Integrated Wastewater Treatment in Lignocellulosic Biorefineries

Tyler Tobin

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Committee:

Richard Gustafson

Renata Bura

Heidi Gough

Anthony Dichiara

Program Authorized to Offer Degree:

School of Environmental and Forest Sciences

University of Washington

Abstract

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Tyler Tobin

Chair of the Supervisory Committee:

Professor Richard Gustafson

School of Environmental and Forest Sciences

Production and use of bio-based products offer a number of advantages over conventional petrochemicals, yet the relatively high cost of production has restricted their mainstream adoption. Optimization of waste treatment processes could reduce capital expenditures, lowering the barrier to market entry for lignocellulosic biorefineries. This paper characterizes waste production from lignocellulosic ethanol production and analyzes potential wastewater treatment operations. It is found that organic material is intrinsic to bioconversion wastes, supplying up to 260 kilograms of biological oxygen demand per tonne of feedstock. Inorganic material, however, is largely added to waste streams throughout the bioconversion process as a result of pretreatment and pH adjustment operations which increase the inorganic loading by 44 kilograms per tonne of feedstock. Adjusting unit operations to limit addition of inorganic material can reduce the demands and therefore cost of waste treatment. Various waste treatment technologies – including those that take advantage of ecosystem services provided by feedstock production – are evaluated in terms of capital and operating costs, as well as technical feasibility. It is concluded that waste treatment technologies may be better integrated with conversion processes and even feedstock production. In general, there should be an effort to recycle resources throughout the bioenergy supply chain through application of ecosystem services provided by adjacent feedstock plantations and recovery of resources from the waste stream to reduce overall capital and operating costs of bioconversion facilities.

Funding Acknowledgement

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1. Introduction

Bio-based products have potential to accelerate the sustainable development of the global economy. Bio-based products span a wide range of materials including liquid fuels, plastics, construction materials, adhesives and lubricants among others. Cultivation of biomass feedstocks stimulates rural economies (Demirbas, 2009). Domestic cultivation and processing improves security of scarce resources (Dale & Ong, 2014). Production and end use of bio-based products is typically less polluting in terms of both carbon dioxide emissions and other environmental impacts than conventional petroleum derived products (Budsberg et al., 2016; Papong et al., 2014; von Blottnitz & Curran, 2007).

Despite these benefits, bio-based products have not achieved mainstream adoption. Chief among the various obstacles holding back the bio-based economy is the inability of bio-based products to compete at the low price points of petrochemical alternatives (Limayem & Ricke, 2012). The high cost of bio-based products stems from a combination of feedstock prices and extensive processing requirements, particularly for lignocellulosic feedstocks.

Biochemical conversion, or bioconversion, presents one promising platform to process biomass into a wide range of products. Bioconversion of lignocellulosic feedstocks incorporates four main unit operations: pretreatment to fractionate the biomass, hydrolysis to break down cellulose and hemicellulose fibers into carbohydrate monomers, fermentation to convert carbohydrates into desirable products, and separation to purify the desired products.

Pretreatment is necessary to disrupt the structure of lignocellulosic biomass exposing cellulose fibers for further processing. Effective pretreatment should be inexpensive, function over a range of biomass varieties, require little pre-processing of biomass feedstock, and minimize any destructive losses of biomass components (Ewanick & Bura, 2010). Steam explosion was selected as the pretreatment method in this study as it is well researched and performs well in the qualifications of an effective pretreatment method. During steam explosion pretreatment, biomass is heated and pressurized with steam for a period of several minutes to allow the steam to permeate the biomass. Then, the biomass is expelled from the reactor to a receiving vessel resulting in rapid expansion of the pressurized steam which destroys the structure of the biomass (Alvira, Tomás-Pejó, Ballesteros, & Negro, 2010). Steam explosion can be readily customized to accommodate various feedstocks through adjusting the time, temperature, and use of an acid catalyst. Steam explosion results in fractionation of the biomass into solid and liquid phases. The liquid phase is composed of monomeric and oligomeric sugars derived from hemicellulose and the solid phase is composed of cellulose and lignin (Ewanick & Bura, 2010).

Accessing the fermentable material in the solid phase requires hydrolysis of the cellulose polymer into monomeric glucose. Hydrolysis may be completed with either acid or enzymes, but the toxicity to downstream processes limits the use of acid hydrolysis in favor of the mild conditions of enzymatic hydrolysis (Sun & Cheng, 2002). Enzymes used in hydrolysis of cellulose are known as cellulases and may be sourced from several species of fungi and bacteria. Enzymes are highly specific in function, therefore a cocktail of several cellulases including endoglucanase, exoglucanase and β-glucosidase is necessary for complete hydrolysis (Ballesteros & CIEMAT, 2010).

Microorganisms are used to convert carbohydrate material into a desired product in a process known as fermentation. Fermentation may be performed concurrently to enzymatic hydrolysis dubbed simultaneous saccharification and fermentation (SSF) or following hydrolysis dubbed separate hydrolysis and fermentation (SHF). SSF reduces the number of biological reactors required for production and limits end-product inhibition during enzymatic hydrolysis. SHF allows for reactor conditions to match the ideal parameters for hydrolysis and fermentation, while a SSF reactor must find a compromise of conditions between hydrolysis and fermentation ideals (Manzanares & CIEMAT, 2010).

Following fermentation, product separation is necessary to purify the desired product from the fermentation broth. Separation technologies depend highly upon the product, in the case of ethanol, distillation and an ancillary dehydration process are used to separate a pure ethanol product (H. J. Huang, Ramaswamy, Tschirner, & Ramarao, 2010). Dehydration methods include azeotropic distillation, liquid-liquid extraction and membrane pervaporation. The material stream remaining after distillation is known as stillage which becomes the largest wastewater stream in bioconversion facilities (Humbird et al., 2011). Up to 20 liters of stillage can be generated per liter of ethanol produced (Oosterkamp et al., 2016).

Wastewater from lignocellulosic biorefineries is generally characterized by high strength organic loading but can vary significantly based on feedstock and process implementation (Wilkie, Riedesel, & Owens, 2000). Stillage accounts for 85% of wastewater composition, other sources include flash condensate from steam explosion pretreatment processes, boiler and cooling water blowdown, and cleaning water (Humbird et al., 2011).

Wastewater treatment encompasses a variety of treatment technologies. Physical treatment methods include filtration, adsorption, gravitational settling, membrane separation and evaporation methods. Chemical treatment methods include coagulation, flocculation and precipitation reactions. Biological treatment methods include many different microbial communities which operate over a range of reactor conditions (Burton, Tchobanoglous, Tsuchihashi, Stensel, & Metcalf & Eddy, 2013). Effective wastewater treatment systems may include several treatment technologies to treat waste to meet regulatory requirements.

Conventional starch-to-ethanol and spirits distilleries produce stillage waste similar in composition to lignocellulosic stillage (Bories, Raynal, & Bazile, 1988; Wilkie et al., 2000). Various wastewater treatment methods have been explored for these wastes. One common treatment method is evaporation of the stillage into a syrup and subsequent spray drying of the syrup onto spent grains for production of animal feed known as dried distillers' grains with solubles (DDGS) (Kim et al., 2008). However, lignocellulosic processes do not produce spent grain as a byproduct and therefore are unable to take advantage of DDGS as a coproduct. Another common treatment method for high strength organic wastes is anaerobic treatment. Anaerobic treatment utilizes oxygen-free biological reactors to degrade organic material into a mixture of methane and carbon dioxide known as biogas which may be combusted as a natural gas substitute (Burton et al., 2013). Biogas recovery, coupled with the lower energy demands of anaerobic treatment has made it the focus of lignocellulosic waste treatment research (Humbird et al., 2011; Montague, Slayton, & Lukas, 2002). However, the high capital cost of anaerobic reactors and the need for supplemental treatment escalates wastewater treatment to up to 21% of the total capital cost of a lignocellulosic biorefinery (Humbird et al., 2011). Optimization of wastewater treatment processes could reduce the capital investment required for new facilities, thereby lowering the barrier to market entry for bio-based products.

This study has three primary objectives to better understand wastewater treatment in the context of lignocellulosic bioconversion: first, to determine how upstream processes impact the wastewater profile, second, to identify upstream process changes to minimize waste treatment requirements, and third, to screen waste treatment technologies which may reduce the capital investment required to construct a biorefinery or that may reduce overall operating costs. To achieve these objectives, a system-wide mass balance was generated from lab scale experiments to determine how constituents move through the bioconversion process and during which processes wastes are generated. Using the National Renewable Energy Laboratory's (NREL) *Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol* report and accompanying Aspen Plus process model as a base scenario, process alternatives were evaluated to identify the technical and economic influence of each process alternative.

2. Methods

2.1 Experimental Methods

2.1.1 Raw material

2-year-old 2nd cycle short rotation coppice poplar used in this research is a hybrid of *Populus trichocarpa* and *Populus deltoids* (clone number 5077), obtained from a plantation near Jefferson, OR managed by GreenWood Resources (Portland, OR). The poplar trees were harvested without leaves and chipped in fall 2015. Samples were stored at -20°C until processed.

2.1.2 Steam explosion

Steam explosion was conducted as previously described (Dou, Ewanick, Bura, & Gustafson, 2016). In brief, 300 grams (g) oven-dried (OD) biomass was impregnated with 3% (w/w) sulfur dioxide (SO_2) overnight, and then steam pretreated at 195°C for 5 minutes in a 2.7-liter batch reactor (Aurora Technical, Savona, BC, Canada) (Dou et al., 2016). After steam explosion, the pretreated biomass slurry was separated into solid and liquid phases using vacuum-assisted filtration. The solid phase was then washed with deionized water to remove the free sugars.

2.1.3 Solid Phase Saccharification and Fermentation

Solid phase saccharification and fermentation was performed to simulate commercial enzymatic hydrolysis and fermentation processes where enzymes would remain active through both hydrolysis and fermentation steps. Sterile flasks, media, sterile sampling technique were employed to maintain suitable environment for fermentation and to produce accurate, repeatable results.

Enzymatic Hydrolysis

Enzymatic hydrolysis was carried out using cellulase (Celluclast 1.5 L, Sigma) at 20 Filter Paper Units (FPU)/g cellulose and β-glucosidase (Novozyme 188, Sigma) at 40 cellobiase units (CBU)/g cellulose. The solid phase was hydrolyzed at 10% (w/v) water insoluble content (WIS) in a total volume of 250 milliliters (mL) at 50°C and 175 rotations per minute (rpm) in a shaker. 50 millimolar (mM) citrate buffer was added to maintain the pH at 4.8. After 48 hours (h) of enzymatic hydrolysis, the flask temperature was reduced to 30ºC and the pH increased to 6.0 using 1.0 molar (M) sodium hydroxide (NaOH) in preparation for fermentation as described in the following sections.

Yeast strain

Scheffersomyces stipitis ATCC 58376 (also-known-as: *Pichia stipitis* Y-7124) was obtained from ATCC, Manassas, Virginia.

The strain was taken from -80°C stocks and maintained on YPG solid medium (10 g/L yeast extract, 20 g/L peptone, 20 g/L glucose, and 18 g/L agar, Difco, Becton Dickinson, MD) at 4°C and transferred to fresh plates on a weekly basis.

Culture media conditions

Cells were grown to high cell density in foam-plugged 1 liter (L) Erlenmeyer flasks containing 500 mL liquid media with additional trace nutrients (10 gram per liter (g/L) Macron Fine Chemicals Granular Glucose, 20 g/L Sigma-Aldrich D-(+)- Xylose (99%), 3 g/L BD Bacto Yeast Extract, 5 g/L BD Bacto Peptone, 2.3 g/L Fisher Chemical Urea, and 1 g/L Fisher Chemical magnesium sulfate heptahydrate ($MgSO_4$ x 7-H2O)) in an orbital shaker for 48 h at 30°C and 175 rpm, with a concurrent transfer to fresh medium performed every 24 h.

After 48 h of growth, cell culture suspension was centrifuged, and spent media decanted to yield cell pellets. Pellets were then washed three times with sterile distilled water and subsequently adjusted with sterile distilled water to form a concentrated yeast culture. The dry cell weight per liter (DCW/L) per liter of the concentrated yeast culture was measured on a spectrophotometer (Shimadzu UV-1700, Columbia, MD) via standard curves relating 600 nanometers (nm) absorbance to DCW/L concentration.

Fermentation

Yeast culture was added directly to the fermentation flasks without denaturing enzymes to allow for continued hydrolysis throughout the fermentation process. Concentrated yeast culture was added to achieve 5 g DCW/L media. Dry trace nutrients were added to supplement the fermentation media at following concentrations: 3 g/L yeast extract, 5 g/L peptone, 2.3 g/L urea, and 1 g/L $MgSO_4$ x 7-H_2O. Following addition of yeast, flasks were incubated at 30°C and maintained with continuous agitation (175 rpm), and pH value of ~ 6.0.

2.1.4 Liquid Phase Detoxification and Fermentation

Early attempts to perform fermentation on untreated, steam exploded liquid phase were unsuccessful resulting in the need to detoxify the liquid phase prior to fermentation.

Detoxification

Powdered activated carbon (Fisher Scientific C272-500) was added to untreated, steam exploded liquid phase (pH = 1.6 ± 0.1) at a consistency of 10% (w/v) and agitated for 12 hours at 175 rpm. Following treatment, the activated carbon was removed via vacuum filtration through a 0.2 µm sterile bottle filter. The pH was then adjusted to 6.0 using 50% (w/w) NaOH solution.

Fermentation

The same yeast strain, storage, cultivation, and harvest procedures as described above were employed for fermentation of detoxified liquid phase. Trace nutrients (3 g/L yeast extract, 5 g/L peptone, 2.3 g/L urea, and 1 g/L $MgSO_4$ x 7-H_2O) were added to the sterile, detoxified liquid phase to create the fermentation media. Concentrated yeast culture was added to achieve 5 g DCW/L media. Fermentation flasks were incubated at 30°C and maintained with continuous agitation at175 rpm.

2.1.5 Distillation

The resulting fermentation broths from solid phase and detoxified liquid phase fermentation were distilled separately under the same conditions. Distillation was performed using an IKA RV 10 rotary evaporator and accompanying IKA HB 10 water bath (Staufen, Germany). Batches of fermentation broth were distilled 250 mL per batch to accommodate vessel size; 0.5 mL of anti-foam agent (Sigma Antifoam 204) was added to each batch. The rotary evaporator was set to rotate at 20 rpm and maintain a vacuum of 350 millibar. The water bath was maintained at a temperature of 87°C. Distillation proceeded until visual signs of boiling ceased.

2.1.6 Compositional analysis

Several analytical methods were used to determine the composition of each process material stream.

Elemental Analysis

Elemental analysis was conducted to quantitatively determine the inorganic constituents of biomass samples. The analysis was conducted by the University of Washington School of Environment and Forest Sciences Analytical Service Center. Solid biomass samples were ground to 40 mesh particle size and dried completely in a 105ºC oven. Oven dry samples were digested in accordance with Environmental Protection Agency (EPA) Method 3050B (US EPA, 1996). In brief, samples were mixed with concentrated nitric acid and refluxed at 95ºC ± 5ºC for 30 minutes then cooled and concentrated via evaporation. Following concentration, hydrogen peroxide was mixed with the sample digest until the sample was completely reacted, again the sample digest was concentrated via evaporation. Finally, concentrated hydrochloric acid was added to the sample digest and the resulting slurry was filtered. The sample digest filtrate was then analyzed on a Thermo Jarrell-Ash (Thermo Scientific) iCAP 61E Inductively Coupled Plasma Emission Spectrometer for Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Zn, Si, and Ag.

Ash

Ash content of raw biomass samples was measured gravimetrically by heating 20-mesh-milled dry biomass to 575°C for 12 h (Sluiter et al., 2008a).

Solid fraction carbohydrates, acetate groups and acid soluble lignin

The chemical composition of raw biomass and solid fraction was determined according to a modified method derived from TAPPI Standard Method T222 om-11(TAPPI Test Methods, 2011) and NREL protocols (Sluiter et al., 2008b). Briefly, 0.2 g of finely ground, oven dried sample was treated with 3 mL 72% sulfuric acid (H_2SO_4) for 2 h at room temperature, then diluted into 120 mL total volume and autoclaved at 121°C for 60 minutes. Klason lignin contents were determined by gravimetric methods by filtration through tared sintered glass crucibles. After filtration, the carbohydrate and acetyl composition of the filtrate was analyzed by HPLC (Dionex ICS-3000, as described in (Suko & Bura, 2016)) and the acid soluble lignin (phenolics) in the filtrate was analyzed by UV spectrophotometer (Shimadzu, Tokyo, Japan) at 205 nm.

Liquid fraction carbohydrate, ethanol, and degradation products

The concentration of monomeric sugars was determined with a high-pressure liquid chromatography (HPLC) system (Dionex ICS-3000). The concentration of monomeric sugars, ethanol and degradation products, such as acetic acid, furfural and 5-hydroxymethylfurfural (5-HMF) were measured using refractive index detection on a Shimadzu Prominence LC, as described by Suko (Suko & Bura, 2016). Monomeric and oligomeric soluble carbohydrates were determined using NREL LAP TP-510-42623 (Sluiter et al., 2008b). Phenolic concentration in the liquid fraction was assayed by the Folin-Ciocalteu method (Singleton, Orthofer, & Lamuela-Raventós, 1999), using an ultra-violet (UV) spectrophotometer (Shimadzu, Tokyo, Japan) at 765 nm. Gallic acid was used as calibration standard.

Wastewater characteristics

Several wastewater specific parameters were measured from the stillage streams to better characterize the waste stream. These parameters along with the reagents and methods used to perform the analysis are provided in Table 1.

Table 1: Wastewater characterization parameters and methods

Test	Reagents	Method
Total solids, Total volatile solids, Total suspended solids, Volatile suspended solids	--	Standard Method 2540[1]
Biological Oxygen Demand, 5 day	Hach BOD Nutrient Pillows, PolySeed Microbial Culture	Standard Method 5210[1]
Alkalinity	--	Standard Method 2320B[1]
Chemical Oxygen Demand	Hach High Range TNT COD Digestion Vials (0 - 1,500 mg/L)	Hach Method 8000[2]
Reactive Phosphorous	Hach High Range TNT Reactive Phosphorous (1.0 - 100 mg/L PO4)	Hach Method 8114[2]
Total Phosphorous	Hach High Range TNT Total Phosphorous (1.0 - 100 mg/L PO4)	Hach Method 10127[2]
Ammonia	Hach High Range TNT Nitrogen-Ammonia (0.4 - 50 mg/L NH_3-N)	Hach Method 10031[2]
Nitrate	Hach High Range NitraVer 3 Nitrogen-Nitrate (0.2 - 30.0 mg/L NO_3-N)	Hach Method 10020[2]
Nitrite	Hach High Range NitraVer 3 Nitrogen-Nitrite (0.003 - 0.500 mg/L NO_2-N)	Hach Method 10019[2]
Total Nitrogen	Hach High Range TNT Total Nitrogen (2.0 - 150 mg/L N)	Hach Method 10072[2]
Sulfate	Hach High Range SufaVer 4 Reagent Pillows (0.0 - 70 mg/L SO_4)	Hach Method 8051[2]

Notes:
1. (Franson, Clesceri, Greenberg, & Eaton, 1998)
2. (Hach, n.d.)

2.2 Environmental Impact Assessment

SimaPro 8.2 life cycle assessment software was used to compile a rudimentary environmental impact assessment of the treatment alternatives (“SimaPro,” n.d.). The system boundary encompasses only material and energy flows into and out of the wastewater treatment process. No construction, facility usage, or demolition flows were considered in this analysis. Material and energy flows were calculated from process models, then, closely matching unit processes were paired from the EcoInvent database to build unit processes representing each treatment alternative.

2.3 Economic Modeling Methods

Capital equipment costs were sourced from the literature or from personal communication with equipment vendors. All values were converted to 2016 United Stated Dollars (USD) using the Chemical Engineering Plant Cost Index (Chemical Engineering Magazine, 2017).

Operating costs were calculated through aggregation of material and energy costs and fixed costs such as maintenance. Labor costs were not included in this analysis. Chemical prices were adjusted with the US Bureau of Labor Statistics Producer Price Index for Other Inorganic Chemicals (Bureau of Labor Statistics, 2017). Maintenance was assumed to cost 10% of equipment costs annually (Perry & Green, 2008). For comparison purposes energy flows were valorized as either electricity or steam. An electricity price of 0.06 USD per kilowatt-hour (USD/kWh) is within the range of typical industry energy prices in the United States (US Energy Information Administration, 2017a). A steam price of 11.79 USD per 1000 kg of 62 bar, 455ºC steam was calculated using a natural gas boiler at 85% efficiency (US Department of Energy, 2015; US Energy Information Administration, 2017b).

All future cash flows were discounted a rate of 10% to incorporate the time-value of money (Humbird et al., 2011).

This cost estimate attempts to incorporate all major equipment costs and known material and energy streams and may be considered accurate to within -25% and +30% of values presented (Perry & Green, 2008).

3. Results and Discussion

3.1 Carbohydrates and Other Organic Compounds

Figure 1 and Figure 2 provide a summary of the mass flow rate of each measured organic compound throughout the bioconversion process. Pretreatment fractionated the raw biomass into solid and liquid phases. The solid phase accounted for 57.4 ± 1.31% of the raw biomass and was composed of predominately cellulose and acid insoluble lignin. The liquid phase accounted for 42.6 ± 1.31% of the biomass and was composed of hydrolyzed hemicellulose (arabinose, galactose, glucose, xylose, mannose), acetic acid, sugar degradation products (furfural, 5-HMF), and lignin derived phenolic compounds.

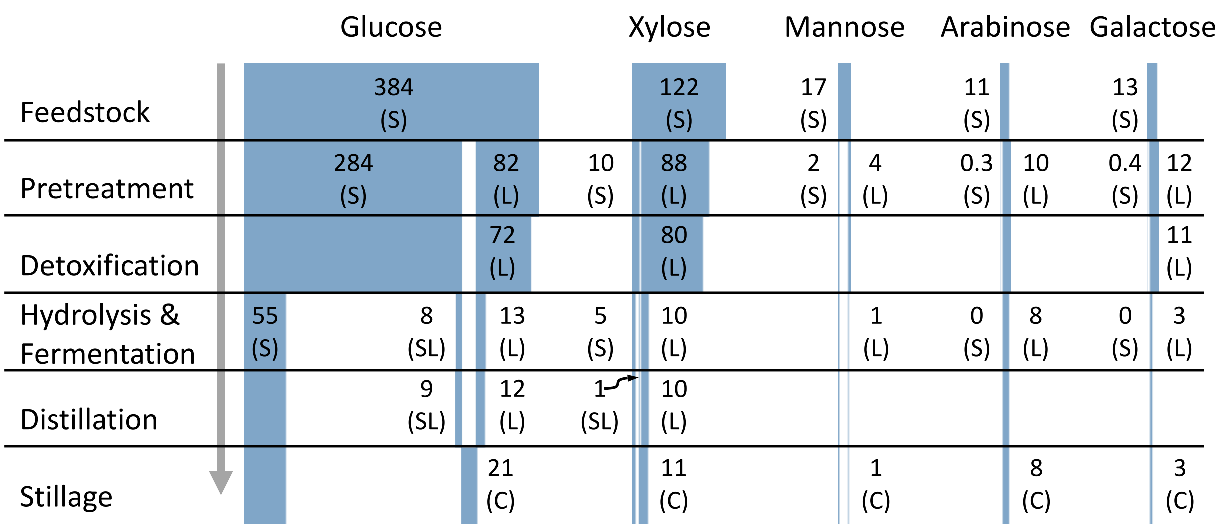

Figure 1: Carbohydrate Material Flows
Notes:
Material flows represented as kg/tonne OD biomass
(S) – solid phase, (L) – liquid phase, (SL) – liquid phase derived from pretreated solid,
(C) – combined stillage
All values are means of triplicates

Previous experiments indicated inhibitory compounds present in the liquid fraction limited the effectiveness of *S. Stipitis* to ferment the liquid phase resulting in an ethanol yield of near 0% (w/w). Therefore, the liquid phase was detoxified with powdered activated carbon which resulted in 100% removal of furfural and HMF, 88% removal of total phenolic compounds, and 22% removal of acetic acid. Detoxification also resulted in a 11% (w/w) loss of the total carbohydrate content of the liquid phase.

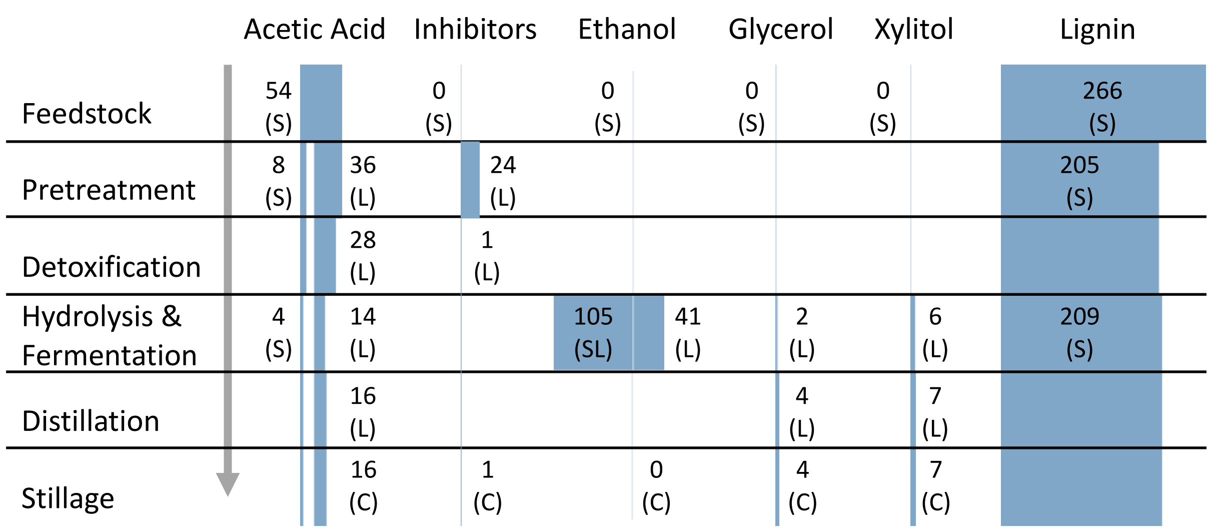

Figure 2: Other Organic Material Flows

Notes:

Material flows represented as kg/tonne OD biomass

(S) – solid phase, (L) – liquid phase, (SL) – liquid phase derived from pretreated solid,

(C) – combined stillage

All values are means of triplicates

The detoxified liquid phase was fermented with an ethanol yield of 25 % (w/w) (gram ethanol per gram total carbohydrate) which equates to 48% of the theoretical yield. Overall, 83% of carbohydrates were consumed during liquid phase fermentation. Of the remaining carbohydrates, 76% were carbohydrate oligomers and, therefore, inaccessible to the yeast during fermentation. The low ethanol yield is likely due to residual inhibitory compounds such as dibutyl phthalate, phthalic acid derivatives (Peng et al., 2015) and acetic acid which will lead to increased stress response mechanisms and reduced normal, ethanol producing metabolism (Hohmann & Mager, 2007; Palmqvist & Hahn-Hägerdal, 2000).

The solid phase was saccharified and fermented with an ethanol yield of 38% (w/w) (gram ethanol per gram total carbohydrate) which equates to 74% of the theoretical yield. Overall, 76% of carbohydrates were consumed during fermentation. Of the remaining carbohydrates, 98% were carbohydrate oligomers and, therefore, inaccessible to the yeast during fermentation.

Rotary evaporation provided 100% (w/w) ethanol removal for both liquid phase and solid phase fermentation broths. The concentration of carbohydrates in the liquid phase and solid phase fermentation stillage following distillation increased twofold, but carbohydrate mass flows remained relatively constant.

The sum of residual carbohydrates in the combined stillage stream amounts to 44 kg/OD tonne feedstock as shown in Figure 1 which represents wasted resources impacting the overall process yield. Improved processing techniques at the commercial scale including mechanical mixing during solid phase hydrolysis (Samaniuk, Tim Scott, Root, & Klingenberg, 2011; Unrean, Khajeeram, & Laoteng, 2016), acclimated yeast strains (C.-F. Huang, Lin, Guo, & Hwang, 2009; Nigam, 2001), and combined solid and liquid phase fermentation (Humbird et al., 2011) could reduce the quantity of carbohydrates in the stillage stream. However, the presence of these residual carbohydrates suggests it would be beneficial to recycle stillage as process water to simultaneously convert carbohydrates to product and reduce the organic load entering wastewater treatment (Alkasrawi, Galbe, & Zacchi, 2002; Mohagheghi & Schell, 2010). Additionally, given the potential for process upsets which result in incomplete fermentation, future biorefineries may want to engineer systems that can recycle stillage to prevent unnecessary loading of the waste stream and to maintain high process yields.

3.2 Inorganic Components

Figure 3 provides a summary of the mass flow rate of the major inorganic compounds measured throughout the bioconversion process. Raw biomass is composed of 1.91 ± 0.04% ash content, measured gravimetrically. Of the ash fraction, calcium, potassium, magnesium, and phosphorous are the largest measured contributors at 47.5%, 35.0%, 6.5%, and 5.7% respectively.

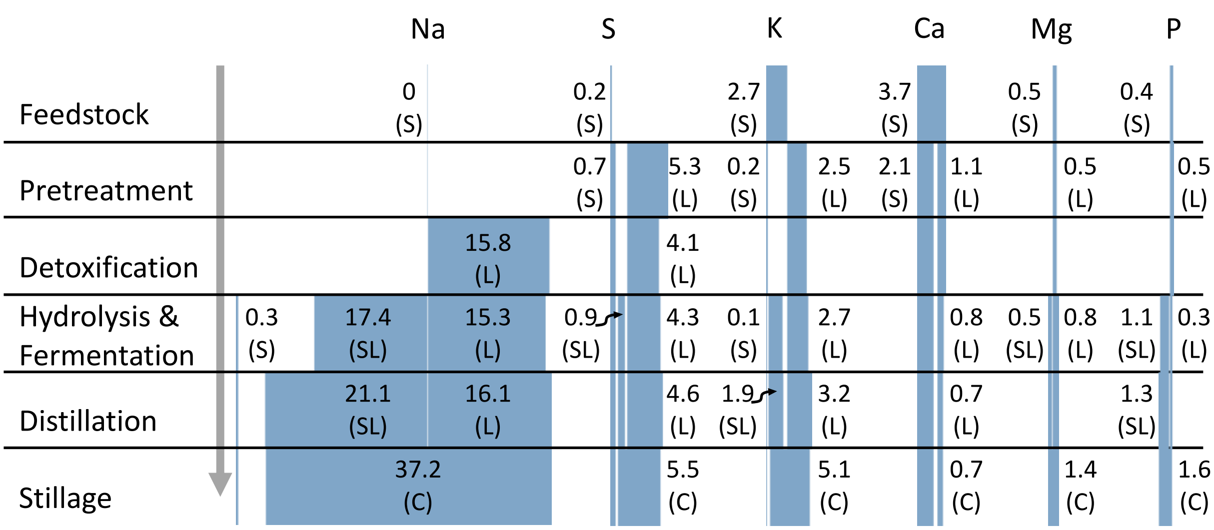

Figure 3: Inorganic Material Flows
Notes:
Material flows represented as kg/tonne OD biomass
(S) – solid phase, (L) – liquid phase, (SL) – liquid phase derived from pretreated solid,
(C) – combined stillage
All values are means of triplicates

Following pretreatment, the inorganic constituent load increased by 72.7% due to the SO_2 impregnation process with sulfur dominating the measured composition at 44.9% and calcium dropping to 24.1% of the total measured components for combined solid and liquid pretreated material. Similarly, pH adjustment (sodium hydroxide) and buffering solution (sodium citrate) additions, as part of the detoxification, fermentation, and saccharification steps, continued to increase the total inorganic loading. Following these steps, sodium became the most prevalent inorganic constituent accounting for 66.1% followed by sulfur at 12.0% including all solid and liquid material streams. The inorganic load remained unchanged following distillation, however, due to ethanol and water loss inorganic concentrations increased by twofold in the combined stillage steam.

Most of the wastewater inorganic load is composed of constituents added during processing, therefore, process engineers have a high degree of control over the inorganic composition of the wastewater.

Pretreatment is one area where inorganic loading may be controlled. SO_2 impregnation results in the addition of over 27 times the original sulfur content of the biomass. The sulfur content of wastewater streams is important, particularly when anaerobic digestion is part of the treatment process. Sulfate is readily reduced to hydrogen sulfide (H_2S) during anaerobic digestion and may compose up to 1.3% (w/w) of biogas produced from lignocellulosic stillage (Humbird et al., 2011). Due to its corrosive nature, it is not recommended to combust fuels containing over 1% (w/w) H_2S (Li, 2015). In addition, biogas with H_2S concentration higher than 0.004% (w/w) is not recommended for integration into natural gas pipelines (Li, 2015). Therefore, H_2S treatment is necessary for any practical application of biogas given current sulfate concentrations.

H_2S treatment can be costly. For example, purchase of lime to operate flue gas scrubbers which entrain sulfur emissions as gypsum ($CaSO_4$) amounts to $2.2 million per year or about 2% of all operating expenditures (Humbird et al., 2011). Pretreatment is the only unit operation which requires the addition of sulfur compounds and biomass has a relatively low sulfur content; removal of the sulfur catalyst from the steam explosion step would withdraw the need for flue gas desulfurization. Substitution of SO_2 with a different acid such as nitric or phosphoric acid is one potential solution (Negro et al., 2014). Additionally, many other sulfur-free pretreatment technologies have been developed: fungal pretreatment, mechanical comminution, organosolv, ozonolysis, ionic liquids, liquid hot water, ammonia fiber explosion (AFEX), wet oxidation, and CO_2 explosion, among others (Alvira et al., 2010). Further development of these technologies and corresponding economic analysis may identify a pretreatment method with overall lower costs than acid-catalyzed steam explosion which adds not only to the pretreatment costs but to downstream treatment as well.

pH adjustment is another unit operation which adds to the inorganic wastewater load. pH adjustment occurs following pretreatment to condition the liquid phase and to buffer pH throughout solid phase saccharification and fermentation. In this study, sodium hydroxide was used to adjust pH and sodium was observed as the most prevalent inorganic constituent in the combined stillage stream. This correlation shows that pH adjustment is a primary driver behind which ions will compose the inorganic fraction of the wastewater. Given this large impact, care should be taken to determine which chemicals are used to adjust pH. Table 2 presents a comparison of several chemicals with respect to chemical cost, neutralization salt parameters, and downstream treatment methods.

Table 2: Neutralization agent comparison matrix

	Ammonium Hydroxide (NH_4OH)	**Sodium Hydroxide (NaOH)**	**Calcium Hydroxide ($Ca(OH)_2$)**	**Potassium Hydroxide (KOH)**	**Calcium Carbonate ($CaCO_3$)**
Chemical Cost[1] (USD/tonne OD feedstock)	18.50[2]	14.50[3]	6.90[2]	153.50[3]	28.60[3]
Primary Salt and Parameters	• $(NH_4)_2SO_4$ • soluble • nutrient[4]	• Na_2SO_4 • soluble • inhibitory[5]	• $CaSO_4$ • insoluble • carbohydrate loss[2]	• K_2SO_4 • soluble • nutrient[6] • inhibitory[5]	• $CaSO_4$ • insoluble • carbohydrate loss[2]
Downstream Treatment Methods	• Biological Nitrogen Removal • Ion Exchange • Reverse Osmosis • Electrodialysis	• Ion Exchange • Reverse Osmosis • Electrodialysis	• Precipitation • Ion Exchange • Reverse Osmosis • Electrodialysis	• Ion Exchange • Reverse Osmosis • Electrodialysis	• Precipitation • Ion Exchange • Reverse Osmosis • Electrodialysis

Notes:

1. Chemical cost was calculated through stoichiometric substitution of each chemical for ammonium hydroxide in the 2011 NREL Aspen Plus model (Humbird et al., 2011)
2. (Humbird et al., 2011)
3. (ICIS Industries, 2008)
4. (International Plant Nutrition Institute, n.d.-a)
5. (Burton et al., 2013)
6. (International Plant Nutrition Institute, n.d.-b)

The salts formed during neutralization are an important operational consideration. This analysis assumes sulfate as the primary anion in solution following SO_2-catalyzed steam explosion pretreatment resulting in generation of sulfate salts during neutralization. Insoluble salts cause additional wear and tear on equipment and are typically removed to limit equipment damage and scaling issues. Removal of insoluble salts requires two solid-liquid separation operations. First, the pretreated slurry must be separated to prevent precipitated salts from becoming entrained in the pretreated solid and then precipitated salts are separated from the conditioned liquid phase. Precipitation of salts has also been shown to cause carbohydrate losses of up to 13% affecting overall process yield (Humbird et al., 2011). Soluble salts, on the other hand, present downstream treatment challenges. Monovalent ions have been shown to cause inhibitory effects on methanogens, an essential microbial community in anaerobic treatment systems, at concentrations as low as 3,500 mg/L (Burton et al., 2013). Soluble salts often require high energy separation techniques such as reverse osmosis or ion exchange processes (Burton et al., 2013). Neutralization salts can be beneficial. They can provide a source for essential nutrients (e.g. N, K, S) which may compliment or offset other nutrient additions necessary for fermentation.

Given the relatively few options available for pH adjustment and their respective advantages and disadvantages it appears ammonium hydroxide or sodium hydroxide would provide the most compatible, treatable, and economical alternatives. If biological wastewater treatment is employed ammonium hydroxide maybe the better alternative for its ease of treatment and nutritional benefits to the fermentation and wastewater treatment processes. If physical wastewater treatment is employed sodium hydroxide may be the better alternative given its lower cost.

3.3 Wastewater Characteristics

Various wastewater characteristics are presented in Table 3. Also shown in Table 3, are values from the 2011 NREL Bioconversion Process report to show how values in this study compare to similar values from the literature. The NREL study used cornstover as a feedstock and adjusted pH with ammonia hydroxide compared to the hybrid poplar and sodium hydroxide used in this study.

Most parameters between the two studies agree over the composition of the waste stream with the exception of total chemical oxygen demand (COD), total solids, total volatile solids, ammonia, total P, and sodium. The total COD, total solids, and total volatile solids differences can be explained through a difference in sample identification. In the NREL study, all parameters were measured following lignin separation, but in this study the total solids were measured while insoluble lignin was still present in the waste stream greatly increasing these values. Differences in ammonia and sodium material flows can be explained by the alternative pH adjustment processes used in the NREL study and this study.

Table 3: Wastewater characteristics

Parameter	Concentration Data (mg/L)		Normalized Data (kg/tonne od biomass)	
	NREL[1]	This study	NREL[1]	This Study
BOD	33,000	32,100	135	160
Soluble BOD	32,600	32,300	130	160
Total COD	87,400	169,100	355	845
Soluble COD	84,600	78,700	340	390
Total Solids	68,433	158,400	280	790
TVS	58,460	128,700	240	640
TSS	1,500	73,100	6.10	365
VSS	1,360	68,500	5.5	342
TDS	66,933	85,200	270	425
Ammonia-N	1,060	160	4.3	0.8
Total P	805	2,030	3.3	10.1
Ortho-P	805	1,275	3.3	6.4
Total Alkalinity	2,750	3,210	11.2	16.0
Sulfate	4,400	1,820	17.9	9.1
Silica	1,580	10	6.4	0.1
Al	ND	ND	ND	ND
Ba	0.0147	0.927	0.00	0.00
Cd	0.0005	ND	0.00	ND
Ca	6.79	146	0.03	0.73
Cr	0.177	2.33	0.00	0.01
Cu	0.005	ND	0.00	ND
Fe	0.814	11.9	0.00	0.06
Pb	0.0025	ND	0.00	ND
Mg	4.63	298	0.02	1.49
Mn	0.0957	0.373	0.00	0.00
K	498	1020	2.03	5.10
Cl	2473	NA	10.06	NA
Na	15.8	7450	0.06	37.17
St	0.0863	ND	0.00	ND

Notes:
NA – not analyzed, ND – not detected, NREL – National Renewable Energy Laboratory,
BOD – biochemical oxygen demand, COD – chemical oxygen demand,
TVS – total volatile solids, TSS – total suspended solids, VSS – volatile suspended solids,
TDS – total dissolved solids

1. Data reproduced from (Steinwinder, Gill, & Gerhardt, 2011)

3.4 Wastewater Treatment Alternatives

While examining how unit operations impact wastewater composition provides insight into how waste treatment costs could be controlled, the potential capital cost savings are quite low when compared to the overall cost of the waste treatment system. Therefore, this study decided to approach wastewater treatment from a fresh perspective and compare three wastewater treatment alternatives: the treatment system proposed in the 2011 NREL study which centers on anaerobic treatment, an oxidation ditch treatment system, and a wastewater evaporation system.

3.4.1 Design Tenets

The design tenets for the anaerobic treatment designed by NREL were primarily to remove process contaminants to a level sufficient to recycle effluent for process water and secondarily to recover energy in the form of biogas (Steinwinder et al., 2011). These objectives sought to preserve fresh water and optimize efficiency of the overall bioconversion process, but resulted in a capital-intensive treatment process.

This study altered those constraints to encourage more economical treatment alternatives and creative use of recovered resources. Primarily, the treated effluent should be used in some meaningful way; second, the treatment system should strive for simplicity of design; finally, to employ industrial ecology concepts wherever possible to connect the various aspects of the bioenergy supply chain including agricultural feedstock production, bioconversion processes, energy production, and waste management.

3.4.2 Treatment Technology Overview and Design

Anaerobic Treatment

A process flow diagram of the anaerobic treatment system is presented in Figure 4 as specified by NREL (Humbird et al., 2011; Steinwinder et al., 2011). In brief, an anaerobic reactor converts 91% of organic waste into biogas and cell mass. Activated sludge reactors are used to convert most of the remaining organic waste into carbon dioxide and cell mass while simultaneously converting ammonium to nitrate. A membrane bioreactor separates the activated sludge from the partially treated wastewater which proceeds to a reverse osmosis (RO) system for final treatment of salts and residual organic waste. Waste sludge is dewatered with a press and incinerated in the boiler. RO reject is evaporated and crystallized and disposed of off-site. The treated water is recycled back into the bioconversion process.

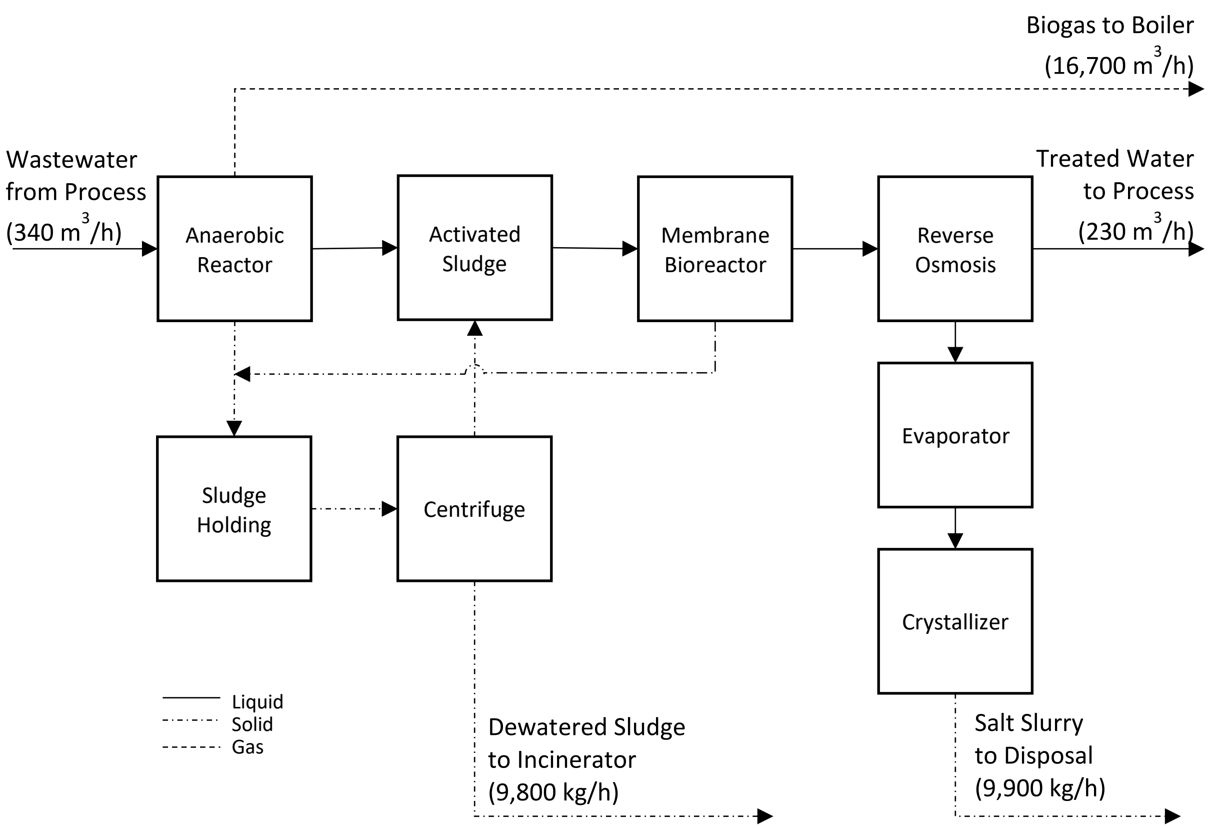

Figure 4: Anaerobic Treatment Process Flow Diagram

Oxidation Ditch Treatment

Given the design tenet for simplicity and generally rural setting proposed for most bioconversion facilities, facultative lagoons presented themselves a possible low-tech, functional treatment system. However, initial design calculations indicated that the high organic loading of the bioconversion wastewater would quickly over-load a facultative pond driving the system to anaerobic conditions. Anaerobic ponds are not advised for temperate climates due to slow reaction rates (US EPA, 2000). Therefore, an activated sludge treatment system was evaluated instead.

An oxidation ditch was evaluated for its simplicity and robust treatment capabilities. The oxidation ditch is a mature technology with more than 9,200 municipal installations in the United States in 1998 (Water Environment Federation & American Society of Civil Engineers, 1998). Oxidation ditches consist of an elliptical, or similarly shaped, basin with aerators which provide both circulation and oxygen transfer of the media (US EPA, 2000).

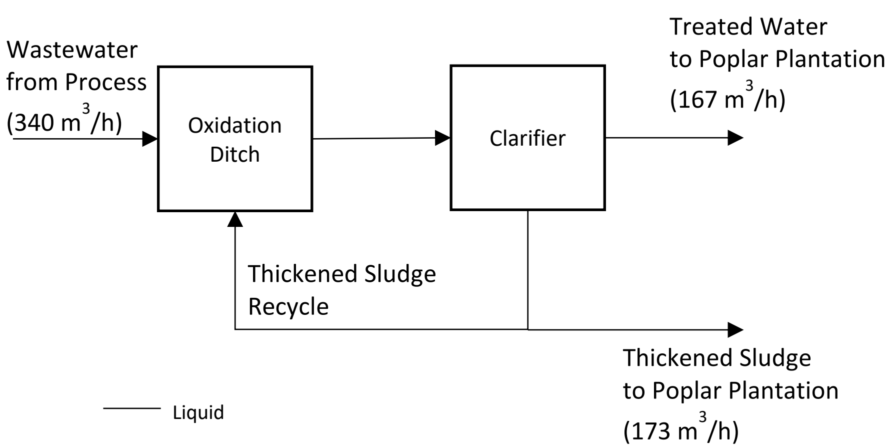

Figure 5: Oxidation Ditch Treatment Process Flow Diagram

A process flow diagram of the proposed oxidation ditch treatment system is shown in Figure 5. Wastewater will directly enter the oxidation ditch where biological oxidation will take place. Effluent from the oxidation ditch will flow to a clarifier to separate biomass from the treated effluent. Treated effluent will be discharged to adjacent poplar plantations for use as reclaimed irrigation water. Clarifier underflow will be split to provide biomass recycle to the oxidation ditch and to waste sludge. Wasted sludge will also be discharged directly onto an adjacent poplar plantation for final treatment and to function as fertilizer and irrigation for the plantation.

Reclaimed water treatment requirements vary widely from region to region. As a case study, the oxidation ditch was designed to provide treatment to at least 30 mg/L BOD and TSS to meet the Class B reclaimed water standards in Washington State (McGowan, 2015). In the absence of treatability data on biorefinery wastewater, all design calculations were executed using a Monte Caro-type analysis over uniformly-distributed, typical kinetic coefficients for activated sludge as described by *Wastewater Engineering: Treatment and Resource Recovery* (Burton et al., 2013) and EPA design guidance (US EPA, 2000). For design purposes, the oxidation ditch was treated as a completely mixed system, however, if desired, the reactor could be operated at conditions approaching plug-flow (US EPA, 2000). All design and kinetic values are provided in Table 4 along with treated effluent characteristics.

Table 4: Oxidation design parameters

Parameter	Unit	Range	Mean	SD
Input				
Influent BOD, S_{in}	mg/L	--	32,300	--
Effluent BOD, S_{out}	mg/L	--	30	--
Influent Flow Rate, Q	m^3/day	--	8,160	--
Max Substrate Utilization, k	mg bsCOD / (mg VSS * d)	4 - 12	--	--
Half Saturation Constant, K_s	mg/L BOD	20 - 60	--	--
Yield, Y	mg VSS / mg BOD	0.4 - 0.8	--	--
Endogenous Decay Coefficient, b	mg VSS / (mg VSS * d)	0.06 - 0.15	--	--
Fraction of biomass that is debris, f_d	mg VSS / mg biomass	0.10 - 0.15	--	--
Reactor Biomass Concentration, X	mg VSS / L	2,500 - 5,000	--	--
Recycle Biomass Concentration, X_r	mg VSS / L	25,000 - 50,000	--	--
Effluent Biomass Concentration, X_e	mg VSS / L	--	30	--
Aeration Efficiency, AE	kg O2/kWh	2.0 - 2.6	--	--
Output				
Solids Retention Time, SRT	days	0.2 - 2.4	0.6	0.3
Reactor Volume, V	m^3	7,480 – 76,250	23,400	9,990
Waste Sludge Flow Rate, Q_w	m^3/day	1,700 – 8,150	4,150	1,200
Waste Sludge Mass Flow Rate, P_x	kg VSS/day	82,500 – 207,500	150,000	30,500
Total Oxygen Demand, O_2	kg/day	344,500 – 519,000	426,000	43,500
Aeration Power, PO_2	kWh/day	133,000 – 258,000	186,500	24,000

Notes:
SD – standard deviation, BOD – biochemical oxygen demand

A clarifier will be necessary to separate biomass from the treated effluent and to provide activated sludge recycle to maintain the desired solids retention time. Assuming a typical surface overflow rate of 16 m^3/m^2*d for extended aeration systems and a flow rate of 8.2 x 10^6 L/d, the clarifier would occupy an area of approximately 500 m^2 (Burton et al., 2013).

Industrial sludges are regulated under Resource Conservation and Recovery Act (CFR Title 40 Part 257) which regulates land disposal and treatment of solid wastes (e-CFR, n.d.-a). Characterization of the waste shows no hazardous compounds within the waste, so waste activated sludge may be applied directly to an adjacent poplar plantation without the need for dewatering or sludge stabilization operations (e-CFR, n.d.-b). However, permitting and monitoring requirements determined at the state level must be followed. Studies have shown poplar tree growth is not negatively impacted by application of sludge and that the trees are able to provide adequate treatment of nitrogen and phosphorous (Dimitriou & Aronsson, 2011; Moffat, Armstrong, & Ockleston, 2001).

Similar to the waste sludge, treated effluent will be applied to adjacent poplar plantations as reclaimed water for irrigation purposes. A bioconversion facility which processes 1,000 tonnes per day would require approximately 17,000 hectares of plantation assuming poplar productivity of 22 OD tonnes per hectare per year (Greenwood Resources personal communication). Utilizing all reclaimed water for irrigation distributed over the plantation would provide about 0.02 hectare-meters of irrigation, or about 6.5% of the average irrigation rate at the Greenwood Resources poplar test plot in Clarksburg, CA (Greenwood Resources personal communication).

Poplar trees are robust plants with tolerance to harsh conditions. Poplars are adept at capturing and absorbing nutrients (N and P) from the soil and have been used for phytoremediation purposes to reduce nutrient run-off (Castro-Rodríguez et al., 2016; Dimitriou & Aronsson, 2011). Poplars have also been shown to have little growth impairment up to total dissolved solids (TDS) content of 6,000 mg/L in irrigation water and remain tolerant to TDS content up to 12,400 mg/L (Patterson, Chanasyk, Mapfumo, & Naeth, 2008; Shannon et al., 1999). Since no direct treatment of TDS is provided in this treatment scheme most inorganic constituents are expected to pass through the system yielding a predicted TDS content of up to 10,400 mg/L, within the TDS tolerance of poplar trees.

Wastewater Evaporation Treatment

Evaporation is commonly used in corn ethanol facilities where thin stillage is concentrated into a syrup called condensed distillers' solubles which is later incorporated into animal feed (Kim et al., 2008). Evaporation has been evaluated for lignocellulosic ethanol production but has not gained much traction due to high energy costs and limited availability of boilers suited for high ash combustion (Humbird et al., 2011; Merrick & Company, 1998).

Evaporators come in many different varieties and configurations. Multi-effect systems arrange several evaporator units in series using the latent heat of the vapor from the previous unit to drive the next unit resulting in far greater efficiencies than single-effect systems (Geankoplis, 2003). The steam economy (kg vapor evaporated / kg steam feed) is increased roughly proportionally to the number of effects in the system, however the benefit of greater economy is balanced by increased capital cost for each effect.

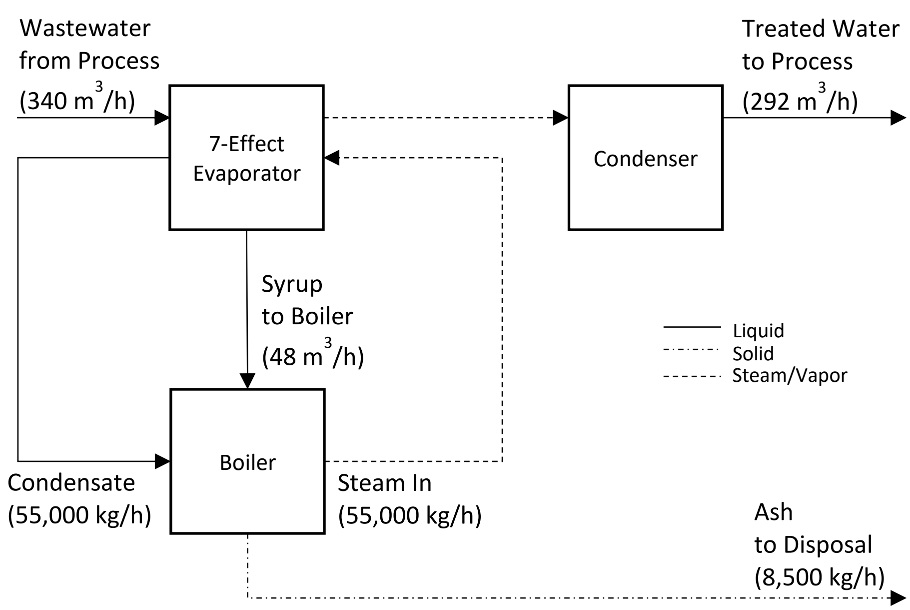

Figure 6: Evaporation Treatment Process Flow Diagram

A process flow diagram of the wastewater evaporation system is provided in Figure 6. Most of the suspended solids (insoluble lignin) will have been removed from the waste stream leaving behind a thin stillage with approximately 8.5% dissolved solids; roughly 70% of dissolved solids are organic and 30% are inorganic.

The stillage is concentrated from 8.5% dissolved solids to approximately 60% solids with a 7-effect evaporation system. The system was modeled in WinGEMS software to determine the evaporator surface area and steam requirements (Metso Automation, 1990). Table 5 presents a list of inputs and outputs from the WinGEMS model. The steam requirement to run the evaporators is 55,200 kg/h which accounts for 23.5% of the steam production of the boiler currently specified by the NREL model (Humbird et al., 2011). Use of this steam for evaporation purposes would still allow the boiler and turbo-generator to meet all process steam and electricity demands of the biorefinery, but would reduce the quantity of excess power exported to the grid from 13 MW to 8.3 MW.

Table 5: Evaporator design parameters

Parameter	**Unit**	**Value**
Input		
Influent Flow Rate, Q	L/h	340,000
Influent Temperature, Q_{temp}	ºC	80
Influent Fraction Solids, Xin	--	0.085
Steam Pressure, S_{press}	bar	4.4
Steam Temperature, S_{temp}	ºC	115
Output		
Steam Demand, S_{in}	kg/h	55,200
Evaporator Area, SA	m^2	2,500
Effluent Fraction Solids, X_{out}	--	0.61
Effluent Pressure, Pout	bar	0.28
Capacity, C	kg/h	295,000
Economy, E	kg/kg	5.34
Syrup Flow Rate, Q_{syrup}	L/h	47,700
Condensate Flow Rate, Q_{out}	L/h	292,000

The 60% solids syrup produced from the evaporators will be combusted in the furnace. Assuming the organic solids of the syrup have a heating value similar to dried sewage sludge (12.56 MJ/kg) then the 60% solids syrup will have an estimated lower heating value of 4.43 MJ/kg (Vesilind & Ramsey, 1996). Ash from the furnace will be disposed of at an off-site landfill.

Vapor from the evaporation process will be condensed and recycled into the bioconversion process. The condensed liquid will contain organic compounds volatilized during the evaporation process. Studies have shown that use of stillage derived condensates for process water have little to no impact on fermentation yields (Larsson, Galbe, & Zacchi, 1997; Palmqvist et al., 1996). Therefore, the condensates will receive no further treatment prior to integration with bioconversion process water.

3.4.3 Technical Assessment

There are several advantages to anaerobic treatment of wastewater. Aeration is often one of the most expensive operations in wastewater treatment. Anaerobic treatment degrades organic material in the absence of oxygen alleviating this burden while simultaneously producing biogas which can be utilized for heat and power generation. The biogas produced from wastewater treatment may be able to supply up to 36% of the fuel for the boiler specified in the NREL model (Humbird et al., 2011). Furthermore, anaerobic treatment combined with aerobic and RO polishing operations provides a very high level of water treatment allowing for direct reuse of treated water in the bioconversion process.

The downsides of the NREL anaerobic treatment method stem from its complexity. Anaerobic treatment is sensitive to inhibitory compounds and shock loads, either of which may interrupt treatment efficiency or biogas production given a shift or disruption in upstream processing. Given this sensitivity, and the scale of the treatment process, skilled operators will be required to closely monitor and operate the treatment system. The treatment system will also occupy a large amount of space for the 31 million gallon anaerobic reactor and three 6.5 million gallon aerobic basins.

The oxidation ditch design plays counterpoint to the anaerobic treatment system in many ways with its own set of advantages and disadvantages. The primary advantage of an oxidation ditch treatment systems is its simplicity of operation. The single large, well-mixed reactor is very resistant to shock loads and will rapidly dilute inhibitory compounds to less harmful concentrations. Instead of producing energy, oxidation of organic matter requires large amounts of energy to properly aerate the reactor.

The engineered level of treatment for the oxidation ditch is much lower than the anaerobic treatment system preventing the effluent from being recycled into the bioconversion process. However, this allows for a transition of engineered treatment to natural treatment provided by the poplar plantation. For example, the low solids retention time caused by the high organic loading into the system will limit nitrogen treatment from occurring, but nitrogen compounds will be readily absorbed by the poplar plantation providing protection to receiving water bodies. Addition of ecosystem services provided by the plantation increases its intrinsic value while recirculating water, carbon and nutrients within the bioenergy supply chain.

Physical treatment of wastewater, such as evaporation, presents its own benefits and challenges. Evaporation does not rely on microorganisms to provide treatment and therefore is a consistent, reliable, familiar unit operation to facility operators. Evaporation requires more energy than biological treatment processes, but the organic rich syrup produced can be combusted for net energy benefit. However, locating a boiler design capable of accommodating the high ash content of syrup while meeting the specifications for the bioconversion process may be difficult, although recovery boilers used in Kraft pulp mills regularly accommodate high ash conditions. In addition, it is possible to use acid catalysts and neutralization bases in the conversion process that will significantly reduce the ash content of the syrup.

3.4.4 Environmental Impact

An environmental impact assessment was completed to determine the relative environmental demand of each treatment alternative. Table 6 presents the EcoInvent unit processes used to quantify each treatment alternative for global warming potential and fossil fuel depletion. Freshwater utilization was calculated from the water balances presented in Figure 4, Figure 5 and Figure 6. Figure 7 shows the relative impact of each treatment alternative. Anaerobic treatment provides the greatest offset to global warming potential from biogas recovered during treatment coupled with the relatively low energy demand of the system. The oxidation ditch is the only system to contribute to global warming potential due to its high energy demand and lack of resource recovery. Similar trends are observed for fossil fuel depletion. All three alternatives offset freshwater utilization through recovery of treated water. The oxidation ditch achieves the greatest freshwater utilization offset contingent upon the need, and ability, to irrigate an adjacent poplar plantation. At locations where irrigation is not necessary, or possible, reclaimed water would likely be discharged to the environment and exit the bioconversion supply chain. Both anaerobic and evaporation treatment provide lower offsets to freshwater utilization, but retain all reclaimed water within the biorefinery.

Table 6: Environmental impact EcoInvent unit process parameters

EcoInvent Process Name	**Description**	**Amount**	**Unit**
Evaporation			
Steam, for chemical process, at plant/RER U	Allocation for steam generated from syrup combustion	62,143	kg
Steam, for chemical process, at plant/RER U	Steam demand for evaporation unit	55,226	kg
Oxidation Ditch			
Electricity, bagasse, sugarcane, at fermentation plant/BR U	Electricity demand for aeration generated at biorefinery	3,284	kWh
Electricity, medium voltage, at grid/US U	Electricity demand for aeration generated offsite	4,480	kWh
Electricity, bagasse, sugarcane, at fermentation plant/BR U	Electricity demand for other processes generated at biorefinery	3,050	kWh
Anaerobic Treatment			
Steam, for chemical process, at plant/RER U	Allocation for steam generated from biogas combustion	86,040	kg
Steam, for chemical process, at plant/RER U	Steam demand to heat anaerobic digester	265	kg
Steam, for chemical process, at plant/RER U	Steam demand for evaporation/crystallizer unit	1,012	kg
Electricity, bagasse, sugarcane, at fermentation plant/BR U	Electricity demand for aeration generated at biorefinery	4,283	kWh
Electricity, bagasse, sugarcane, at fermentation plant/BR U	Electricity demand for RO generated at biorefinery	47	kWh
Electricity, bagasse, sugarcane, at fermentation plant/BR U	Electricity demand for sludge handling generated at biorefinery	0.58	kWh
Electricity, bagasse, sugarcane, at fermentation plant/BR U	Electricity demand for other processes generated at biorefinery	3,050	kWh
Sodium hydroxide, 50% in H_2O, production mix, at plant/RER U	Caustic demand for alkalinity adjustment	4,486	kg

Notes:
U – unit process, RER – European region, BR – Brazilian region,
US – United States region, RO – reverse osmosis

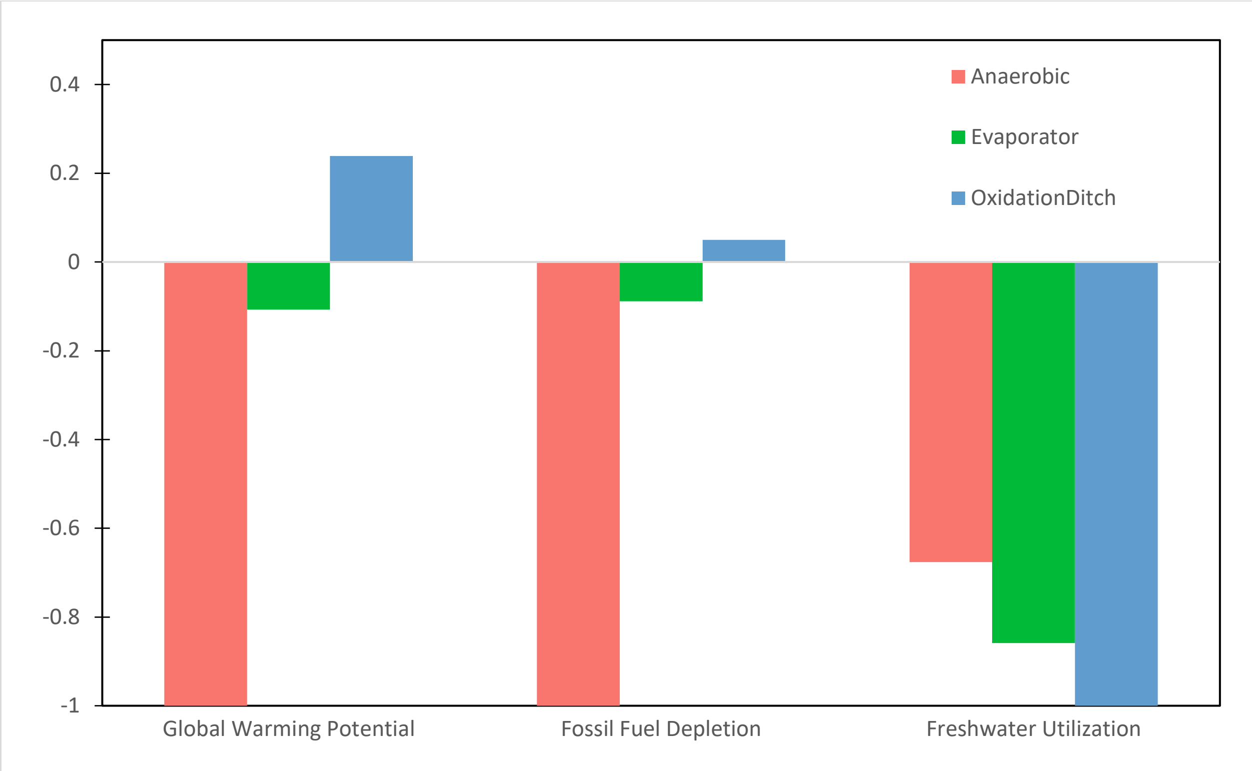

Figure 7: Relative Environmental Impact
Notes:
Positive values indicate use of environmental resources. Negative values indicate offset environmental resources. Values of 1 or -1 represent the alternative with the largest impact in each category. Values between 1 and -1 represent the value of each other alternative normalized to the largest impact in each category. (Ex. The Evaporator treatment offsets about 10% of the global warming potential as Anaerobic treatment.)

3.4.5 Economic Analysis

A summary of the installed and operation costs for each treatment alternative is presented in Table 7 and a breakdown of operating costs is presented in Table 8. Energy is the major driver of operation cost for all three treatment alternatives.

Table 7: Summary of equipment, installed and operating cost for treatment alternatives

Treatment Alternative	Installed	Operation Cost
Anaerobic Treatment	50,000,000[1]	3,182,000
Oxidation Ditch	14,000,000[2]	6,218,000
Evaporator	45,000,000[3]	814,000

Notes:

1. (Humbird et al., 2011; Steinwinder et al., 2011)
2. (US EPA, 1980)
3. Personal communication with Lundberg, LLC | A Dustex Company

Incremental analysis was performed to determine the economic viability of each treatment alternative. Treatment alternatives were ordered by ascending capital cost: oxidation ditch, evaporator, and anaerobic treatment. Then a return on investment (ROI) was calculated for each adjacent pair of alternatives. The ROI for the oxidation ditch/evaporator pair is 65% indicating that the lower operating cost of the evaporator warrants the higher capital cost when compared to the oxidation ditch. There is no ROI for the evaporator/anaerobic treatment pair given the anaerobic treatment is both more capital and operationally intensive than the evaporator. The evaporator appears to be the most economical treatment alternative from this straightforward analysis.

Table 8: Operation cost breakdown

Unit Operation	Material/Energy Flows	Units	Value	Cost per Unit	Cost per Hour	Annual Cost	Notes and Sources
Anaerobic Treatment						3,182,000	
Anaerobic Reactor	Biogas (out)	kg/h	-86,000	0.0118	-1,015	-8,534,500	credited as steam / 1,2,3
	Heat (in)	kg/h	265	0.0118	3	26,300	billed as steam / 1,2,3
	Caustic (in)	kg/h	2,240	0.2217	497	4,176,500	1
Aerobic Reactor	Aeration Electricity (in)	kWh/h	4,280	0.06	257	2,159,700	1,4
Sludge Handling	Electricity (in)	kWh/h	1	0.06	0	500	1,4
	Sludge (out)	kg/h	9,760		0	0	not accounted
Reverse Osmosis	Electricity (in)	kWh/h	50	0.06	3	25,200	1,4
Evaporator	Heat (in)	kg/h	1,010	0.0118	12	100,200	billed as steam / 1,2,3
Crystallizer	Salts (out)	kg/h	9,870	0	0	0	not accounted
Other	Other Electrical	kWh/h	3,050	0.06	183	1,539,000	1,4
	Maintenance	--	--	--	--	3,688,800	10% of equipment capital
Oxidation Ditch						6,218,000	
Oxidation Ditch	Aeration Electricity (in)	kWh/h	7,760	0.06	466	3,915,700	4
Clarifier	Sludge (out)	kg/h	6,250	0	0	0	not accounted
Other	Other Electrical	kWh/h	3,050	0.06	183	1,539,000	4
	Maintenance	--	--	--	--	763,500	10% of equipment capital
Evaporation						814,000	
Evaporator	Steam (in)	kg/h	55,225	0.0118	652	5,480,400	billed as steam / 2,3
	Syrup (out)	kg/h	-62,140	0.0118	-733	-6,166,700	credited as steam / 2,3
	Ash (out)	kg/h	1,200	0	0	0	not accounted
Other	Maintenance	--	--	--	--	1,500,000	10% of equipment capital

Notes:

All costs in USD, Assumes 8,410 hours of operation annually

1. (Humbird et al., 2011)
2. (US Energy Information Administration, 2017b)
3. (US Department of Energy, 2015)
4. (US Energy Information Administration, 2017a)

Despite these predictions, cost estimation is an inherently uncertain procedure. Figure 8 shows the present worth of each treatment alternative over the 30-year facility lifetime, uncertainly is represented by the shaded region. There is a great deal of overlap in uncertainty between all three treatment alternatives; therefore, more accurate cost estimates are recommended to gain a better understanding of the true cost of each treatment alternative.

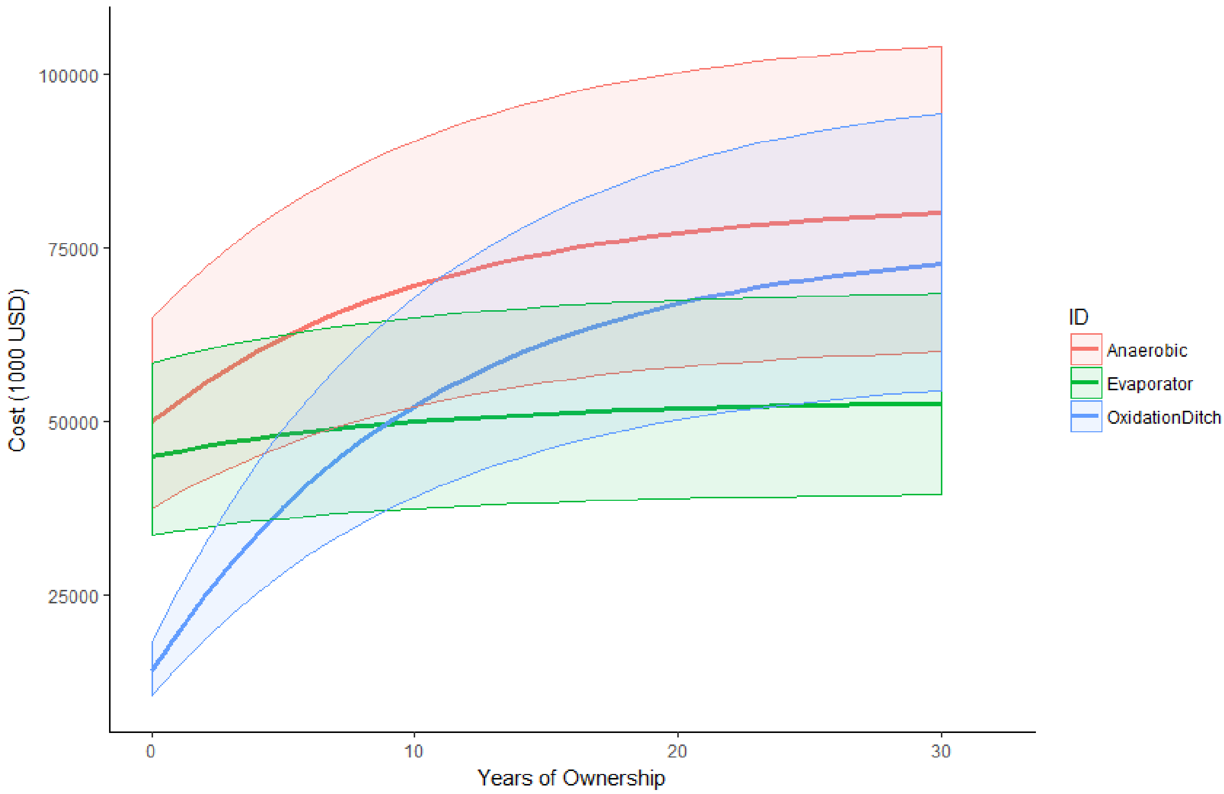

Figure 8: Wastewater Treatment Alternative Cost of Ownership
Notes:
Bold line indicates predicted cost of ownership.
Shaded area indicates estimation uncertainty (-25%, +30% of predicted).
Cost of ownership calculated as net present value of installed cost plus operational costs discounted at 10% IRR.

4. Conclusion

Wastewater management will play a large role in the commercial development of lignocellulosic biorefineries. Analysis of bioconversion material flows shows that the composition of the waste stream can be manipulated through process adjustments. Efforts to reduce inorganic additions to the waste stream during pretreatment and pH adjusting processes may significantly reduce treatment demands and lower treatment cost.

Alternative treatment methods may also offer solutions to lower treatment demands. Utilization of feedstock plantations for tertiary treatment may help externalize treatment costs away from engineered systems into natural systems, while simultaneously improving crop yield.

5. Future Work

The objectives of this study were to characterize bioconversion material streams in the context of wastewater treatment and then screen process alternatives and treatment technologies to better manage wastewater. These objectives were intended as a step toward identifying areas of interest for further research to improve wastewater treatment in lignocellulosic biorefineries. These areas of interest include:

- Techno-economic analysis on the impact of sulfur-free pretreatment methods including substitution of the SO_2 catalyst with other acids such as phosphoric acid or nitric acid and acid-free methods such as ammonia fiber explosion and CO_2 explosion.
- Further investigation into pH adjustment, particularly on interaction effects of neutralizing agents with various pretreatment methods. For example, substitution of SO_2 with nitric acid catalyzed steam explosion and subsequent neutralization with $Ca(OH)_2$ would result in $Ca(NO_3)_2$, a readily soluble salt without the processing issues associated with $CaSO_4$.

- Treatability studies to determine how the microbial communities employed during biological wastewater treatment interact with lignocellulosic stillage would provide improved kinetic coefficients for more accurate design of biological waste treatment technologies.
- Investigation into the long-term impacts of using ecosystem services of poplar plantations to aid in wastewater treatment; particularly, how inorganic constituents cycle and potentially accumulate in the environment and bioconversion process.

Finally, evaluation of more nuanced treatment methods using this study as a framework may identify even more cost effective treatment technologies. For example, anaerobic treatment was shown to provide significant benefits to the bioconversion process from biogas recovery, but the effluent polishing steps resulted in a capital intensive treatment alternative. A reimagined anaerobic treatment method which incorporates ecosystem services may result in a treatment alternative which is both low cost and recovers valuable resources.

6. References

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