Investigating Grey Water Footprint for the Production of Gasoline and Diesel from Biomass via Fast Pyrolysis

Energy Systems Division

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CONTENTS

FIGURES

TABLES

ACRONYMS AND ABBREVIATIONS

AOB	Ammonia oxidizing bacteria
APHA	American Public Health Association
AS	Acute standard
AWWA	American Water Works Association
BETO	Bioenergy Technology Office
BOD_5	Biological oxygen demand (5-day test)
COD	Chemical oxygen demand
CO_2	Carbon dioxide
CS	Chronic standard
ft^3/s	Cubic foot per second
d.m.t./d	dry metric tons/day
DEMON	DEMON®, de-ammonification process
DOE	Department of Energy
EISA	Energy Independence and Security Act
GHG	Greenhouse gaseous
GPD	gallons per day
GREET	Greenhouse Regulation, Energy, Emissions in Transportation model
H_2S	Hydrogen sulfide
HPLC	High-performance liquid chromatography
IPCB	Illinois Pollution Control Board
LCA	Life Cycle Assessment
MMGY	Million gallons per year
MMGD	Million gallons per day
MWWTP	Municipal Wastewater Treatment Plant
NH_3-N	Ammonia nitrogen
NPDES	National Pollutant Discharge Elimination System
PNNL	Pacific Northwest National Laboratory
PSA	Pressure swing absorption
R&D	Research and development

TEA   Techno-economic analysis
TKN   Total Kjeldahl nitrogen, the sum of organic nitrogen, ammonia (NH_3), and
            ammonium (NH_4^+)
TSS   Total suspended solids

US EPA   United States Environmental Protection Agency

WEF   Water Environmental Federation
WWTP   Wastewater treatment plant

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INVESTIGATING GREY WATER FOOTPRINT FOR THE PRODUCTION OF GASOLINE AND DIESEL FROM BIOMASS VIA FAST PYROLYSIS

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EXECUTIVE SUMMARY

To ensure long-term sustainable biofuel production that will maximize the economic, environment, and social benefits associated with the use of biofuel, natural resource sustainability must be considered in the early stage of technology research and development. The U.S. Department of Energy's Bioenergy Technology Office (BETO) has been focused on the need to select new production pathways by not only considering economic viability, technical feasibility, and market needs but also by considering ways to protect the soil, water, and ecosystem. Because of the nature of chemical reactions, a variety of organic and inorganic compounds would be present in the wastewater as a result of the thermochemical process used in the production of biofuel. The options for handling the wastewater could impact local water quality, strain municipal wastewater-treatment capacity, and affect refinery cost. In that context, the discharge of wastewater from biorefineries is an increasingly vital parameter to address in terms of ensuring biofuel sustainability. This parameter is particularly relevant to the complex reaction steps that occur in the multiple-unit operations required for biomass conversion, such as biomass fast pyrolysis, hydrotreating, and downstream separation. Findings from this study provide a basis for understanding the grey water footprint and developing a biofuel sustainability index for the pyrolysis biofuel production pathway.

This report investigates the grey water footprint of biofuels produced from fast pyrolysis. The system boundary consists of raw biomass handling and pre-processing, fast pyrolysis, oil vapor condensation, two-stage hydrotreating, and hydrocracking to produce a mixture of gasoline, diesel, and jet fuel. The study analyzes the feasibility of wastewater treatment options and identifies limitations on ultimate discharge to the surface stream under water quality standards and pollutant discharge regulations. The grey water footprint for the pyrolysis biorefineries was estimated for biological oxygen demand (BOD_5), total suspended solids (TSS), and ammonia nitrogen, and the dominant grey water component was identified. A maximum allowable grey water concept is proposed to factor in the regulatory discharge permit for various regulated components. A range of refineries with production capacities of 10, 25, 50, 80, and 90 MMGY and wastewater streams with various concentrations were evaluated for the feasibility of treating their wastewater in a 1-MMGD local municipal wastewater treatment plant equipped with a secondary treatment process. The study further examined interactions among production scale and concentration, efficiency of pollutant removal in MWWTP, costs associated with treatment, and challenges in meeting water quality standards to gain a deep understanding of key considerations in refinery facility siting.

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1. INTRODUCTION

Biomass pyrolysis is believed to be a near-term option — mandated by EISA — for producing infrastructure-compatible drop-in liquid transportation fuels from biomass to displace fossil fuels in the transportation sector (Czernik and Bridgwater, 2004; US Congress, 2007). The U.S. Department of Energy's Bioenergy Technology Office (BETO) has committed to achieving the EISA goal by supporting technology development, engineering economics analysis, and sustainability assessment to "convert biomass to fuels, chemicals and power via thermal and chemical processes such as gasification, pyrolysis and other non-biochemical processes" (DOE, 2012). Although extensive research has been conducted on the fast pyrolysis step by using a variety of cellulosic biomass as feed, a greater opportunity exists to upgrade bio-oil to gasoline-grade transportation fuel. Several critical reviews by Czernik and Bridgewater (2004) and Mohan et al. (2006) concluded that, as of 2006, oil upgrading was still in its infancy and not economically attractive.

Recent advances in research and development have shown that pyrolysis-based biofuel can be cost-effective in comparison with gasoline under large-scale implementation (Jones et al., 2009; Wright et al., 2010). To achieve long-term sustainable production at a large scale and maximize the economic, environment, and social benefits, it is critical that natural resource sustainability be considered in the early stage of development to help ensure that the new production pathways are based on not only economic viability and market needs but also on environmental sustainability. Therefore, a comprehensive evaluation has been developed and continuously updated for the process through techno-economic assessment (TEA) and life cycle assessment (LCA). Life cycle assessment for the process demonstrated promising net energy value and significant environmental benefits in the reduction of GHGs (Hsu, 2012). These results have been incorporated into the latest version of the GREET model (Han et al., 2011). Even so, there have been few water assessments estimating water consumption and the impact of water quality on the pyrolysis process.

Water is a vital component to consider when addressing the environmental sustainability of biofuels because it is essential to the biomass feedstock and fuel production supply chain. Increased biofuel production through new feedstock development would inevitably be accompanied by changes in land use, which shapes the type and the amount of water used. The spatial shift of water use would result in impacts on ecological service. At the conversion stage, biorefinery water use could strain local water resources and alter regional water demand. Non-point source discharge from feedstock production could change the nutrients and chemical distribution in the water system. The wastewater discharge from a biorefinery could affect water quality locally and downstream. Current analysis of conventional and cellulosic biofuel from biochemical or gasification/mixed alcohol processes revealed extensive regional variability and process dependency in the impact of fuel production on water — including water quality, water quantity, and water availability. Initial TEA analysis of fast pyrolysis has estimated the process water requirement at the pyrolysis stage (Jones et al., 2009). Process wastewater, which becomes increasingly central to the biofuel sustainability portfolio, remains less understood.

Like many novel forms of fuel generation, fast pyrolysis process requires water input and, at the same time, generates wastewater through chemical reaction and input water use during multiple process steps and unit operations. Because the process occurs at relatively high temperatures in the absence of oxygen, it allows for the formation of a wide variety of both organic and inorganic

1

molecules. During the process, lignin and cellulosic material are converted to a range of chemical compounds, such as organic acids, sugars, ketones, alcohols, aldehydes, phenols, polyaromatic compounds, low concentration of sulfur species, and nitrogen species (Bu et al. 2011; Bu et al. 2012). The chemistry changes with the variation of process conditions. Although research revealed that the wastewater from slow pyrolysis is toxic to biological systems (Nakaia et al., 2007; Tiililkkala et al., 2010), the water chemistry of wastewater from fast pyrolysis is not well known. Several researchers have attempted to recover the chemicals from the waste stream. Plant material Kenaf has been evaluated for the adsorption of small-molecular-weight phenolic compounds and poly aromatic hydrocarbons (Holmes et al., 2013); catalytic hydrodeoxygenation of lignin-derived phenols (Bu et al. 2012) in the wastewater generated from pyrolysis is under investigation. Activated biochar from pyrolysis could be another option for recovering organic compounds (Gu and Wang, 2012). Nevertheless, water recycling and reuse options are constrained by the cost of treatment. Thus, it is important to assess wastewater generated from specific fast-pyrolysis at the process development stage by first quantifying its chemical composition to further develop strategies or designs for wastewater treatment, recycle, recovery, or reuse.

Findings from the present study provide a basis for the development of the grey water footprint and biofuel sustainability index for the production of biofuel through pyrolysis. Results can support process development and decisions made on refinery projects on the basis of not only economics and infrastructure but also on water resource sustainability.

2. SCOPE OF THE STUDY

This assessment focuses on a modeled fast pyrolysis process. It considers all stages, starting from raw biomass handling and processing to fast pyrolysis and then followed by oil vapor condensation and bio-oil upgrading and conversion to produce a mixture of a wide-boiling-range hydrocarbon product with less than 2wt% oxygen. For this study, the hydrocarbon product is further separated into gasoline and diesel blendstocks. Jet fuel blendstocks will be considered in future studies. The aqueous waste stream is discharged from the hydrotreating stage (Figure 1). The scope of the study includes:

- Defining a system boundary and analysis approach.
- Selecting appropriate water quality constituents for analysis.
- Developing options for treating the waste stream in a municipal WWTP.
- Evaluating the feasibility of this option by comparing a range of concentrations of BOD, TSS, and ammonia nitrogen in the wastewater stream from pyrolysis biorefineries of 10MMGY-90MMGY.
- Estimating potential grey water footprint for ammonia nitrogen, BOD_5, and total suspended solids (TSS) against the regulatory standard for each case and identifying dominant grey water.
- Finally, estimating the cost of the wastewater treatment scheme.

3. DESCRIPTION OF FAST PYROLYSIS AND UPGRADING PROCESS

Fast pyrolysis of cellulosic biomass is a process during which thermal decomposition of carbonaceous material in the absence of oxygen produces char, gas, and a liquid product rich in oxygenated hydrocarbons. As seen in Figure 2, fast pyrolysis requires biomass drying, flash pyrolysis under high temperature, bio-oil hydrotreating under high pressure with the presence of catalyst, and hydrocracking. Hydrotreating and hydrocracking are typically regarded as "upgrading." The upgrading step involves contacting the bio-oil with hydrogen under pressure and at moderate temperatures (<400°C or 750°F) over fixed bed reactors.

In first-generation fast pyrolysis, biomass is rapidly heated in a fluidized bed reactor to temperatures around 400–500°C in the absence of oxygen, causing thermal decomposition of the biomass and yield vapors, which are condensed and ultimately result in a liquid bio-oil. This bio-oil resembles crude oil in appearance but has higher oxygen content and is more acidic. It is subsequently processed in the upgrading step, which involves hydrotreating and hydrocracking to produce hydrocarbon biofuel-blend stocks, in which bio-oil contacts a catalyst with high-pressure hydrogen, over a catalyst, at moderate temperatures. In hydrotreating, hydrogen is reacted with the bio-oil (hydrodeoxygenation) to remove oxygen (Equation 1) with the presence of sulfide catalyst. Sulfur must be added to the system to maintain the sulfidation required to keep the catalyst active. The deoxygenated bio-oil undergoes a separation step, and the heavy fraction of the hydrogenated biooil is reacted again with hydrogen in order to create smaller chains of hydrocarbons (decarboxylation, Equation 2) to increase the amount of gasoline blendstock produced and to improve the quality of the diesel pool.
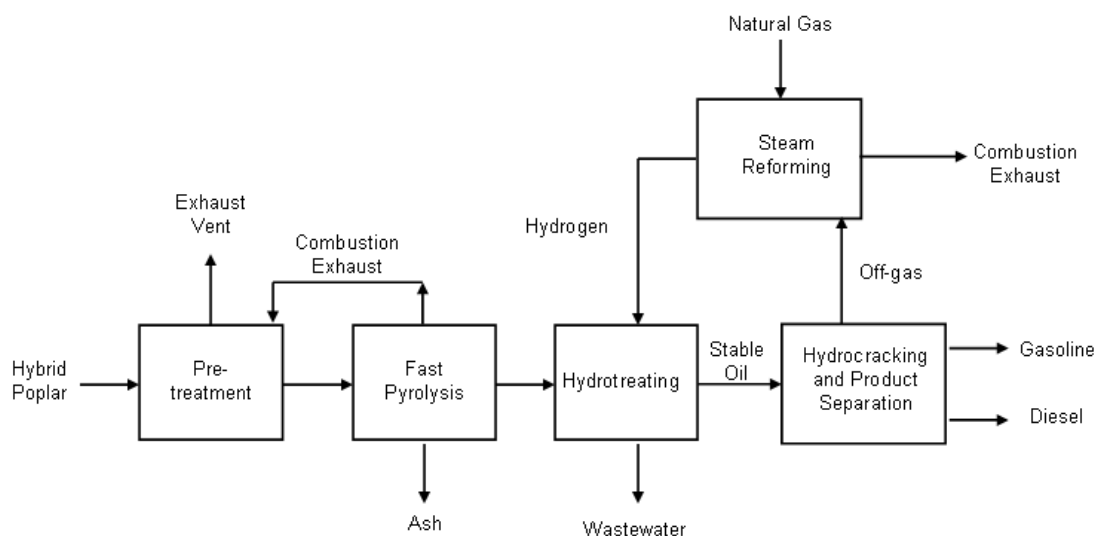
Figure 1.   Process schematics of fast pyrolysis, hydrotreating, and hydrocracking (adapted from Jones et al., 2009).

$$\text{C}_n \text{COOH} \xrightarrow{\text{Catalyst / 3H}_2} \text{C}_{n+1} + 2\text{H}_2\text{O} \qquad \text{Hydrodeoxygenation, Equation 1}$$

$$\text{C}_n \text{COOH} \xrightarrow{\text{Catalyst / H}_2} \text{C}_n + \text{CO}_2 \qquad \text{Decarboxylation, Equation 2}$$
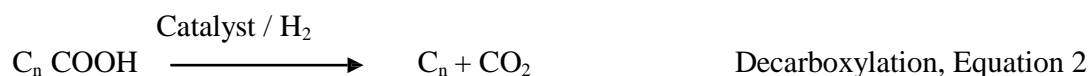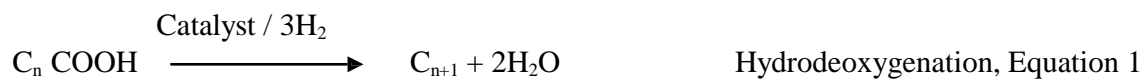
A small amount of water is produced during the de-oxygenation. Water is generated during the oxygenation step. As indicated in Equation 1, two moles of water are produced for every additional mole of c-c bond formed and two oxygen molecules are removed from the raw bio-oil. These water molecules immediately mix in with other organic and inorganic compounds in the hydrotreating unit and hence become a part of process wastewater. However, as fully de-oxygenated bio-oil molecules have little solubility in water, they readily separate from the wastewater.

Variations of the fast pyrolysis and hydrotreating/hydrocracking have been proposed (Figures 2). These designs center on hydrogen production, which is an essential pathway for oil upgrading via hydrotreating and hydrocracking. Hydrogen can be produced by reforming bio-oil's aqueous phase from a pyrolysis unit or sourced from external supply. Under the former option, aqueous-phase oil is mixed with steam before entering a high-temperature pre-reformer to be converted to syngas, producing hydrogen via the water-gas shift followed by pressure swing adsorption (PSA) (Figure 2). That design features varying proportions of bio-oil reforming. Alternatively, hydrogen can be purchased to maximize oil yield (Wright et al., 2010). In this case, a conventional petroleum refinery nearby could provide the hydrogen for plant needs. Process model simulation showed that generating hydrogen from aqueous-phase bio-oil would result in a final fuel product containing 38% (wt/wt) of gasoline and diesel, and the remaining content would be water, CO_2, and a light fraction. In comparison, supply hydrogen from an external source would lead to a fuel fraction of 42% (wt/wt) in the final output (Wright et al., 2010). This change in fuel fraction is also accompanied by a decrease in light ends, water, and CO_2, from 66% to 60% (Wright et al., 2010). Unfortunately, further breakdown of water fraction in the output wastewater stream is not available.
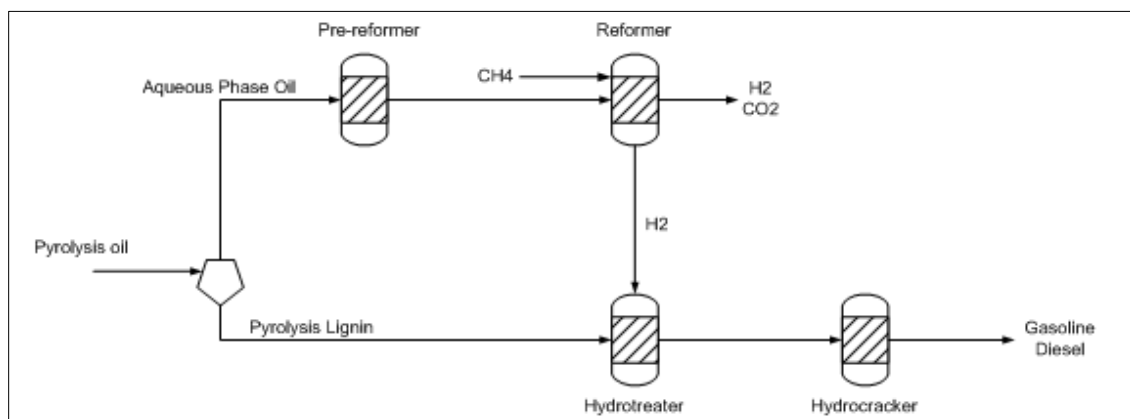
Figure 2. Schematic of pyrolysis oil separation for upgrading and reforming (adapted from Wright et al., 2010).

4. WATER FOOTPRINT CONSIDERATION

The concept of water footprint has been well accepted (Chapagain and Hoekstra, 2004; Gerbens-Leenes et al., 2009; Evans and Cohen, 2009; Misra and Ye, 2011; Wu et al., 2012; Chiu and Wu, 2012). Theoretically, the biofuel water footprint during the crop growing and refinery conversion stages can be partitioned into three compartments, including green water, blue water, and grey water. Green water refers to the amount of rainfall lost to support crop growth through evapotranspiration (ET), and blue water represents surface water and groundwater used by the irrigation and conversion process. Blue water in a biorefinery is that lost through evaporation and drifting in cooling tower, steam lost through evaporation, and the water incorporated to product and solid waste. Grey water is defined as the volume of freshwater that is required to assimilate the load of nutrients/chemicals discharged from the production process to meet the acceptable concentration standard in streams, on the basis of water quality standards established by a regulatory body, such as the U.S. Environmental Protection Agency (EPA). Grey water from feedstock production includes chemical run-off and/or leaching from field to stream. In a biorefinery, the grey water contains blowdown from cooling (recirculating cooling system is dominant in biorefinery) and boiling systems.

A method for grey water footprint estimate was proposed by Hoekstra et al. (2004), on the basis of chemical/pollutant input to the water system, discharge standard, and natural background of the chemical/pollutant in local streams. The grey water footprint reflects both feedstock production and refinery conversion stages. In a study by Wu et al. (2012), the authors summarized the research in nine significant papers on the water footprint of biofuels in the United States and identified the grey water footprint as a key gap in existing water footprint analysis. This gap is largely the result of limited data availability. In particular, information on wastewater characterization of the new developing process is limited in the public domain.

Recently, researchers have addressed the gap in multiple biofuel studies. In the feedstock production stage, studies focused on nitrogen-based grey water only because fertilizer is the biggest concern and a major contributor to the composition of grey water. Early assessment of nitrogen-based grey water relies on a simplified approach, in which a fixed fraction of the total fertilizer applied to a farm is allocated as the fertilizer is leached into the water system. Lately, attempts have been made to estimate the amount of fertilizer leaching into the water system by using field monitoring data and hydrologic modeling (Wu et al., 2012; Argo et al., 2013) and statistic modeling (Chiu and Wu, 2012). Chiu and Wu (2013) have also evaluated the footprint of grey water as a result of applying nitrogen fertilizer to forest woods-based feedstock. Their work provides a breakdown of the grey water footprint for a mixed feedstock (wood residue, round wood, thinning) containing softwood, hardwood, and short-rotation woody crop from pine, which is believed to be a desirable candidate for biofuel production via the thermochemical conversion process (pyrolysis, gasification).

Another gap in grey water assessment is grey water from the biorefinery process. As biofuel technology advances, the complexity of new conversion processes often leads to a much broader range of contaminants in the process wastewater. Water chemistry and the amount of compounds in the wastewater stream can vary significantly, depending on conversion process technology. Multiple organic and inorganic compounds in varying quantities could be present in a single stream. Furthermore, the composition of grey water is controlled by regulatory standards and is based on the natural background concentrations of specific compounds of interest, which is information that

requires an extensive spatial dataset. All of the parameters stated above add complexity to the accounting of the grey water footprint. In the past, wastewater flow discharge from feedstock conversion has largely been considered as negligible. On the other hand, the development of new processes for feedstock conversion has been intensely focused on yield, process efficiency, and energy use. In terms of water use, the process water requirement is often the focus. However, wastewater has been of minimal focus in process R&D.

In fast pyrolysis, with or without hydrogen import, water for cooling and steam would be needed. In particular, steam drum will be necessary to provide raw boiler water for recovering extra heat from process streams, generating steam and generating power. It also generates water through chemical reaction (hydrodeoxygenation, Equation 1), which ends up in the wastewater stream. Therefore, the total refinery wastewater stream would be a composite of cooling and boiling water blow-down and hydrotreating discharge (Figure 1). Blowdown from a steam drum is nominally treated and recycled to the cooling system in the process design. Because fast pyrolysis is still in the R&D stage, commercial operating parameters regarding cooling water treatment and its blow-down water quality are not available. Under the assumption that the cooling tower effluent discharges to the surface water or is reused in accordance with applicable state and local regulations, this study focuses on process wastewater. Additional analysis is necessary once the cooling water data become available. Jones et al. (2009) estimated that during hydrotreating, approximately 48 lb of water and 44 lb of upgraded oil (a mixture of gasoline and diesels) are produced from every 100 lb of wet pyrolysis oil. From a fuel production point of view, this would translate to a fuel-to-water ratio of 1:1.09. Thus, in a biorefinery with fast pyrolysis and upgrading, for a gallon of fuel production, about an equal amount of water is produced. As discussed above, the wastewater from fast pyrolysis contains oil, organic, and inorganic compounds (Bu et al. 2011 and 2012; Snowden-Swan, 2013; Gu, 2013); therefore, an appropriate treatment scheme is necessary before the hydrotreated water can be discharged to surface stream.

In this study, we attempt to estimate the grey water footprint for a range of organic and inorganic constituents to identify the dominant source of grey water. Because the water sample characterization was not publically available at the time of the study, we developed assumptions for the contaminants on the basis of literature. The analysis focuses on, in particular, BOD_5, TSS, and ammonia. BOD_5 and TSS are two key parameters regulated by EPA for wastewater discharge, while ammonia would be one of the major nitrogen components remaining in the water phase of the reactor discharge flow because its solubility. Ammonia can be oxidized to nitrate, potentially leading to a concentration limit in rivers set by US EPA (EPA 2009). We assume that a majority of hydrocarbon can be recovered from the wastewater stream.

5. METHODS

5.1 DATA SOURCES AND ASSUMPTIONS

The calculation of grey water footprint is based on a daily waste stream from pyrolysis under refinery sizes of 10, 25, 50, 80, and 90 MMGY operated 330 days a year. It is assumed that one gallon of process wastewater is generated from hydrotreating for one gallon of fuel (gasoline and diesel) produced. The wastewater stream is transported to a local municipal wastewater treatment plant (MWWTP) equipped with a secondary treatment process, where it is blended with the influent

of the MWWTP for treatment. Effluent of the MWWTP is discharged to a surface stream next to the facility. The MWWTP receives a medium-strength wastewater of 20 mg/L of ammonia, 200 mg/L of BOD5, and 200 mg/L of TSS at 1 MMGD.

A wide range of concentrations for the pyrolysis wastewater is selected for evaluation, taking into consideration the water quality from typical medium-strength municipal wastewater to high-strength wastewater of biological feedstock with ammonia. Table 1 summarizes the components evaluated and their concentrations.

Table 1.   Ranges of contaminants concentration and biorefinery size evaluated in this study.

Parameter	Values
BOD_5 (mg/L)	200, 500, 1000, 2000
TSS (mg/L)	200, 400, 600
Ammonia (mg/L)	20, 50, 100, 200, 500
Biorefinery capacity (MMGY)	10, 25, 50, 80, 90

To evaluate the technical feasibility of the proposed off-site treatment option for the wastewater streams, several steps were taken to screen for most critical components affecting the treatment. Flow and concentration of the components of interest were determined and compared with those of the MWWTP. Loadings (lb per day) were calculated for BOD and ammonia nitrogen of the model biorefinery waste stream for the refinery capacities and concentrations listed in Table 1. A set of initial screening criteria for each pollutant were applied to the waste stream based on loadings. Selected streams went through the treatment schemes, and their effluents were compared with BOD discharge limits. For ammonia, the dilution factor between effluent and the receiving stream flow and their concentrations was also considered. To illustrate the wastewater treatment issue associated with the model pyrolysis biorefinery, we chose the state of Illinois as an example. For a biorefinery to be built in other states, the corresponding ammonia standard can be obtained from the state government.

The discharge limits of BOD_5 (30 ppm) and TSS (30 ppm) from a municipal wastewater treatment plant are in accordance with the NPDES set by EPA (EPAa, 2009). The water quality standard for ammonia nitrogen is subject to state regulation and varies from region to region. Under the Clean Water Act, the USEPA (USEPAa, 2009) provides guidelines for developing fresh water ammonia criteria by state. Under the guidelines, state governments have established a local water quality standard for ammonia nitrogen. The ammonia nitrogen standard is expressed as a chronic standard (CS) and an acute standard (AS), which vary with temperature and pH. For example, at a water temperature of 25°C and a neutral pH, the AS of total ammonia nitrogen could be 3.75 mg/L, while the CS could be 3.01 mg/L during the Early Life Stage Present period of March through October in Illinois, according to the Illinois water quality standard (ILPCB).

The grey water footprint is estimated by using a method developed by Hoekstra and Chapagain (2011). The natural background value of ammonia in Illinois is estimated to be 0.3 ppm ammonia nitrogen, which is obtained from Mueller et al. (1995); the natural value for both BOD_5 is assumed to be 2 ppm and TSS 20ppm. The model pyrolysis biorefinery does not export electricity or produce other coproducts (Han et al., 2011). Grey water volume for a component is calculated as

7

discharge wastewater loading on the surface stream/(discharge standard concentration – natural background concentration). Grey water footprint for fuel production (L/L) is calculated as grey water volume divided by fuel production volume.

The cost of the wastewater treatment is estimate based on a user charge fee set by MWWTPs to cover the cost of treating and discharge the wastewater. We assume $240 per million gallons, $250 per 1000 pounds of BOD_5, and $165 per 1000 pounds of TSS. Because ammonia nitrogen oxygen demand is roughly 4.7 time of BOD, the charges to ammonia nitrogen are assumed to be 4.5 times that for BOD.

6.   RESULTS AND DISCUSSION

6.1   PYROLYSIS WASTEWATER TREATMENT AT OFFSITE MWWTP

Although fast pyrolysis has been commercialized by Ensyn and VTT, the fast pyrolysis and upgrading process design is still being improved at the pilot scale. On-site wastewater treatment could be an option for fast pyrolysis, which requires additional capital and operational costs. Alternatively, a local municipal WWTP may accept the stream if the water quality is deemed suitable and its capacity allows sufficient dilution. In this section, we explore the off-site wastewater treatment option by examining key factors: wastewater stream loadings, wastewater treatment efficiency, discharge limits, and aquatic water quality standard. We examine the feasibility of wastewater treatment for a biorefinery operating 330 days per year and 24 hours per day. The wastewater stream generated is 1 gallon of wastewater per gallon of fuel produced. The wastewater is treated in a local secondary municipal wastewater treatment plant with a capacity of 1 million gallons per day (MMGD) equipped with an activated sludge process. The plant is operated at 80% capacity and receives typical medium-strength municipal wastewater of 200 ppm BOD_5, 200 ppm SS, and 20 mg/L ammonia nitrogen.

6.1.1   Screening Wastewater Streams Feasible for Treatment in the MWWTP

Wastewater stream flow varies proportionally with refinery scale. As a pyrolysis refinery expands, wastewater flow increases accordingly. Consequently, the pyrolysis wastewater stream becomes less diluted by the municipal WWTP flow. The model pyrolysis biorefinery capacity analyzed ranged from 10 – 90 MMGY. With 1 L of wastewater stream per liter of fuel production, the wastewater flow would span from 0.03 to 0.26 million gallons per day (MGD), which is equivalent to 3–25% of the 1 MGD flow in the MWWTP. Without considering the concentration, flow loading alone could be substantial and strain the MWWTP when the size of the refinery is increased to 80–90 MMGY.

A second factor to consider is the concentration of each component in the wastewater stream. At high range, TSS (600 mg/L) is less than one-third that of BOD (2000 mg/L) (Table 1). Because discharge limits for both TSS and BOD are the same (30 mg/L), the impact of TSS on selecting wastewater streams for treatment in the MWWTP is small. Our initial results showed that with a treatment efficiency of 80–90%, TSS in effluent is well below the discharge limits for all of the refinery sizes and concentrations evaluated (Table 2). In comparison, the concentration of ammonia

nitrogen in the wastewater stream (20–500 mg/L) could reach 25 times that of the MWWTP influent (20 mg/L). Therefore, the remaining analysis focuses on BOD and ammonia nitrogen.

Although concentration by itself is important, the loading – which is a combination of concentration and flow – is typically used to estimate and analyze wastewater treatment operations. To down-select the refinery sizes and streams that are feasible for off-site treatment in the MWWTP, loadings of BOD and ammonia nitrogen from the wastewater streams were calculated for the concentration range and refinery scales studied. These loadings are further compared with the model MWWTP typical influent concentrations of BOD 200 ppm and ammonia nitrogen 20 ppm, to derive the proportion of waste stream loading to that of MWWTP. As illustrated in Figure 3, the waste loadings – determined by both conversion process and refinery size – will result in wide range of chemical loadings to the plant, spanning from a small fraction of the MWWTP loading to well beyond the full treatment capacity of the plant.

Table 2.   Comparison of TSS in the model refinery wastewater stream and effluent of MWWTP at the studied concentration range, refinery scales, and TSS removal efficiencies.

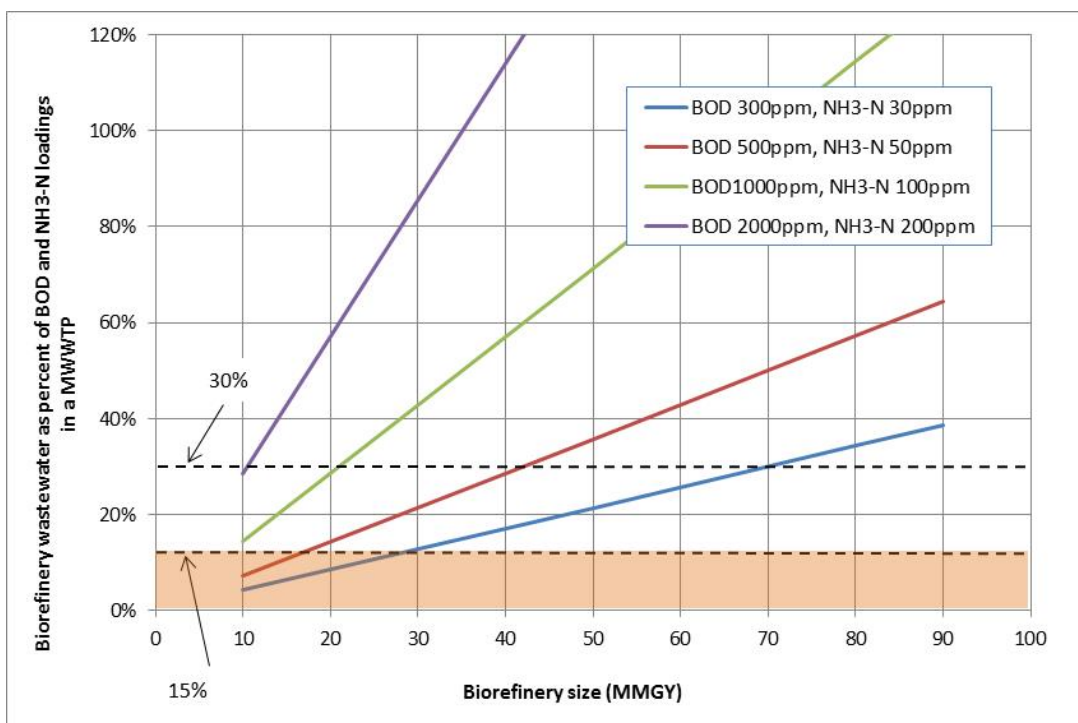| Refinery Size	TSS Concentration in Waste Stream (mg/L)	MWWTP Influent (combined, mg/L)	MWWTP Effluent with 80% Removal (mg/L)	MWWTP Effluent with 85% Removal (mg/L)	Effluent with 90% Removal (mg/L)
10 MMGY	90	22	4.41	3.31	2.21
	150	24	4.76	3.57	2.38
	200	25	5.06	3.79	2.53
	300	28	5.65	4.24	2.82
	400	31	6.24	4.68	3.12
	600	37	7.41	5.56	3.71
25 MMGY	90	25	4.99	3.74	2.49
	150	29	5.83	4.37	2.92
	200	33	6.54	4.90	3.27
	400	47	9.35	7.01	4.68
	600	61	12.17	9.13	6.08
50 MMGY	90	29	5.84	4.38	2.92
	150	37	7.42	5.57	3.71
	200	44	8.74	6.55	4.37
	400	70	14.00	10.50	7.00
	600	96	19.26	14.45	9.63
90 MMGY	90	35	7.00	5.25	3.50
	150	48	9.57	7.18	4.79
	200	59	11.71	8.79	5.86
	400	101	20.29	15.21	10.14
	600	144	28.86	21.64	14.43

Figure 3. BOD and ammonia nitrogen loadings of refinery wastewater streams with various concentrations relative to a MWWTP in refinery sizes from 10 to 90 MMGY. Note the MWWTP wastewater influent contains 200 ppm BOD and 20 ppm ammonia nitrogen. Orange shaded area indicates down-selected stream loadings.

To accept an industry wastewater stream for treatment, local MWWTP operators must be certain that normal performance can be maintained to meet the discharge limits and water quality standard after the wastewater stream is added to the facility. MWWTP operation takes into consideration the plant's capacity for accommodating the additional stream flow, loading, and associated operation and inputs requirements. Extensive throughput could be detrimental to the system and destabilize the plant performance and operation. Therefore, we applied the criterion that BOD and ammonia loadings exceeding 30% of the MWWTP influent would not be acceptable to the facility. This down-selection eliminates high-concentration streams while still allows a 300-ppm BOD stream from a 60-MMGY refinery, a 1000-ppm BOD stream from a <20-MMGY refinery, and other loading streams in between (Figure 3).

In addition to BOD, ammonia concentration is another concern associated with this waste stream. Extensive ammonia loading increase could disturb microbial community in the activated sludge process by disproportionly promote growth of nitrifiers which leads to possible imbalance of the microbial population. It also causes an increase in oxygen demand. In addition, ammonia nitrogen at high concentration could severely inhibit the microbial community that is critical to the activated sludge process in a secondary treatment plant. The USEPA developed inhibition values for screening the incoming wastewater stream (USEPAb, 2004). According to the guideline, the concentration of ammonia in activated sludge should not exceed 480 mg/L. Considering the dilution factor between the refinery wastewater stream and a MWWTP plant of 1 MMGD flow, the concentrations of ammonia in the WWTP plant would be significantly decreased. Still, compared with typical

municipal wastewater influent of 20 mg/L of ammonia nitrogen, the inhibition concentration would be about 24 times higher. In fact, treatment facilities are not likely to take the high risk to accept ammonia nitrogen loadings that far exceed its influent level. We further down-select wastewater streams by limiting ammonia nitrogen loading to 15% relative to the MWWTP influent. As a result, feasible refinery streams are limited to BOD of 300 mg/L from a 30-MMGY refinery, 500 mg/L BOD streams from less than 20-MMGY plant (Figure 3). Ammonia concentrations in the influent reduced to 30-50mg/L. Clearly, ammonia nitrogen criteria play a major role in determining the feasibility of treating the waste stream from the model refinery.

6.1.2   Removal Efficiency and Effluent Discharge Dilution Factor

In the MWWTP, removal efficiency can vary because of incoming wastewater stream volume and quality, facility design, and operational parameters. The U.S. EPA requires that wastewater treatment facilities achieve 80% removal of BOD and TSS. In reality, depending on the plant design and operation, removal efficiency could vary from 80% up to 95%. The down-selected wastewater streams were further examined under several typical treatment efficiencies for BOD and ammonia nitrogen. Results in Figure 4 showed that effluent concentration increases with wastewater stream concentration. The wastewater stream could not meet discharge requirements for BOD with 80% removal efficiency (Figure 4a). At 85% removal efficiency, only the wastewater stream containing 300 mg/L BOD can be treated to meet the BOD discharge limit. As BOD concentration increases to 500 ppm, the effluent concentration exceeds limit slightly. However, when the removal efficiency increases to 90%, all of the effluent would comply with BOD requirement (Figure 4a). If a MWWTP facility is operated at 85% removal efficiency only, the number of feasible wastewater streams for treatment would be further reduced to BOD concentrations of less than 300 mg/L for a 10-MMGY biorefinery. Coincidentally, current thinking of deployment plans for fast pyrolysis biorefinery lean toward the small/modular systems, in which economies of mass production are achieved by centralizing the upgrading process. Nevertheless, a treatment facility with a minimal of 85% removal efficiency is required for the biorefinery wastewater streams.

Ammonia nitrogen in effluent for the 30-mg ammonia nitrogen/L wastewater streams can meet the water quality standard in most cases (Figure 4b). Similarly, the treatment would be satisfactory at 90% removal efficiency. In fact, a higher-concentration ammonia nitrogen discharge stream may still comply with the water quality standard at 80% removal efficiency. As the wastewater effluent is discharged to the surface water, its concentration is usually diluted by the receiving stream. Conversely, the water quality standard applies to the receiving stream, rather than the discharge effluent from the MWWTP. The extent to which the discharge chemical is diluted would be governed by local stream water quality, flow, and regulations. If the surface water stream receiving the MWWTP effluent has sufficiently large flow compared with the discharge flow, the final concentration of ammonia in the surface water can be reduced to meet or be below the water quality standard. Factoring in dilution, meeting the water quality standard requires a receiving stream flow of 0.01–0.11 MGD and 0.35–0.48 MGD for the selected streams from 10–25-MMGY refineries with 85% and 80% removal efficiencies, respectively. This amount of flow is equivalent to 0.02–0.17 ft^3/s (85% removal efficiency) and 0.54–0.74 ft^3/s (80% removal efficiency) (Table 3). Because of significant regional variability in stream flows, this range could be a hurdle in regions with limited water resources. For example, the Chicago River in Niles, IL, has a flow of 39 ft^3/s, and the Des Plaines River in Gurnee, IL, has a flow of 46 ft^3/s flow (http://waterdata.usgs.gov/il/nwis/rt). Both of the stream flows would be more than adequate to receive this range of the ammonia effluent

11

by providing 100-fold dilutions. On the contrary, small streams with flows of 1–3 ft^3/s are also quite common in the same region. Although the required receiving stream flow for ammonia nitrogen dilution in this study is less than 0.7 ft^3/s (Table 3), as the stream may also receive other discharge from the region, which may easily strain its ability to renewal. Therefore, the feasibility of the treatment option depends greatly on the existing local municipality, local water quality standard, and local surface stream flow, in addition to the efficiency of the treatment process.
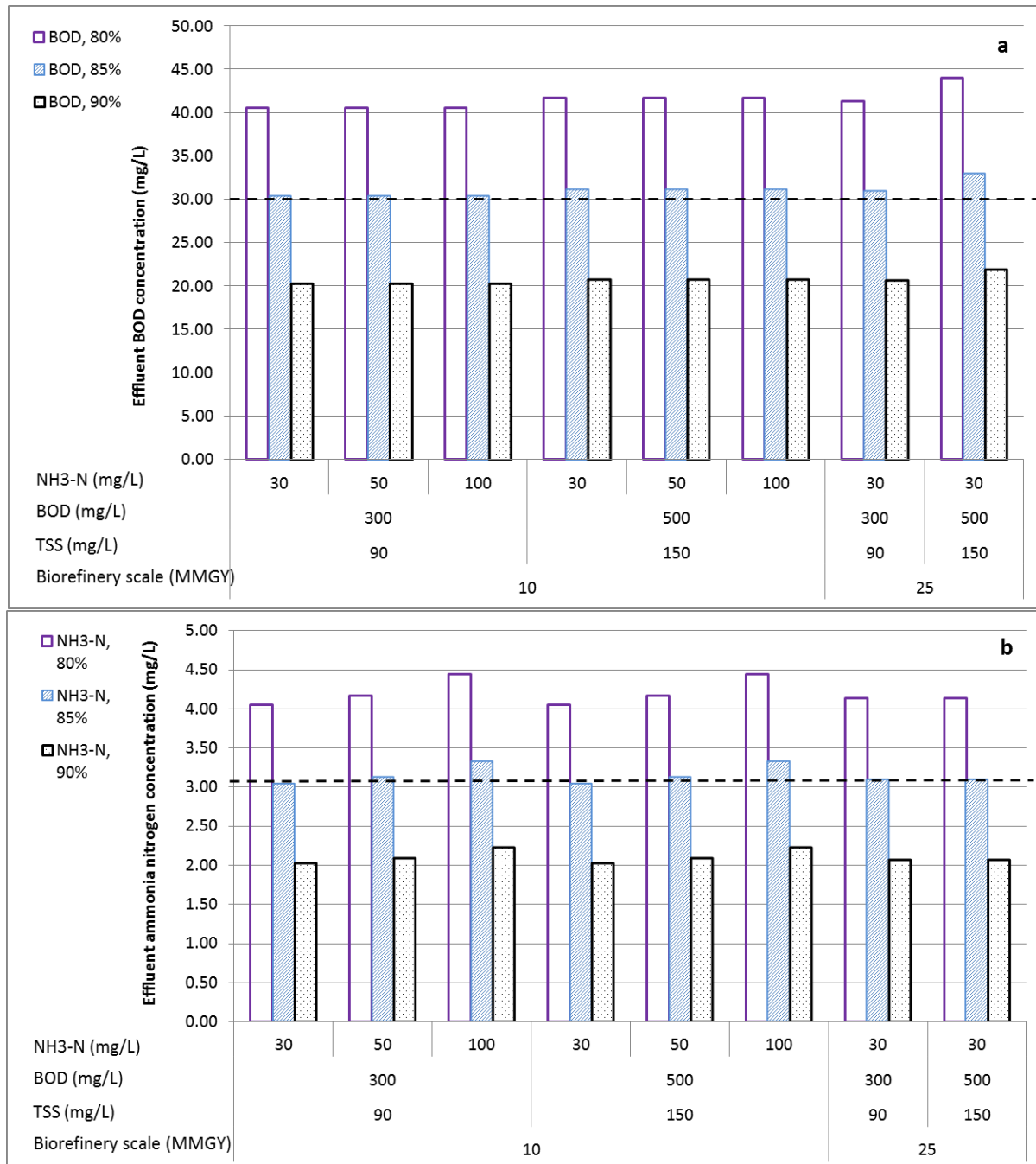

Figure 4. **Water quality of treated wastewater at various process removal efficiencies for the wastewater concentrations and refinery sizes studied: (a) BOD; (b) ammonia nitrogen. The**

12

horizontal axis represents wastewater streams being treated in the MWWTP Dashed lines are discharge limits or water quality standards.

Table 3.   Influence of receiving stream flow on ammonia concentration.

Refinery size[a] (MMGY)	Refinery wastewater ammonia nitrogen (mg/L)	Effluent ammonia concentration from MWWTP (mg/L)		Receiving stream flow rate required to meet regulation (ft^3/s)	
		80% removal	85% removal	80% removal	85% removal
10	30	4.06	3.04	0.54	0.02
	50	4.17	3.13	0.59	0.06
	100	4.44	3.33	0.74	0.17
25	30	4.13	3.10	0.58	0.05

[a]   Process wastewater is generated at 1 L per L of fuel produced.

In the development of a biofuel refinery project, decision makers typically select a plant location on the basis of infrastructure and economic considerations. Recently, the water resources requirement for process water use has become more of a constraint as a result of concerns about decreased levels of ground water. The present study further suggests that local stream flow should also be factored in when determining how to effectively treat and discharge biorefinery wastewater. In that regard, considerations about water sustainability for the pyrolysis biorefinery would cover a range of issues, including process water sourcing, process water use, wastewater treatment, and treated effluent discharge. These considerations can be addressed via both technology and refinery siting. From a water quality and water resource availability perspective, refinery location is critical to the water sustainability of biofuels.

6.3   GREY WATER FOR PYROLYSIS WASTEWATER AT VARIOUS LEVELS OF TREATMENT

The natural water system has the ability to renewal itself by degrading and decomposing a certain level of complex organics through a series biological and chemical reactions occurring in the water and sediments. Chemicals and pollutants in question can be absorbed by the water system up to a level without harming the environment. This concept is already reflected in various state and local water quality standards, such as TMDLs. Thus, it is essential to recognize the self-renewal capability of natural water systems. To illustrate this in the context of grey water footprint, we define a *maximum allowable grey water* as the amount of grey water allowable to be released to ecosystem by water quality regulation, below which discharging of the water would not cause harm to water quality. As illustrated in Figure 5, the grey water volume would be a serious concern only when it exceeds the *maximum grey water*. Thus, the *maximum grey water* can be obtained when the concentration of a pollutant in the discharge wastewater stream equals the water quality standard for the region. A net grey water footprint value can be calculated using the available wastewater data and regulatory standard. Introducing the maximum grey water concept provides a practical approach in considering different attributes of grey water, which allows a representation of the self-renewal

capability of a natural water system and regulations applied to industrial discharge stream or the surface water stream.
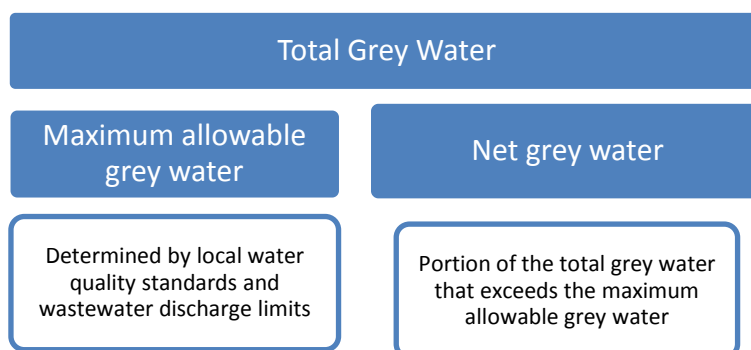

Figure 5.   Conceptual diagram of maximum allowable grey water for regulated substances

Previous grey water assessment has been limited to nitrogen fertilizer grey water for which the nitrate drinking water standards for the surface stream was used. In this study, we attempt to expand the fertilizer-based grey water estimate to encompass a wider range of chemicals by incorporating the perspective of wastewater treatment industry. This information is especially important in estimating the water footprint of products/energy that is produced via various industrial processes; each generates a distinct wastewater stream that also is governed by different regulatory standards. In addition, it enables officials to address regional specific water quality issues by including local standards for water quality.

Grey water footprint of the process wastewater streams that are treated in the MWWTP was estimated for ammonia nitrogen, BOD_5, and TSS. The maximum allowable grey water footprint for BOD is calculated to be 1.1 L/L of biofuel and 1.11 L/L for ammonia nitrogen (State of Illinois) (Figure 6). For TSS, the maximum value is 3 mg/L. With 85% removal efficiency in the MWWTP, the total grey water footprint for ammonia nitrogen and BOD for the down-selected wastewater streams are minimal, ranging from 1.1 to 1.3 L/L biofuel produced. As removal efficiency was reduced to 80%, the total grey water footprint increased slightly to 1.4–1.8 L/L (Figure 6). The TSS grey water footprint is approximately half of the ammonia nitrogen/BOD grey water footprint — less than 0.6 L/L for 85% removal and less than 0.8 L/L for 80% removal, respectively, at the refinery range. The net grey water footprint – the differential between the maximum allowable value and the total grey water (Figure 5) — is further determined.

As illustrated in Figure 6, the net grey water footprint for BOD and ammonia nitrogen is very small. At 80% removal efficiency, it takes 0.7 L of net BOD grey water to produce 1 L of biofuel from the pyrolysis/hydrotreating process for the highest effluent stream. The largest net ammonia nitrogen grey water footprint is 0.5 L/L. In reality, the ammonia grey water is even lower when the dilution factor is taken into consideration. As for TSS, since the maximum allowable grey water is 3 L/L while the total calculated grey water for these streams is below 0.8 L/L, there is no net generation of TSS grey water.

Determining the maximum grey water for BOD_5 and TSS in other regions of the world where discharge limits are established is rather straightforward because the standard is based on the effluent discharge stream from MWWTP. If these regulatory compliances are met, total grey water of BOD and TSS would be at or below the maximum grey water, resulting in zero net grey water footprint. In contrast, the ammonia nitrogen maximum grey water would vary extensively from region to region, depending on the local water quality and water pH, climate, and local regulations. The range of maximum grey water value discussed in this study applies only to a fast pyrolysis refinery built in Illinois. For the refinery to be built in other states, local regulatory standards apply.
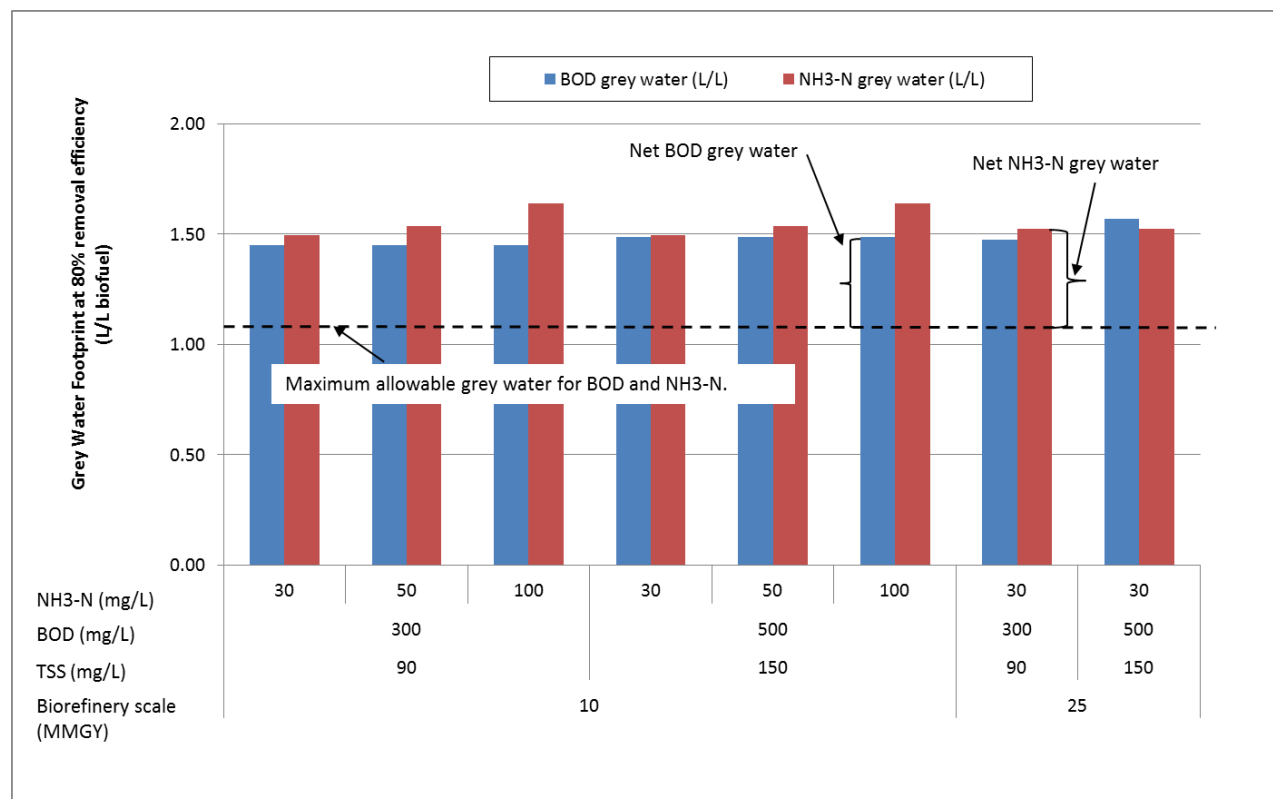

Figure 6. Net grey water footprint of fast pyrolysis/hydrotreating wastewater treated in the MWWTP with 80% removal efficiency.

6.4   WASTEWATER TREATMENT COST

Following the consideration of technical feasibility, the treatment expense bared by the pyrolysis biorefinery must be examined. Treating process wastewater in a local municipality would incur costs. Typically, the MWWTP charges the wastewater stream provider a user rate for the wastewater treatment and discharge. The user rate is normally determined on the basis of the flow and concentration of the wastewater stream, which represents the mass loading to the treatment facility. As flow or concentration of the wastewater stream increases, the total loading increases — and so does the total treatment cost to the wastewater stream provider. While most MWWTP charges are based on BOD_5, TSS, and flow, some facilities also charge for ammonia treatment. We develop an estimate on the basis of the assumptions that the MWWTP has 1-MMGD flow capacity with a user charge rate $240 per million gallons of wastewater treated, $250 per 1000 pounds of BOD, $165

per 1000 pounds of TSS. A fee for treating ammonia nitrogen is also applied, which is 4.5 times that for BOD, $1125 per 1000 pounds of ammonia nitrogen.

Figure 7 shows that the cost for BOD dominates in this wastewater stream, accounting for approximately 80% of the total. The impact of flow on the cost is minimal, given the relative low user charge rate. The overall cost associated with the treatment of the wastewater stream increases significantly with wastewater concentration and is relatively less sensitive to refinery size. Since BOD concentrations of 1000 mg/L or above from 10- and 25-MMGY plants have been excluded because of loading constraints (Figure 3), the largest portion of cost is attributed to treating a 500-mg/L BOD. A biorefinery of 25 MMGY requires 688 dry tonnes of feed per day with a fuel yield of 417 L/dry tonne feed (Hsu, 2011; Han et al., 2011); a wastewater stream containing 500 mg/L BOD translates to a daily charge of $126 for wastewater treatment (Figure 7). The cost falls to $76 at a 10- MMGY plant. On annual basis, the total cost of wastewater treatment would range from $22,000 to $42,000 for the two refineries. Therefore, even though it is technically feasible to treat the waste in a local MWWTP, adequate excess capacity, and considerable receiving stream flow, the associated user charge may still be a limiting factor in large-scale operation. Further investigation is needed to explore alternative treatment options and technologies to lower the cost. Because 80% of the cost is incurred in BOD_5 treatment, process wastewater recycle and reuse to reduce the organic carbon concentration is the key to cutting down the cost for the option of treating the wastewater in a MWWTP facility. Moreover, analysis to examine the economic viability under various water treatment regimens by integrating TEA and water footprint assessment would provide valuable insights.
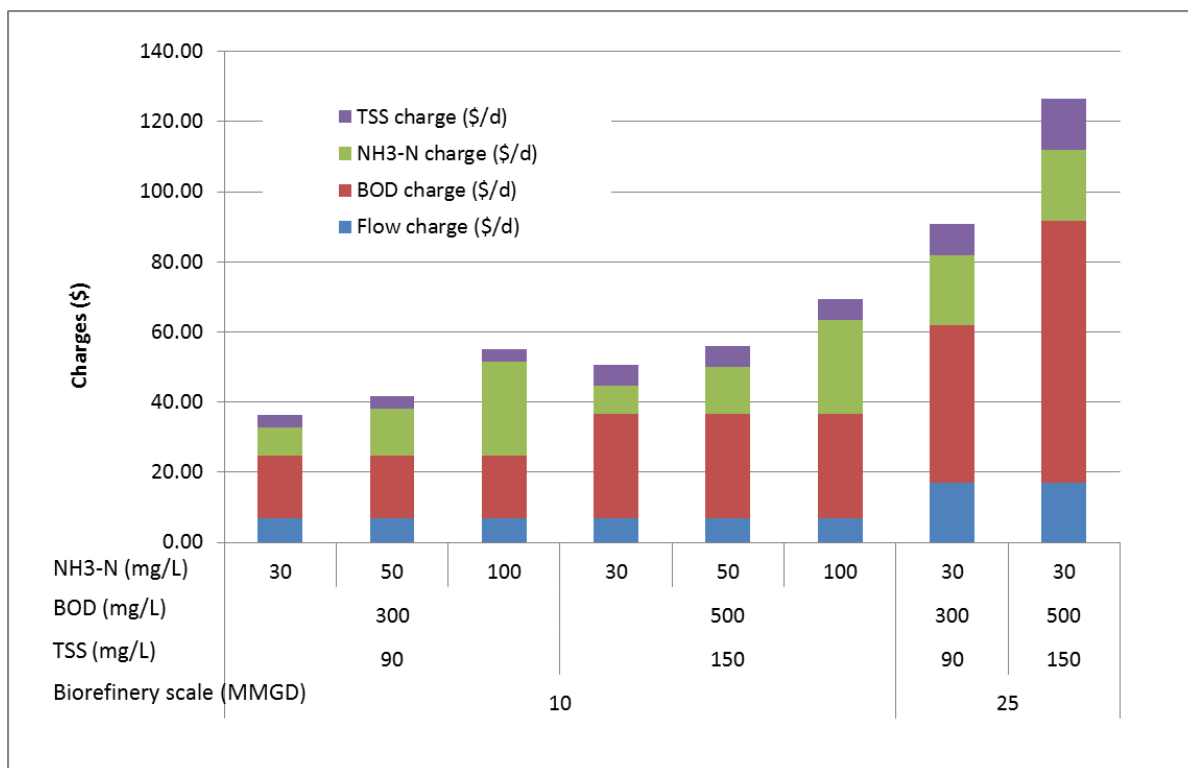

Figure 7.   Estimated daily cost to biorefinery associated with process wastewater treatment in a MWWTP for the wastewater streams.

7. UNCERTAINTIES AND ISSUES

Pyrolysis wastewater reportedly contains phenolic compounds and other organic carbon compounds (Gu and Wang, 2012). However, quantitative characterization of the contaminants was not available at the time of this study. Although the nature of the feedstock (wood) would likely yield biodegradable components in the water phase, we could not rule out the presence of some level of phenolic compounds and associated toxicity, which could be inhibitory to the microbial community in the activated sludge process. Therefore, pretreatment may be required to remove the phenolic compounds. The extent of the pretreatment depends on their concentration in the mixed influent. The toxicity of the wastewater stream may make the option of off-site treatment in MWWTP undesirable. In that case, the wastewater must be treated on-site with a non-biological treatment scheme. Advanced water treatment technologies capable of removing contaminants to an acceptable level in the biorefinery are readily available. Nevertheless, the associated cost for a refinery with a wastewater treatment plant could be a major hurdle and even prohibitive at certain scale.

8. CONCLUSION

We examined wastewater treatment for the process wastewater generated from fast pyrolysis biorefineries in a MWWTP by considering multiple factors. Feasibility of the treatment option depends on wastewater flow from the refinery, concentration of the wastewater, loadings, capacity and flow of the local WWTP, treatment efficiency, and stream flow of the receiving water body. In the refinery scale and concentration ranges studied, ammonia nitrogen loading is a major factor in selecting feasible wastewater streams. Removal efficiency could also limit the choice of wastewater streams. Meeting ammonia nitrogen water quality standard relies on both treatment and dilution during effluent discharge. The grey water footprint of the wastewater stream is sensitive to the dominant components, water quality standard, discharge limits, and natural background concentrations of the components of interest. In the cases analyzed, ammonia nitrogen plays an critical role in selecting feasibility for treatment and BOD is the determining factor for the grey water footprint.

Previous grey water assessment has been limited to nitrogen fertilizer grey water for which the nitrate drinking water standards for the surface stream was used. In this study, we attempt to expand the fertilizer-based grey water estimate to encompass a wider range of chemicals by incorporating the perspective of wastewater treatment industry. This information is especially important in estimating the water footprint of products/energy that is produced via various industrial processes; each generates a distinct wastewater stream that also is governed by different regulatory standards.

This study further suggests that refinery decision makers should also consider local receiving stream flow, which is an important factor in determining the level of treatment required for ammonia removal. In that regard, considerations about water sustainability for the pyrolysis biorefinery would cover a range of issues, including process water sourcing, process water use, wastewater treatment, and treated effluent discharge. These issues can be addressed via both technology advancement and

refinery siting. From the perspective of water quality and water resource availability, refinery location is critical to the water sustainability of biofuels.

Finally, treatment cost could be a significant factor in sustainable operation of the biorefinery. BOD treatment accounts for a major cost for the biorefinery wastewater, if it is treated at MWWTP. The recycling and reuse of process wastewaters to reduce the organic carbon concentration is the key to decreasing the cost for the option of treating the wastewater in a MWWTP facility. We recommend addressing this issue through an integrated analysis of TEA and water footprint assessment.

On the basis of the above analysis, we came to the following conclusions:

- Feasibility of the wastewater treatment option depends on the existing local municipality, local water quality standard, and local surface stream flow, in addition to the efficiency of the treatment process. It must be examined individually case by case.

- The wastewater from a 25-MMGY refinery with a BOD concentration of 500 mg/L or less and an ammonia concentration of 30 mg/L or less can be treated in a 1-MMGD MWWTP equipped with secondary wastewater treatment at a removal efficiency 85% or above to meet water quality regulations. At 10-MMGY biorefinery, ammonia concentration in the influent can be increased up to 100 mg/L. The waste streams cannot be treated in a MWWTP with 80% removal efficiency.

- At the concentration levels studied, meeting the ammonia water standard requires the treated effluent to be discharged to a receiving stream flow of 0.6–0.8 ft^3/s or higher, if the removal efficiency is 80%.

- The treatment cost based on user rate alone varied from $22,000 to $42,000 per year for the down-selected wastewater streams.

- A maximum allowable grey water footprint concept is proposed to consider self-renewal capability in the natural water system. This level complies with water quality standards and discharge limits set by regulatory agencies and can therefore be applied to broader range of chemicals in the wastewater streams that are regulated by government bodies in various regions. Below the maximum grey water volume, the grey water does not pose imminent threat to the eco-environment. Net component-specific grey water is derived from the total grey water and maximum grey water.

- BOD and ammonia nitrogen grey water footprint of the selected streams that are treated by MWWTP are small. Net TSS grey water generation is zero, and the net BOD and ammonia nitrogen grey water footprint is less than 1 L/L biofuel produced.

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19

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