \$)					\$422.80	\$368.85	\$432.40

Table A3. Biomass Selling Price

\$•Ton⁻¹ (AFDW)							
	Biomass Cost	Ash Removal (CAPEX)	Ash Removal (OPEX)				Selling Price
			Other	Biomass Loss	De-ash Chemicals	Waste Water Treat.	
No De-ash	\$462.67	NA	NA	NA	NA	NA	\$462.67
Water Wash, 25°C	\$462.67	\$27.75	\$15.47	\$5.76	\$0.00	\$0.00	\$511.64
1.0% NaOH, 25°C	\$462.67	\$29.14	\$16.84	\$36.68	\$154.18	\$100.98	\$800.50

*all costs reported in 2014\$

Table A4. Energy Consumption

Energy Consumption (KW)			
Equipment Title	Water Wash	1% NaOH	No De-ash
De-ash			
Tanks	0	0	0
Heat Exchangers	0	0	0
Belt Filter Press	954	946	0
Piping	0	0	0
Pump	431	431	0
De-ashing Total	1385	1377	0
Downstream			
HTL Total	47144	36913	60849
Hydrotreating	12684	11897	12684
Hydrocracking	930	872	930
Hydrogen plant	34401	32268	34461
Fuel Storage	0	0	0
Steam Turbine	-10230	-8010	-13204
CHG			
CHG energy Required	62611	48399	81981
Gas energy produced by CHG	-32552	-30534	-32552
CHG TOTAL	30059	17865	49426
	Water Wash	1% NaOH	No De-ash
Total (KW)	116373	93183	145150

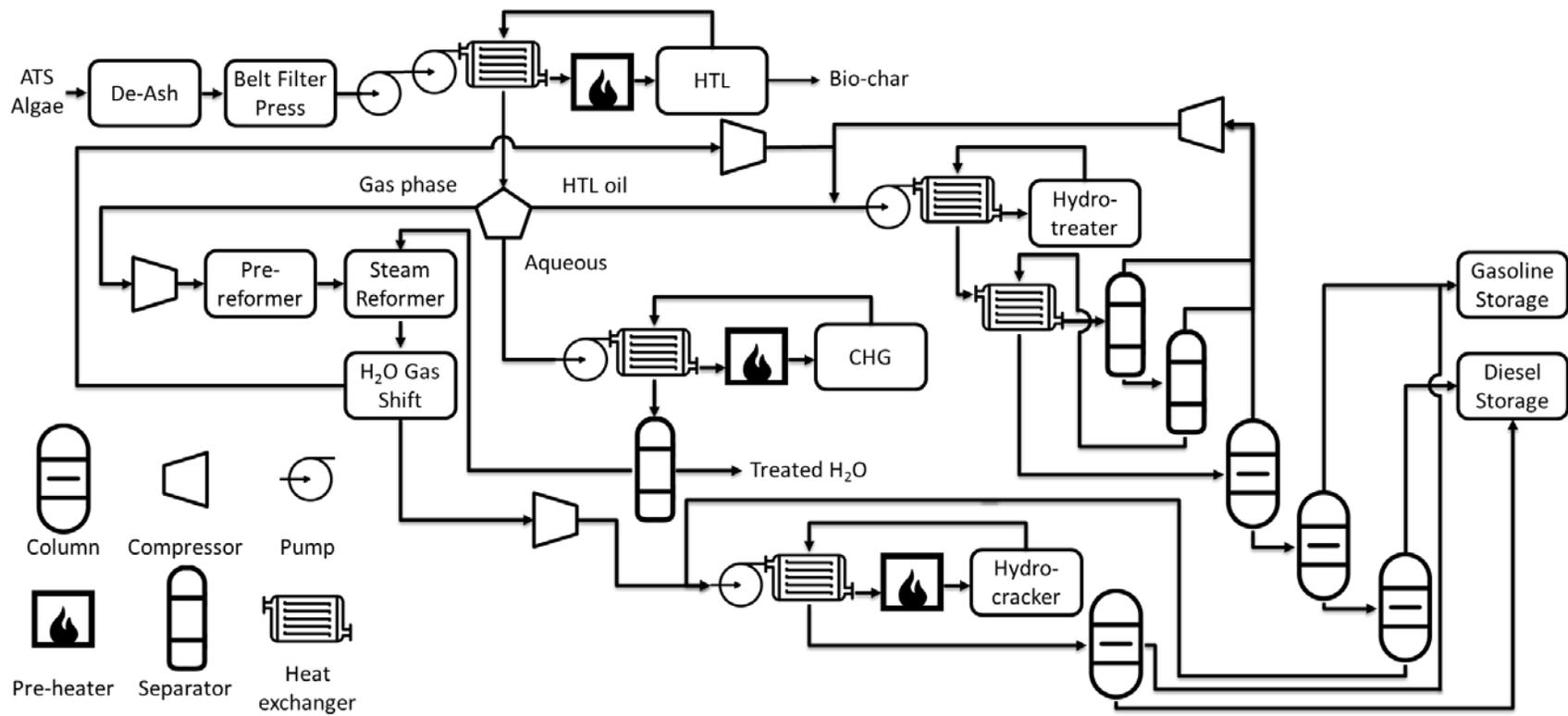


Figure A1. Process model of a microalgae biorefinery incorporating a de-ashing system.