



# WPI

## **An Evaluation of Influential Variables on the Energy Efficiency of Hydrothermal Liquefaction**

A Major Qualifying Project  
Submitted to the faculty of  
WORCESTER POLYTECHNIC INSTITUTE  
In partial fulfillment of the requirements for the  
Degree of Bachelor of Science  
In  
Chemical Engineering

By:  
Emma Bennett  
Jenna Hirshfeld  
Amanda Wetmore

April 2, 2021

WPI Faculty Advisor:  
Professor Michael Timko

*This report represents work of WPI undergraduate students submitted to the faculty as evidence of a degree requirement. WPI routinely publishes these reports on its web site without editorial or peer review. For more information about the projects program at WPI, see*

*<http://www.wpi.edu/Academics/Projects>*

## Abstract

The need for clean, renewable energy is becoming increasingly crucial due to the negative environmental impacts associated with burning fossil fuels and the depleting supply of nonrenewable energy sources. Hydrothermal liquefaction (HTL) is an energy producing process that has the potential to replace nonrenewable energy sources. HTL is a thermochemical conversion process that converts biomass such as algae, wood, and sewage sludge into liquid biocrude. HTL, compared to other thermochemical conversion methods, is especially attractive because it allows for a wet feedstock. Sewage sludge is a cheap and abundant waste that can be used as feedstock for HTL due to its high water content. Although HTL is a promising source of clean, renewable energy, more information is needed on its energy efficiency and factors that contribute to the efficiency of the process.

In this study, we used energy return on investment (EROI) to measure the energy efficiency of HTL and determined which factors in the process were most impactful on EROI. We then included the energy required for biocrude upgrading into the study as a correction factor for EROI and projected EROI values for literature studies based on their specific process conditions. Our study revealed that biocrude yield, feedstock solids loading, and biocrude higher heating value have the most influence on the EROI of HTL. When determining EROI we varied biocrude yield from 10-60%, feedstock solids loading from 0.075-0.325 wt fraction, and biocrude higher heating value from 35.6-43.5 MJ/kg. The resulting EROI values ranged from 0.91 to 20.81 and the trends demonstrated that EROI increases with increasing biocrude yield, solids loading, and heating value. Including the upgrading process as a correction factor drastically decreases the EROI, making the new range 0.64-3.43.

## **Acknowledgments**

We would first like to thank our project advisor, Michael Timko, for his guidance and recommendations throughout this process. Next, we want to thank Pacific Northwest National Laboratory for sharing their data from a previous study with us and allowing us to use it as the basis for our calculations. This project would not have been possible without their willingness to share their information and research with us. We would also like to thank Cheng Feng for allowing our team to have access to his extensive HTL literature datasheet. Lastly, we would like to thank Kelly Hering and Charm Industrial for their guidance on the applicability of our project in industry.

# Table of Contents

<b>ABSTRACT</b>	<b>I</b>
<b>ACKNOWLEDGMENTS</b>	<b>II</b>
<b>TABLE OF CONTENTS</b>	<b>III</b>
<b>LIST OF FIGURES</b>	<b>V</b>
<b>LIST OF TABLES</b>	<b>VI</b>
<b>NOMENCLATURE</b>	<b>VII</b>
<b>CHAPTER 1. INTRODUCTION</b>	<b>1</b>
<b>CHAPTER 2. BACKGROUND</b>	<b>3</b>
<b>2.1 The Problems Associated with Nonrenewable Energy Sources</b>	<b>3</b>
<b>2.2 Biomass as an Alternative Energy Source</b>	<b>4</b>
2.2.1 Waste as a Feedstock	6
2.2.2 Thermochemical Conversion Methods	6
<b>2.3 Hydrothermal Liquefaction (HTL)</b>	<b>9</b>
2.3.1 Process Overview for Sludge HTL	11
2.3.2 Process Overview for Biocrude Upgrading	12
<b>2.4 The History of HTL and Current Applications</b>	<b>13</b>
<b>2.5 Importance of Sludge Water Content</b>	<b>15</b>
<b>2.6 Evaluating Energy Efficiency of Energy Processes</b>	<b>17</b>
2.6.1 Emergy	17
2.6.2 Exergy	18
2.6.3 Energy Payback Period	18
2.6.4 Energy Return on Investment for HTL	18
<b>CHAPTER 3. METHODS</b>	<b>21</b>
<b>3.1 Developing the HTL Process</b>	<b>21</b>
<b>3.2 Calculating the EROI Base Case</b>	<b>23</b>
3.2.1 Pump	24
3.2.2 Heat Exchangers	24
3.2.3 Reactor	25
3.2.4 Calculating EROI	25
<b>3.3 Sensitivity Analysis</b>	<b>26</b>
<b>3.4 Analyzing Important Process Variables</b>	<b>27</b>
3.4.1 Upgrading	28
<b>3.5 Literature Projection</b>	<b>28</b>
<b>CHAPTER 4. RESULTS AND DISCUSSION</b>	<b>29</b>
<b>4.1 Sensitivity Analysis</b>	<b>29</b>
<b>4.2 The Effect of Yield with Solids Loading on EROI</b>	<b>29</b>
<b>4.3 The Effect of Heating Value with Solids Loading on EROI</b>	<b>30</b>
<b>4.4 The EROI of Upgraded Biocrude</b>	<b>31</b>
<b>4.5 Literature Projection</b>	<b>33</b>
<b>4.6 EROI Comparison with Other Processes</b>	<b>35</b>
<b>CHAPTER 5. CONCLUSION</b>	<b>38</b>
<b>CHAPTER 6. RECOMMENDATIONS FOR FUTURE WORK</b>	<b>40</b>
<b>REFERENCES</b>	<b>42</b>

<b>APPENDICES</b>	<b>49</b>
<b>Appendix A. Base Case Calculations</b>	<b>49</b>
Appendix A.1 Basic Flow Information	49
Appendix A.2 Feedstock $C_p$ Data	49
Appendix A.3 Pump Calculations	50
Appendix A.4 Feed/Product Heat Exchanger Calculations	50
Appendix A.5 Feed Heater Calculations	51
Appendix A.6 Reactor Calculations	51
Appendix A.7 Biocrude Cooler Calculations	51
Appendix A.8 EROI Calculations	52
<b>Appendix B. Upgrading energy inputs from PNNL used as correction factor</b>	<b>53</b>
<b>Appendix C. Energy output of upgrading process used as a correction factor</b>	<b>54</b>
<b>Appendix D. Data for the effect of yield with solids loading graph</b>	<b>54</b>
<b>Appendix E. Data for the effect of HHV with solids loading graph</b>	<b>55</b>
<b>Appendix F. Data for the effect of yield with solids loading on EROI with upgrading</b>	<b>55</b>
<b>Appendix G. Literature projection data</b>	<b>57</b>

## List of Figures

Figure 1. Thermochemical Conversion Pathways (Verma et al., 2012)	7
Figure 2. Temperature ranges for thermochemical conversion processes (Zhang and Zhang, 2019)	8
Figure 3. Process diagram for HTL of sludge (Seiple et al., 2017)	11
Figure 4. Process diagram for upgrading of HTL biocrude (Seiple et al., 2017)	12
Figure 5. Biocrude yields for various feed moisture contents for isothermal HTL (Qian et. al., 2017)	16
Figure 6. Boundaries of various EROI analyses (Hall et. al., 2013)	20
Figure 7. Bench scale HTL process used by PNNL (Snowden-Swan et al., 2017)	22
Figure 8. Simplified HTL process	23
Figure 9. Sensitivity analysis of hydrothermal liquefaction	29
Figure 10. The effect of yield with solids loading on EROI	30
Figure 11. The effect of heating value with solids loading on EROI	31
Figure 12. The effect of yield with solids loading on the EROI of upgraded biocrude	32

## List of Tables

Table 1. Literature EROI values for HTL process	2
Table 2. Feedstocks and their corresponding biofuels (Zhang and Zhang, 2019)	5
Table 3. Types of gasification summary (Zhang and Zhang, 2019)	9
Table 4. HTL base case conditions	23
Table 5. Temperature and pressure properties of HTL streams	24
Table 6. Specific heat capacity values for various HTL components	25
Table 7. Variables' Minimum and Maximum Values for Sensitivity Analysis	27
Table 8. EROI Comparison with various conversion methods	36

## Nomenclature

<b>Symbol</b>	<b>Definition</b>	<b>Units</b>
$C_P$	specific heat capacity	BTU/lb*°F
$h$	pump head	ft
$m$	mass flow rate	lb/hr
$P$	pressure drop	psi
$Q$	volumetric flow	gal/min
$q$	specific gravity	-
$SG$	temperature	°F
$T$	work	HP
$W$	efficiency	-
$\varepsilon$	heat exchanger duty	BTU/hr



## Chapter 1. Introduction

Today society relies heavily on nonrenewable energy sources such as coal, oil, and natural gas. These sources are limited and are continuously depleting as the global population and energy consumption increase. These nonrenewable energy sources are also detrimental to the environment and produce harmful emissions that contribute to climate change and the global climate crisis. It is essential to find clean, renewable energy sources that don't emit dangerous gases into the atmosphere and will sustain the world for years to come.

Biomass is one potential source for the production of clean energy. Biomass includes wood, algae, food waste, sewage sludge, and other similar substances and can be used as an alternative to coal, oil, and natural gas. Biomass is favored over nonrenewable sources because it takes carbon out of the air as it is growing and then returns it when it is burned, making it carbon neutral. It is also a renewable energy source meaning that it has an infinite supply. Waste biomass, such as sewage sludge, is an especially promising feedstock because it is constantly being generated and is very cost effective.

Multiple thermochemical conversion methods exist to generate biofuels from biomass. The main processes include carbonization/ torrefaction, liquefaction, pyrolysis, gasification, and combustion. Although these methods are promising, further research and advancement in technology is needed to make them both economically and energetically competitive with existing forms of nonrenewable energy.

Hydrothermal liquefaction (HTL) is a type of thermochemical conversion method that uses hot, pressurized water to break down the biomass into liquid biocrude. HTL is an effective conversion method for sewage sludge because it utilizes a wet feedstock. This provides a very economically promising option because it uses a cheap waste as a feedstock that does not require any type of drying, saving time, energy, and money. As previously mentioned, it is crucial for sustainable fuels to have a competitive energy efficiency with the production of conventional fuels. Energy Return on Investment (EROI) is a valuable way of measuring the energy efficiency of energy processes. EROI gives a ratio of the energy supplied by a biofuel to the energy that was used in making that biofuel. It is a simple and straightforward measurement of how much energy is produced compared to how much energy is consumed.

Despite the potential for effective and efficient energy production, there are very few studies that currently exist evaluating energy return on investment for HTL. Studies that have

been published on the energy efficiency of HTL only evaluate the EROI of a single set of process conditions. Table 1 displays examples of HTL studies that have calculated an EROI for their specific process conditions. As seen in Table 1, the EROIs of HTL range from 0.5 to 3.3. There is a lack of information on trends in EROI for HTL and how various factors can impact the process's energy efficiency. To assess HTL as a competitive energy process, more research is needed on its energy efficiency and the impact of process variables on EROI.

In order to close these gaps in our knowledge, this study will determine the main factors that impact the EROI of HTL and analyze the EROI based on these factors. This information will allow anyone looking at our study to see a range of possible EROIs for HTL and project the EROI for their specific set of process conditions. With biofuels rising in popularity and importance, this information will be extremely useful for those interested in using HTL technology.

*Table 1. Literature EROI values for HTL process*

<b>Source</b>	<b>Feedstock</b>	<b>Process Conditions</b>	<b>Energy Input</b>	<b>EROI</b>
Liu et. al, 2013	Algae	Stochastic life cycle model built using excel. Data collected from Sapphire Energy pilot plant.	Algae cultivation, main energy consuming units of the HTL system, biocrude refining	~1
Anastasakis et. al, 2018	Miscanthus	Aarhus University pilot-scale HTL reactor system	Main energy consuming units of the HTL system (trim heater, reactor, and feed pump) - does not include cultivation	2.8
Anastasakis et. al, 2018	Spirulina	“	“	3.3
Anastasakis et. al, 2018	Sewage Sludge	“	“	0.5
Sawayama et. al, 1999	Japanese Oak	Liquefaction was performed using a stainless autoclave with 100 or 300 ml capacity using 0–5 wt% Na <sub>2</sub> CO <sub>3</sub> as a catalyst.	Main energy consuming units of HTL	1.8
Sawayama et. al, 1999	Sewage Sludge	“	“	2.9
Sawayama et. al, 1999	Kitchen Garbage	“	“	0.7

## Chapter 2. Background

### 2.1 The Problems Associated with Nonrenewable Energy Sources

The world population is projected to increase to 8.6 billion in 2030, 9.8 billion in 2050, and 11.2 billion in 2121 (*World Population Prospects: The 2017 Revision*, 2017). This increase in population will increase global energy consumption and will require more resources to provide power and electricity. Today, the world relies heavily on the burning of fossil fuels to generate power. Fossil fuels are energy sources formed by decayed organic matter such as plants and animals that were buried by layers of rocks. Oil, coal, and natural gas are all examples of fossil fuel energy sources. The type of fossil fuel that is formed depends on what type of matter is decayed, how long it has been buried, and the temperature and pressure conditions under which it decayed (*Fossil*, n.d.). According to the U.S Energy Information Administration, in the last 10 years 80% of the United States energy production came from the burning of fossil fuels (*Fossil Fuels Account for the Largest Share of U.S. Energy Production and Consumption*, 2020).

Because fossil fuels are a nonrenewable energy source, there is a threat of the supply being depleted. One study developed a formula for estimating when fossil fuel sources will be depleted and predicted that the oil, gas, and coal supplies will be depleted by 2040, 2042, and 2112, respectively (Shafiee and Topal, 2009). Due to the diminishing supply of fossil fuels, it is essential to find renewable sources that can provide energy indefinitely. Furthermore, utilizing fossil fuels also has a significant negative impact on the environment. Burning fossil fuels has had an immense contribution to the greenhouse gas effects which contribute to global warming and cause the melting of arctic ice, rising sea levels, extreme heat waves, and frequent occurrences of droughts and desertification (Lam, et al., 2019).

Coal is a popular, inexpensive energy source but there are severe environmental consequences associated with its use. There are multiple ways to collect or obtain coal and these methods impact surrounding habitats and ecosystems. Mountaintop removal, for example, changes the landscape of the environment while also polluting surrounding streams and threatening aquatic wildlife (*Coal and the Environment*, 2020). Underground mines do not affect the landscape as much as other methods, but they require proper ventilation of methane. In 2018, methane emissions from coal mining and abandoned coal mines accounted for about 11% of total U.S. methane emissions (*Coal and the Environment*, 2020). The combustion of coal results in

emissions of several harmful gases. For example, coal combustion produces sulfur dioxide which contributes to acid rain, nitrogen oxide which contributes to smog, and carbon dioxide which is the primary greenhouse gas and contributes to global warming (*Coal and the Environment*, 2020).

Crude oil is another type of fossil fuel that is used for petroleum products such as gasoline, diesel fuel, and heating oil. Crude oil exists in liquid or gaseous form in underground reservoirs, spaces between sedimentary rocks, and near the surface in tar sands. Producing and transporting crude oil can have negative effects on land and marine ecosystems. Fracking is an oil production technique that is used to collect oil from tight geologic formations. This technique requires an abundance of water to release oil from rock strata and also produces wastewater that can contain chemicals and other contaminants. Wastewater produced from fracking is frequently disposed of by injecting the water into deep wells, which can cause earthquakes. Oil spills are another devastating result of producing oil and are caused by accidents at oil wells or on transportation vehicles. Oil spills can contaminate soil and water, cause explosions, and lead to fires that devastate habitats (*Oil and the Environment*, 2020).

Natural gas is a fossil energy that contains many different compounds, the largest being methane. Natural gas has many uses in multiple sectors such as the electric power sector and the industrial sector. In the U.S. it is mostly used for heating and electricity. Natural gas is a relatively clean fossil fuel and its combustion results in fewer emissions of air pollutants and carbon dioxide than burning coal and petroleum products. Although it is cleaner than the other fossil fuel options, there are still negative environmental impacts. Because natural gas is mainly methane, natural gas leaks contribute to greenhouse gas emissions. Drilling wells for natural gas production can produce air pollution and disrupt surrounding people, wildlife, and water sources. Drilling wells can also result in large amounts of contaminated wastewater requiring proper handling and treatment (*Natural Gas and the Environment*, 2020).

## **2.2 Biomass as an Alternative Energy Source**

Because of the harmful effects of burning nonrenewable fossil fuels, finding an alternative energy source is necessary to protect the planet and ensure that future generations have access to renewable energy. Researchers have discovered that the conversion of biomass into biofuel is a viable option to replace fossil fuels as an energy source. Biomass sources include wood wastes, energy crops, aquatic plants, agricultural crops and their waste products,

and municipal and animal wastes (Gollakota, et al., 2018). Several processes are being explored that convert these feedstocks into bioenergy or biofuel. The term biofuels includes a range of fuels such as biogas, biodiesel, bioethanol, biohydrogen, etc. Biofuels can exist in different forms: solids, liquids, and gases. Solid biofuels refer to the raw biomass fuels and the residue after the conversion of biomass. Conversion methods produce the liquid and gas biofuels known as bio-oil and syngas, respectively (Zhang and Zhang, 2019). Table 2 below describes different types of feedstocks and the biomass and biofuels that correspond to them.

*Table 2. Feedstocks and their corresponding biofuels (Zhang and Zhang, 2019)*

<b>Class</b>	<b>Biomass</b>	<b>Biofuels</b>
Edible feedstock	Starch (wheat, barley, corn, potato); sugars (sugarcane, sugar beet); oil crops (rapeseed, soybeans, sunflower, palm, coconut, used cooking oil, animal fats)	Bioethanol, biodiesel
Nonfood-based	Forest and forest residue; agricultural biomass (straw, grass); energy crops (jatropha, cassava, miscanthus); municipal solid waste (MSW); animal manure	Hydrocarbon fuels, hydrogen, methanol, alcohols, F-T (Fischer-Tropsch) fuel, aviation fuel, olefins
Aquatic biomass	Microalgae; seaweed; microbes	Naphtha, diesel, hydrogen, methanol, ethanol
Feedstock based on nonarable land	Engineered photosynthetic microorganisms; synthetic living factories	Various tailored biofuels (in conceptual stage)

The biofuel produced from thermochemical conversion methods of biomass has multiple environmental advantages over fossil fuels. Biomass takes carbon out of the atmosphere while it is growing and returns it as it is burned which means it is CO<sub>2</sub> and greenhouse gas neutral. Additionally, plant biomass conversion results in insignificant amounts of sulfur oxide emissions. Bio-oil fuels also generate much lower nitrogen oxide emissions than diesel oil (Xiu and Shahbazi, 2012).

### 2.2.1 Waste as a Feedstock

Waste management solutions are becoming increasingly necessary as landfill space fills up and society puts an emphasis on combating climate change largely caused by burning fossil fuels. Utilizing this waste as biomass feedstock for conversion processes could help alleviate the problems associated with burning fossil fuels in addition to those associated with waste buildup. According to the United States Department of Energy, there are 77 million dry tons of waste generated each year and only 27 million dry tons are being used beneficially. This waste includes sludge/biosolids, animal manure, food waste, and fats, oils, and greases (*Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities*, 2017).

One reason that biofuels are less competitive than diesel from fossil fuels is because of the high price associated with the feedstocks (Bora et al., 2020). Sewage sludge is a promising feedstock because of its low cost and availability (Bora et al., 2020). According to the United States DOE, approximately 14 of the 77 million dry tons of waste are wastewater residuals (sewage sludge) (*Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities*, 2017). With an increase in population and industrialization, there is an increase in wastewater treatment plants and an increase in the amount of sewage sludge produced. It was reported that China saw an annual sludge growth of 13% over 9 years and anticipated 60 million tons in 2020. Additionally, the European Union and the United States produce around 50 million and 40 million tons of sewage sludge annually, respectively. Previous sewage sludge management techniques have included incineration, ocean disposal, landfilling, and agricultural usage. These management techniques have significant environmental impacts that disturb marine life and threaten safe agricultural products (Bora et al., 2020). Sewage sludge can be used as the feedstock for thermochemical processes providing an alternative to fossil fuels and a sustainable option for waste management.

### 2.2.2 Thermochemical Conversion Methods

There are five categories of thermochemical conversion methods: carbonization/torrefaction, liquefaction, pyrolysis, gasification, and combustion (Zhang and Zhang, 2019). Figure 1 displays the pathways of each of the five categories.

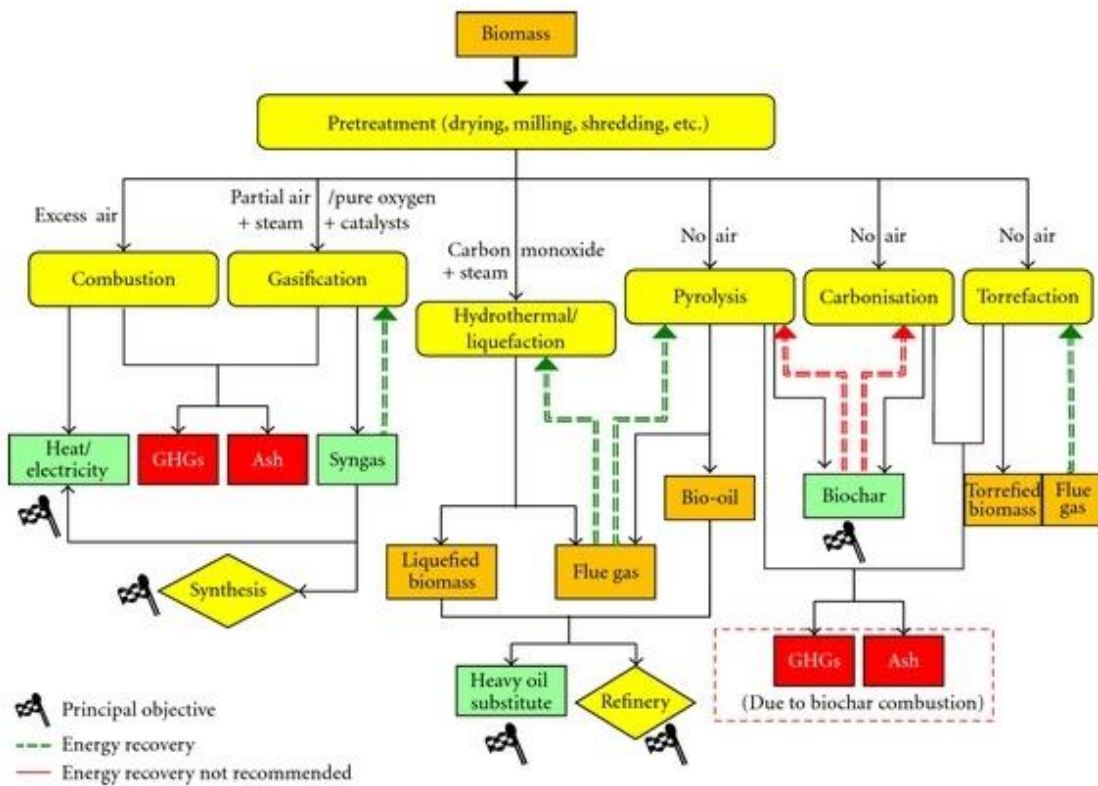


Figure 1. Thermochemical Conversion Pathways (Verma et al., 2012)

The methods are differentiated by and dependent on temperature, heating rate, and residence time (Zhang and Zhang, 2019). The temperature range for each category is shown in Figure 2.

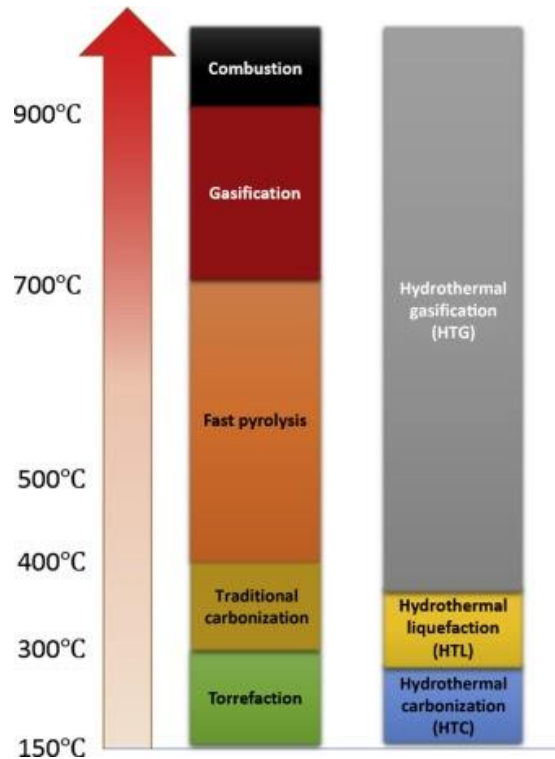


Figure 2. Temperature ranges for thermochemical conversion processes (Zhang and Zhang, 2019)

Torrefaction is a pretreatment method of biomass that improves the energy and grinding qualities of raw materials by removing moisture. This process is conducted under inert conditions, between 200°C and 300°C, and at a low heating rate. The product of this process is called torrefied biomass and it has a reduced volatile content and increased energy density (Zhang and Zhang, 2019). Carbonization is a thermochemical process to convert biomass to biochar. Compared to torrefaction, carbonization is a long-term conversion that requires a low heating rate but a high temperature above 300°C. Torrefaction and carbonization are similar processes but can be differentiated by their purpose. According to Zhang and Zhang (2019), “torrefaction targets maximizing the total energy and mass yields of biomass without severe decomposition of biomass structure.” In contrast, “carbonization aims at maximizing the fixed carbon and minimizing hydrocarbon content of the treated biomass.”

Liquefaction, also known as hydrothermal liquefaction (HTL), is the next category of thermochemical conversion processes and will be explained in detail in section 2.3. Compared to carbonization, HTL requires a lower heating rate, higher temperature, and higher pressure. The main product from HTL is bio-oil which is produced with char and gases as byproducts (Zhang



and Zhang, 2019). An important aspect of HTL is that it can convert wet biomass directly into fuels without the need for pretreatment which is important in differentiating HTL from pyrolysis. Pyrolysis is a process that occurs in the complete absence of oxygen at a high temperature range between 400°C and 700°C and at atmospheric pressure (Zhang and Zhang, 2019). Pyrolysis produces bio-oil, char, and noncondensable gas as the main products. The amount of each type of product that is produced depends on the operating conditions and the type of feedstock used. As previously stated, pyrolysis requires a dry feedstock, which means more energy is required to prepare the feed by drying compared to HTL (Zhang and Zhang, 2019).

Different from HTL and pyrolysis, gasification converts biomass directly into fuel gases that are a mixture of carbon monoxide, hydrogen, methane, and carbon dioxide. There are multiple types of gasification which are summarized in Table 3. The production of hydrogen and syngas by gasification is an economical option and the syngas can be used for methane production as well. The fuel gas produced can be combusted for power and heating (Zhang and Zhang, 2019).

*Table 3. Types of gasification summary (Zhang and Zhang, 2019)*

Process	Working conditions	Products	Heating value (MJ/m <sup>3</sup> )
Partial oxidation with air	700°C–900°C; ST atm	CO, CO <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> , tar	~5
Partial oxidation with oxygen	700°C–900°C; ST atm	CO, CO <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub> , tar	~10–12
HTG	≥ 370°C; ≥ 22 MPa	CO, CO <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub> , tar	~15–20

Direct combustion is the last and most common method for converting biomass to energy and involves burning biomass in open air or in the presence of excess air (Lam et al., 2019). This method converts the photosynthetically stored chemical energy of the biomass into heat, mechanical power, and electricity. This process is carried out in furnaces, boilers, and steam turbines at around 800-1000°C (McKendry, 2002). Direct combustion requires pretreatment of the biomass such as dehydrating, cutting, and crushing, which makes the cost slightly higher than other methods such as pyrolysis and gasification (Lam et al., 2019).

### **2.3 Hydrothermal Liquefaction (HTL)**

As briefly discussed, Hydrothermal Liquefaction (HTL) is a thermochemical conversion method used to convert wet biomass into biocrude, an oil product that can be upgraded into

biofuel. HTL uses hot, pressurized water to break down the solid biopolymeric structure of the biomass into primarily liquid components. Average processing conditions range from 523-627 K for temperature and 4-22 MPa for pressure, which are just below the critical point of water at 647 K and 22 MPa (Elliott et al., 2014). At this temperature and pressure, water becomes a better solvent for nonpolar materials, including organic compounds that are contained in the biomass feedstock. Subcritical water also supplies a source of hydrogen and increases the concentration of reactive protons and hydronium ions in liquefaction reactions. In this manner, it can act as both a catalyst and a reagent for HTL and is therefore instrumental to the process (*Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities*, 2017).

Due to the use of water in the energy conversion process, HTL provides an opportunity to convert biomass into oil without the need to remove water from the feedstock, making it suitable for wet feedstocks. Similar to the above processes, potential feedstocks for HTL can include algae, agricultural waste, sewage waste, and other biomaterials with a significant water content. A study from the Biological and Agricultural Engineering Department at Louisiana State University compared dairy manure, poultry litter, pine sawdust, tallow seeds, switchgrass, peanuts, and vegetable oil as feedstocks to determine which types of biomass generate the best results. The study found that dairy manure produced the highest energy recovery of 70.8% and determined that effective energy conversion through HTL does not require a feedstock with high oil content or high lipid concentrations, making waste feedstocks a viable and low-cost option (Midgett et al., 2012).

In addition to the potential of using low-cost feedstocks, the actual conversion process of the waste feedstock to biofuel is economically feasible when compared with current energy costs. The Pacific Northwest National Laboratory completed an in-depth economic analysis of sludge HTL and centralized biocrude upgrading and concluded that it has “the potential to be competitive with fossil fuels” (Seiple et al., 2017). The estimated selling price for biofuel produced through this process is \$3.46/gasoline gallon equivalent (gge), which is within the +0.49/gge tolerance of the \$3/gge cost target for biofuel developed by the Bioenergy Technologies Office (BETO) through the U.S. Department of Energy (Seiple et al., 2017). The opportunity to produce biofuel from sludge HTL while remaining within BETO’s cost targets provides a strong groundwork for this process and encourages further investigation.

### 2.3.1 Process Overview for Sludge HTL

Along with completing an in-depth economic analysis of sludge HTL and biocrude upgrading, the Pacific Northwest National Laboratory outlined a detailed method for these processes based on designs for HTL of wood and algae feedstocks. The figure below displays their model of the general process of sludge HTL.

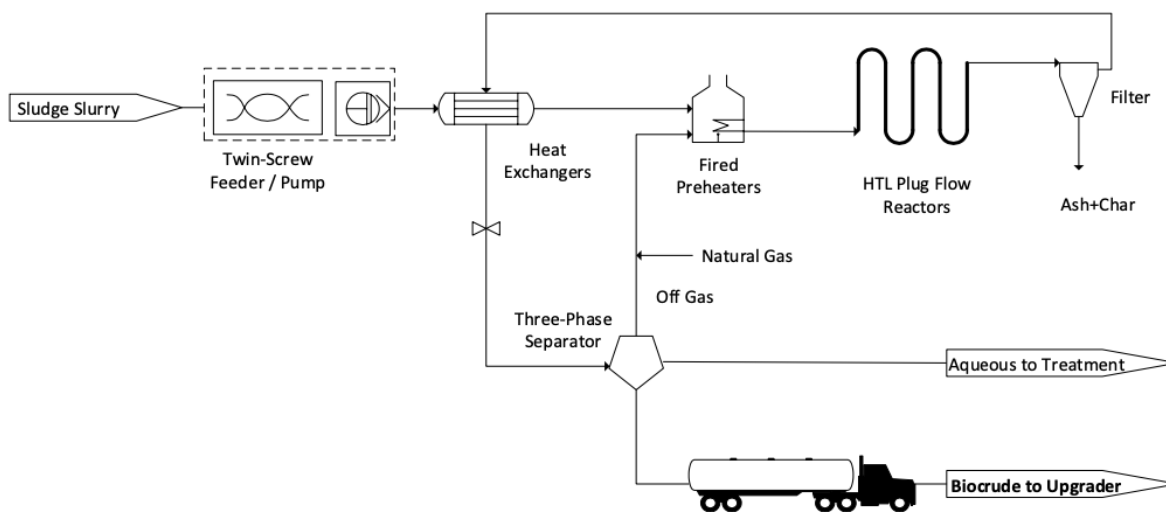


Figure 3. Process diagram for HTL of sludge (Seiple et al., 2017)

As demonstrated in Figure 3, the slurry feed enters the process through a pump and is then preheated using heat from the liquid biocrude product stream. A fired heater using heat from the reactor off-gas as well as additional natural gas is then used to bring the feed up to the reactor temperature of 656°F (347°C). Once the feed is heated and pressurized, it enters the HTL reactor and is converted into an organic biocrude phase, an aqueous phase, solid waste (ash + char), and off-gas. The biocrude phase consists of fatty acids, amides, ketones, hydrocarbons, phenols, alcohols, as well as other components. According to Seiple et. al at the Pacific Northwest National Laboratory, the HTL reaction generally consists of three parts:

1. Depolymerization of the biomass components
2. Decomposition of biomass monomers by cleavage, dehydration, decarboxylation, and deamination
3. Recombination of reactive fragments

The effluent from the reactor enters a hot filter which removes the solid waste stream that contains 60-70% water plus additional ash, char, and a small amount of organics lost from the biocrude and aqueous phases. After the solids have been filtered out, the biocrude and aqueous

gas mixture are cooled before entering a three-phase separator to divide the biocrude, aqueous, and off-gas streams. The biocrude is stored to be later upgraded and the off-gas is recycled back into the system to be used for preheating. The aqueous stream contains water, traces of soluble organics, ammonia, and metal salts and is sent to a treatment plant (Seiple et al., 2017).

### 2.3.2 Process Overview for Biocrude Upgrading

Once biocrude is produced through the Hydrothermal Liquefaction process, it must go through upgrading to remove oxygen, nitrogen, and sulfur to make it a viable fuel. Upgrading uses a catalytic process and is also known as hydrotreating. Upgrading is typically done on a larger scale than HTL, allowing one upgrading facility to process biocrude from approximately ten HTL plants. Before upgrading can take place, a desalting process is needed to remove inorganic compounds from the biocrude to eliminate interference with the hydrotreating catalyst. Once the desalting process is complete, upgrading follows the process illustrated in Figure 4 below.

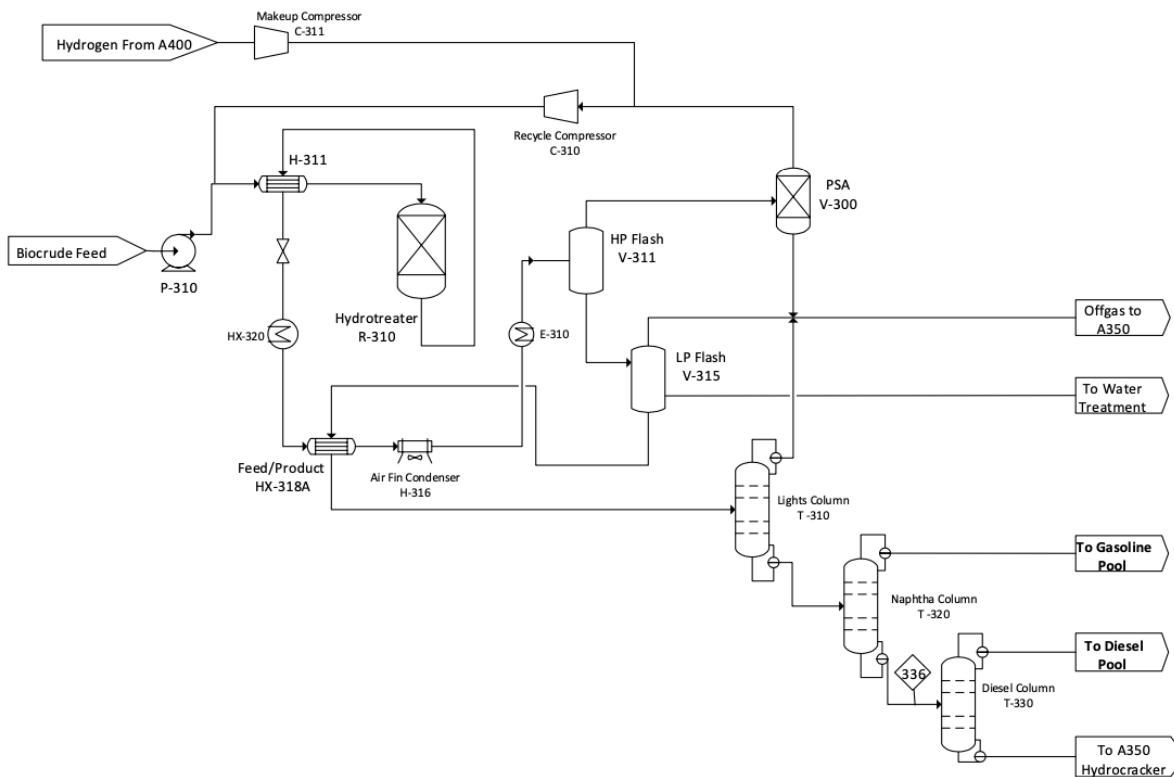


Figure 4. Process diagram for upgrading of HTL biocrude (Seiple et al., 2017)

The desalted biocrude enters the process through a pump to increase pressure, is mixed with compressed hydrogen, and then preheated to the reactor temperature. Hydrogen can be produced onsite by purifying the off-gas and supplemental natural gas. In the hydrotreater, biocrude oxygen reacts to become CO<sub>2</sub> and water, nitrogen reacts to become ammonia, and sulfur reacts to become hydrogen sulfide. The resulting stream contains paraffins, olefins, naphthenes, and aromatics. After the biocrude reacts in the hydrotreater, it is used to heat the feed stream and then is sent to a guard bed to remove soluble iron. Some sludge feedstocks may not contain soluble iron, and a filter can be used for mineral removal instead. This stream is then cooled to condense the water and hydrocarbons. A series of distillation columns are used to fractionate the organic phase into four streams with varying boiling points: C4 minus, naphtha range, diesel range, and heavy oil range material. The heavy stream is sent to a hydrocracker to yield more naphtha and diesel range products. The produced wastewater contains high levels of ammonia and is sent to another area to be treated (Seiple et al., 2017).

## **2.4 The History of HTL and Current Applications**

As discussed in section 2.2.2, a variety of processes have been extensively explored to produce biofuel, and HTL is no exception. Research on HTL began as early as the 1930s and expanded in 1970 at the Pittsburgh Energy Research Centre where a process to convert a commercial scale of cellulose biomass to heavy oil was introduced. This process was further developed by various researchers in the following years, most notably Beckman and Elliot in 1985 who discovered the effects of changing parameters such as temperature, pressure, time, and the catalyst on the product output, and Dote et al. in 1994 who pioneered HTL of microalgae with high lipid content. Algae then became a popular feedstock for HTL, and still remains popular. Despite the popularity of algae, Itoh et. al developed a scale up for HTL of sewage sludge in 1994 leading to the investigation of various feedstocks. Many other researchers have contributed more recently to the advancement of HTL technology through experimentation related to specifications of different parameters, applications, and feedstock possibilities. Despite this exploration, gaps still remain in the knowledge of the reactor mechanisms (Gollakota et al., 2018). Continued research hopes to fill these gaps as well as discover additional advancements to further refine the process.

Currently, HTL has started to enter industry and is in the early stages of commercialization. The Pacific Northwest National Laboratory is one of the leaders in the

technology and has developed a continuous HTL reactor for various biomass feed slurries. The University of Aalborg possesses a pilot plant designed to operate at supercritical conditions with a focus on recycling the water phase (Beims et al., 2020). Furthermore, the Danish-Canadian company Steeper Energy at the University of Aalborg has developed the Hydrofaction™ process which also operates above the supercritical point of water and recycles both the oil and process water effluent. This process uses primarily hardwood and softwood forest and mill residues as feedstock and can achieve a 45% oil yield on a mass basis and 85+% on an energy basis (*Hydrofaction® – Steeper Energy*, n.d.). Additionally, the Australian company Licella and the American company Genifuel have also developed HTL processes and begun commercialization (Beims et al., 2020).

While some companies have already started HTL operations, others are becoming interested in the technology as it becomes more well-known. Charm Industrial is a California-based company with a mission to return the atmosphere to 280 ppm CO<sub>2</sub>, which is equivalent to the level of CO<sub>2</sub> prior to the industrial era. Charm Industrial is currently focused on converting waste biomass into bio-oil through pyrolysis and also works to inject bio-oil underground to contribute to negative emissions. In addition to sequestering the bio-oil, the company is able to reform it to produce green hydrogen which can act as a fuel or an industrial chemical (*Charm Industrial*, n.d.). Pyrolysis has proven to be an effective method of converting wet biomass to bio-oil, but Charm Industrial has identified HTL as a potential alternative method.

Although HTL is making progress in industry, there are some challenges associated with scaling up the process. First, biomass has a low density and therefore can be expensive to use as a feedstock. For example, bark and sawdust have a density of about 0.32 and 0.2 tons/m<sup>3</sup> while petroleum has an average density of 0.88 tons/m<sup>3</sup>. The low density of the biomass requires extremely large volumes of feedstock which can be expensive to transport and process. Additionally, the presence of solids in the product stream makes separation difficult and time-consuming. If the separation is not properly executed, the solids can block the reactor outlet or other parts of the system downstream. Lastly, as previously discussed, upgrading is required to obtain a usable bio-oil. This is an expensive and complicated step, which can deter or hinder companies from using HTL. (Beims et al., 2020). Despite these challenges, HTL has the potential to provide a bio-oil with a higher carbon content and greater energy capacity, although

further analysis is needed to determine the factors that affect biocrude yield and the favorability of the energy trade-off when taking into consideration the energy needed for production.

## **2.5 Importance of Sludge Water Content**

As HTL becomes widely used across companies like Charm Industrial and Steeper Energy, it is important to understand the different factors that can affect biocrude yield. According to Qian et. al. (2017) and Akhtar and Amin (2016), a wide range of factors have been found to impact the yield of biocrude including water loading, sludge moisture content, recovery solvent, reactor residence times, rate of biomass heating, size of biomass particles, and additives. While all factors hold significant importance when it comes to product yield, sludge moisture content was found to have a larger impact not only on biocrude yield but also on energy input to the system.

As mentioned previously, HTL was designed to handle high moisture contents in biomass as opposed to using costly dehydration methods for pyrolysis (Akhtar and Amin, 2016). Because HTL is known to liquefy biomass with any level of moisture content, it becomes important to find the ideal water loading that produces the most biocrude. An analysis completed by Qian et. al., (2017) used a mini batch reaction system to perform multiple trials on feedstocks with differing water contents. As shown in Figure 5 below, a maximum biocrude (BC) yield (wt%) of 27% was produced with a feed moisture content (wt%) of 85% for conventional isothermal HTL. It is also important to note that biocrude yield only fluctuates slightly with feed moisture content. As seen below, biocrude yield only varies 3 wt% between 24% and 27% with an increase in feed water content. This slight variation in biocrude yield might be due to faster sludge hydrolysis reactions when more water is present. A higher water content also helps to produce more organic compounds, which then increases both the biocrude and aqueous product yields. However, as moisture content reaches 100%, dehydration reactions of water-soluble compounds that help to produce biocrude are suppressed (Qian et. al., 2017). This is why a slight decrease in biocrude yield can be observed from 85% to 100% moisture content. Despite faster hydrolysis reactions in the presence of high moisture contents, too much water will result in the suppression of biocrude producing reactions. Because feed moisture content does not play a large role in the yield of biocrude, it becomes important to look at other factors that impact the HTL process.

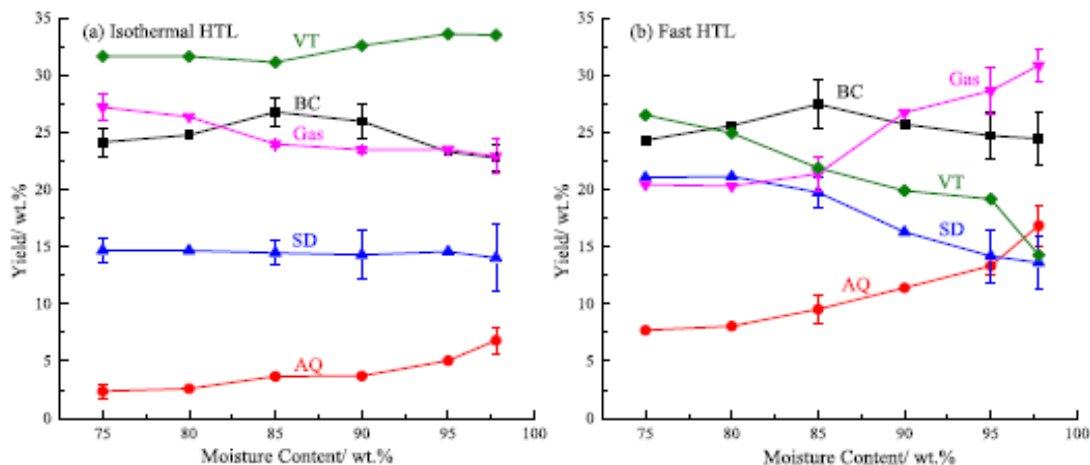


Fig. 3. Effect of moisture content on product fraction yields, VT = volatiles, BC = biocrude, SD = solids, AQ = aqueous phase products: (a)  $T = 673\text{ K}$ ,  $t = 60\text{ min}$ , vol% water = 34.0%; (b) set-point  $T = 773\text{ K}$ ,  $t = 1\text{ min}$ , vol% water = 10.9%.

Figure 5. Biocrude yields for various feed moisture contents for isothermal HTL (Qian et al., 2017)

While feed moisture content can directly affect the biocrude yield, it also plays a large role in the equipment and energy required for the process. The HTL process is mainly composed of pumps and heat exchangers to account for the large temperature increases and pressure differentials required for biocrude production. Looking into pumps, Snowden-Swan et al. (2016), found that a maximum of 20% total solids is possible while still enabling effective pumping. This value was obtained as any solids content greater than 20% would likely clog any pumps in the system leading to maintenance costs or equipment replacement. However, reducing feed water content so that feed solids is greater than 20% would reduce the total mass flow to the plant. This effectively reduces equipment sizing, associated capital costs, and operating costs. These two perspectives on pump operation make it difficult for companies to optimize their feed solids content. While a higher solids content helps to reduce the energy in operating the pump, too little water in the feed will result in pump failure.

Another factor that greatly impacts energy consumption for HTL is the use of heat exchangers. Because HTL must run at temperatures between 523-627 K, the amount of water in the feed has a substantial impact on the heat required to run the exchangers (Elliott et al., 2014). The main factor affecting the heat required for the exchangers is specific heat capacity. Specific heat capacity is the ratio of the quantity of heat required to raise the temperature of a body one degree to that required to raise the temperature of an equal mass of water one degree (Davis et. al., 1995). While the specific heat of water is 4.186 J/g K, the average specific heat of



biomass required for HTL is 1.13 J/g K (Domalski et. al., 1986). Because the specific heat of water is much greater than that of biomass, it takes much more energy to heat feedstocks with greater water contents. However, many HTL feedstocks are harvested with water contents from 90%-99% (wt%), which means the feedstock must be dried or pressed before it can be used. This then creates a tradeoff between using higher water contents in the HTL process to reduce the energy needed in the drying process or using drier feeds to reduce the energy needed in the heat exchangers and pumps.

## **2.6 Evaluating Energy Efficiency of Energy Processes**

There are several performance metrics involved in evaluating the energy efficiency of different energy processes. Product yield is one of the most important metrics and demonstrates how much product, in this case bio-oil, is created from the feedstock. Other metrics include temperature, the cost of the feed, the value of the products, and the amount of energy input into the process. These metrics display how efficient the process is in creating energy as well as how cost-effective the process is. There are several different methods of combining these metrics to evaluate an energy process, including measuring emergy, exergy, energy payback period, and EROI. Each of these methods has benefits and limitations, explained in the following sections.

### *2.6.1 Emergy*

Emergy is a method used to evaluate the energy used directly or indirectly to make a product or service. It illustrates all of the energy contributed by the environment to sustain a system. The unit of emergy is emjoules, which refers to the available energy consumed in the past (Chen et al., 2006). This method of analysis places value on the energy invested in creating the process, not only the energy needed to keep it running. According to Sciubba & Ulgiati (2005), “emergy is often used as a measure of sustainability and/or pressure on the environment by the system.” Emergy is effective in providing a comprehensive evaluation of the energy expended to create a process, allowing for an understanding of how many resources are needed. However, it is difficult to calculate and does not provide information on any performance measurements other than energy consumed in the past.

### 2.6.2 Exergy

Another method to evaluate the energy efficiency of an energy system is an exergy analysis. Because the performance of many energy systems cannot be evaluated efficiently with the use of an energy analysis, exergy analyses are often used to enhance standard energy analyses. Exergy can be defined as the maximum amount of work produced by a system while being brought into equilibrium with a reference environment. In other words, exergy can be thought of as a measure of the quality or usefulness of energy produced by a system (Terzi, 2018). An exergy analysis also identifies the locations, magnitudes, and sources of thermodynamic inefficiencies in thermal systems. This attribute in exergy analyses helps to improve not only the overall efficiency of a system but also the cost effectiveness of a system (Tsatsaronis, 1999). The use of exergy to evaluate the efficiency of a system has helped to detect areas in need of improvement. This analysis then helps to evaluate the sustainability of a process and how to improve it (Arango-Miranda et. al., 2018). Despite the value in using exergy to evaluate the sustainability of existing processes, it becomes more difficult to use this analysis for new energy systems.

### 2.6.3 Energy Payback Period

Energy payback period is another method for evaluating the efficiency of an energy system. This method is more commonly used for evaluating solar energy systems such as solar panels. The energy payback period is defined as, “the required period in which the PV system can produce the same amount of electricity (converted into equivalent primary energy) with the energy consumed over its life cycle” (Asdrubali and Umberto, 2019). More generally, energy payback period can be used to determine the time it takes for an energy system to produce the amount of energy that is put into the system. Energy payback period is a useful analysis because it determines whether a system is achieving a net gain of energy (Asdrubali and Umberto, 2019).

### 2.6.4 Energy Return on Investment for HTL

One of the most prominent techniques to measure the energy effectiveness of a process is known as an energy return on investment analysis. Energy return on investment, or EROI, measures the energy quality of various fuels by calculating the ratio between the energy provided by a particular fuel and the energy invested in creating and delivering the fuel (Hall et. al., 2013). Similar to other methods, EROI is also used to assess the feasibility and sustainability of an

energy source. To simply calculate EROI, the energy produced is divided by the amount of energy required to produce that energy. This takes into account both how high the yield of biocrude is as well as how much energy is needed for production. Fuels like oil and gas, coal, and wind energy have an EROI of about 15, 80, and 19 respectively (Beal et. al., 2012). To be produced commercially, new sustainable fuels like biogas and biodiesel must have a competitive EROI with conventional fuels. An EROI study at the University of Texas in Austin found algal biocrude to produce an EROI significantly less than 1 (Beal et. al, 2012). Similarly, the Department of Energy also reported a negative energy return on investment for the conversion of soybeans into biodiesel (Pimentel and Patzek, 2005). Because of the possibility of such low EROIs for certain methods, it becomes increasingly important to analyze processes where a competitive EROI can be achieved for biofuels.

Despite the apparent benefits of using an EROI analysis, there are a few drawbacks and limitations. Hall et. al. (2013) demonstrates the variability in published values of EROI for similar fuels. For example, natural gas was found to have EROI values ranging from 20, to 26, to 38 (Freise, 2011). Despite these differences, the proposed variability can be largely reduced when similar boundaries are used for the assessment. As shown in Figure 6 below, Hall et. al (2013) explores 4 different EROI boundaries and how they are used. A standard EROI (EROI<sub>ST</sub>) analysis divides energy output by the sum of direct and indirect energy used, covering only up to where the fuel leaves the production facility. Point of use EROI (EROI<sub>POU</sub>) includes the costs associated with refining the fuel, therefore decreasing the EROI. Extended EROI (EROI<sub>EXT</sub>) looks at the total energy required to make the fuel as well as transporting and using the fuel. Finally, societal EROI (EROI<sub>SOC</sub>) sums all gains from fuels and all costs of obtaining them. Through consistency with these different approaches to calculate EROI, variability across the same fuels can be greatly reduced.

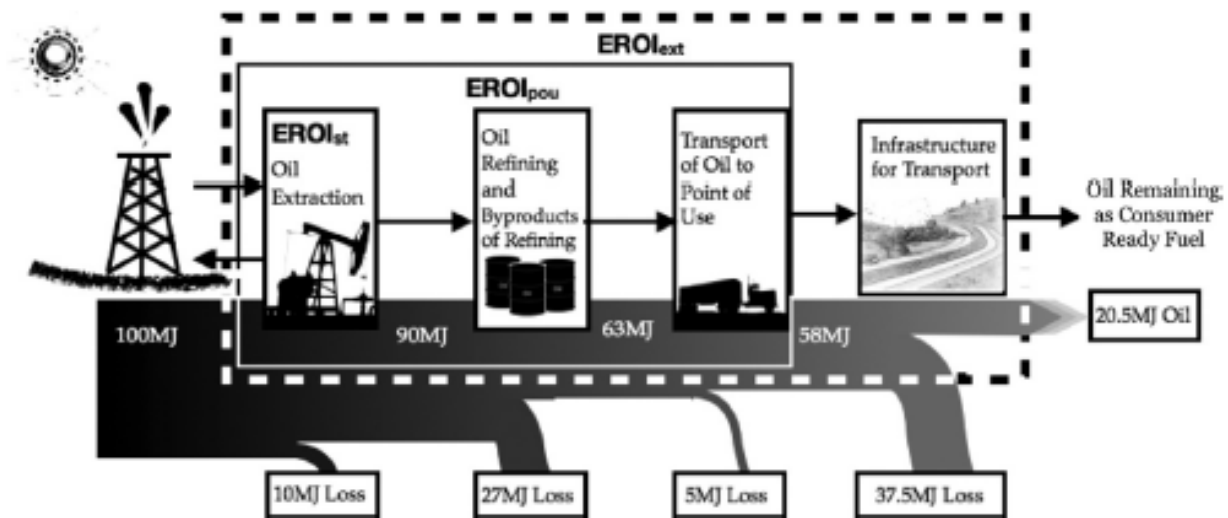


Figure 6. Boundaries of various EROI analyses (Hall et. al., 2013)

Despite some limitations, EROI is a useful analysis when it comes to evaluating HTL as a method of biofuel production. As of 2020, there have been very few studies looking into the EROI of HTL. Liu et. al., (2013) were able to conduct a study on HTL of algae where a stochastic life cycle model was built using Microsoft Excel and data collected at the Sapphire Energy pilot facility. Boundaries for this analysis include the cultivation of algal biomass, hydrothermal liquefaction process, and refining of biocrude constituting a point of use EROI. Using this method, they were able to determine an EROI of around 1 for both biodiesel and biogas based on values collected between 2012 and 2013 in pilot scale operations at the Sapphire facility. Despite the usefulness of this study, a lack of HTL EROI data still exists. With the lack of information on the EROI of HTL, it is difficult to understand how different process variables would impact energy consumption. For HTL to become an energy efficient process, complete EROI analyses will need to be completed, incorporating new technology. New technology possibilities include looking into upgrading technologies that use less energy than conventional refining and improving process and separation efficiencies to minimize waste and emissions (Ramirez et. al., 2015).

## **Chapter 3. Methods**

This study aims to understand the impact of influential variables on the energy return on investment of hydrothermal liquefaction. In order to achieve this, first we explored process variables that impact the energy return on investment for HTL. We then further analyzed the effect of the most impactful variables on trends in energy return on investment. Finally, we incorporated biocrude upgrading as a correction factor then projected EROI values for HTL data from various literature studies.

### **3.1 Developing the HTL Process**

To study the EROI of HTL, we first needed to understand the HTL process. A study from the Pacific Northwest National Laboratory (PNNL), “Conceptual Biorefinery Design and Research Targeted for 2022: Hydrothermal liquefaction Processing of Wet Waste to Fuels” by Snowden-Swan et. al. in 2017 was used as a guide for this analysis. The process of HTL requires heating and pressurizing the feed to produce a reaction, then cooling and separating the product. PNNL’s analysis of HTL uses a bench scale system as shown in Figure 7. The PNNL bench scale system requires two pumps and three heat exchangers to prepare the feed for the reactor. After reacting, the product stream passes through a solids filter, heat exchanger, depressurizing valve, and subsequent condenser before passing through a three-phase separator. This separator splits the existing product stream into three components: an aqueous phase, biocrude, and fuel gas.

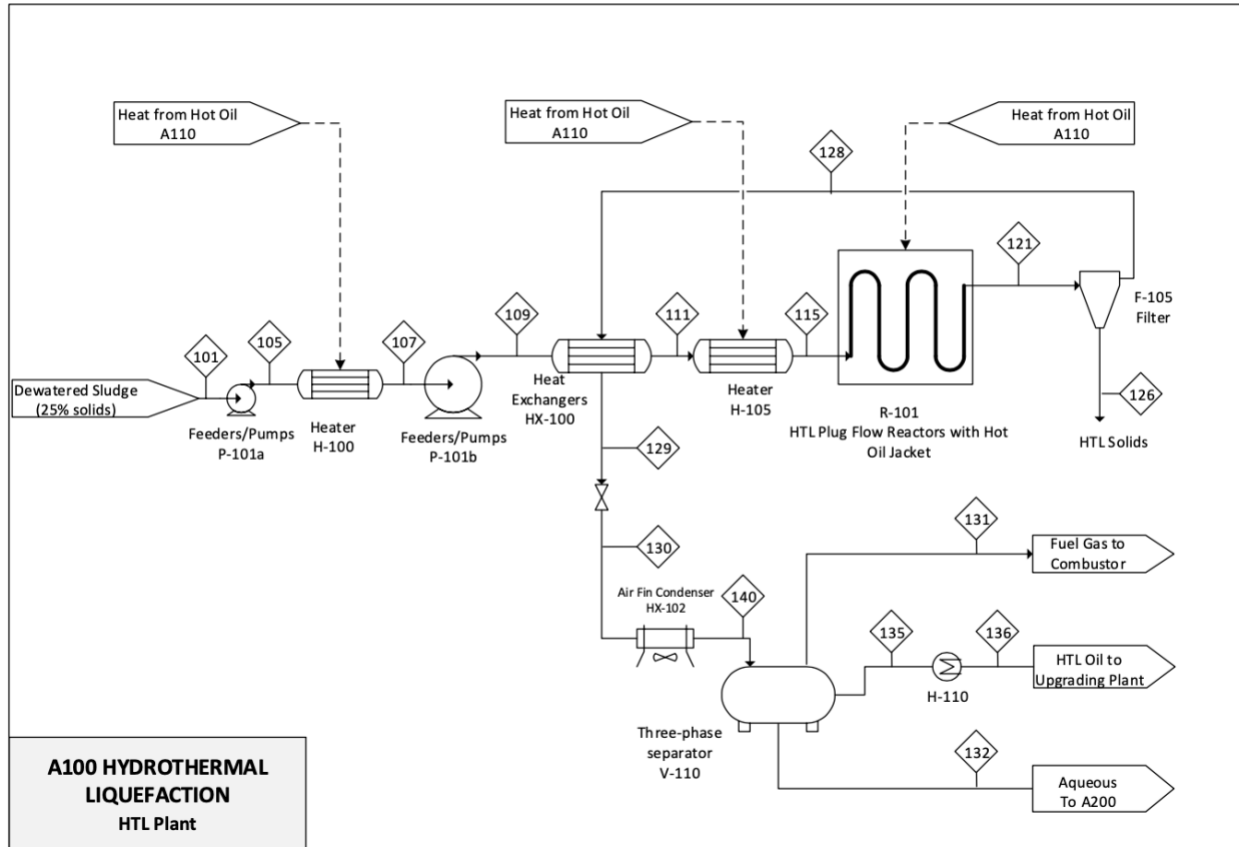


Figure 7. Bench scale HTL process used by PNNL (Snowden-Swan et al., 2017)

Using the PNNL bench scale HTL system for reference, our group simplified the HTL process for ease of calculations and analysis. Figure 8 below shows our simplified HTL process. A singular pump is used to pressurize the feed as opposed to PNNL’s two pump system. Instead of two stand-alone heat exchangers and a heat recovery system, one feed/product heat exchanger is used followed by one stand-alone heat exchanger. After reacting, the solids are filtered out and the remaining products are depressurized and cooled in the same manner as the PNNL process. Next, rather than entering another condenser before being separated further, the products simply enter a three-phase separator where three products are obtained: fuel gas, biocrude, and an aqueous phase. The biocrude phase is then cooled further to allow for transportation and handling. It is also important to note that our analysis does not include the use of hot oil for heat exchangers and the reactor. By simplifying the HTL process, we were able to thoroughly examine multiple variables that have an impact on energy consumption.

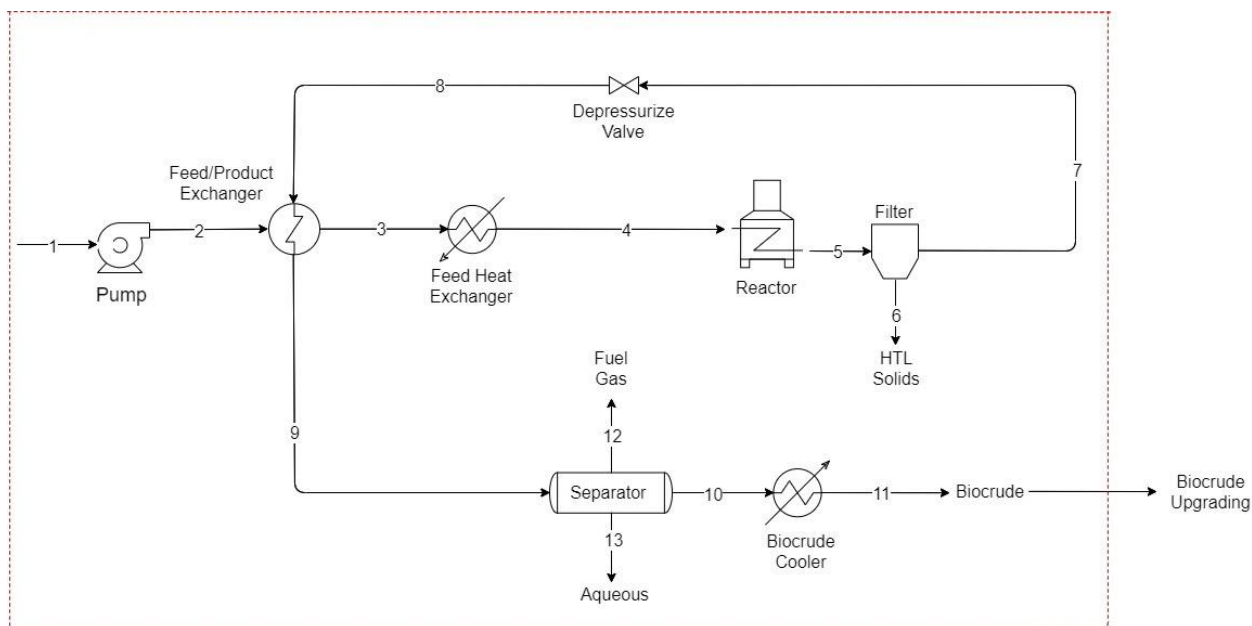


Figure 8. Simplified HTL process

### 3.2 Calculating the EROI Base Case

A base case for EROI was first calculated using the same process conditions as the PNNL study, as shown in Table 4 and Table 5. Our analysis is based around standard EROI which only includes the energy required to produce biocrude via HTL. All energy consuming equipment is involved in the EROI analysis. The setup of our excel model can be found in Appendix A.

Table 4. HTL base case conditions

Operating Conditions and Results	PNNL Experimental Results
Dry Biomass Feed (kg/day)	99,790
Feed Solids (wt%)	25%
Product Yields (wt%)	
Biocrude	44%
Aqueous	31%
Gas	16%
Solids	9%

Table 5. Temperature and pressure properties of HTL streams

Stream Number	1	2	3	4	5	6	7
Temperature (°C)	15.5	15.5	—	346.7	346.7	346.7	346.7
Pressure (MPa)	0.1	20.8	20.8	20.8	20.8	20.8	20.8
Stream Number	8	9	10	11	12	13	
Temperature (°C)	346.7	60	60	43.3	60	60	
Pressure (MPa)	0.2	0.2	0.2	0.2	0.2	0.2	

\*Stream 3 does not have a set temperature as it depends on water content in the feed

### 3.2.1 Pump

The pump duty was calculated in kilowatts using Eqn. 1. The volumetric flow in cubic meters per hour was calculated by dividing feed mass flow by the density of the feed. The density of the feed was calculated using a weighted average between water and sewage solids, where the density of water is 999 kg/m<sup>3</sup> and the density of sewage solids is 1400 kg/m<sup>3</sup> (Dokuz Eylül University, nd.). The pump head in meters was calculated using Eqn. 2. The specific gravity of the fluid was calculated from the density of the feed. Pump efficiency was estimated as 50%.

$$W = \frac{Q * \rho * g * h}{3.6 * 10^6 * \varepsilon} \quad \text{Equation 1}$$

$$h = \frac{\Delta P * 100000}{\rho * g} \quad \text{Equation 2}$$

### 3.2.2 Heat Exchangers

All heat exchanger duties were calculated using Eqn. 3. Specific heat capacity for the feed and product streams was calculated using weighted averages of the components in each stream. Specific heat capacities of sewage solids, water, biocrude, aqueous, and fuel gas can be found in Table 6. Stream 8 was cooled from 347°C to 60°C using cold feed stream 2, which consequently was heated from room temperature. The use of this heat exchanger allowed for heat



recovery in the HTL system. The feed heater was then used to heat feed stream 2 to 347°C. The biocrude product was cooled from 60°C to 43°C to allow for proper transportation and handling.

$$q = m * C_p * \Delta T \quad \text{Equation 3}$$

*Table 6. Specific heat capacity values for various HTL components*

<i>Component</i>	<i>C<sub>p</sub></i> (kJ/kg°C)	<i>Retrieved From</i>
sewage solids	1.13	(Domalski et. al, 1986)
water/aqueous	4.44	( <i>Liquid Water—Properties at various Temperature and Pressure</i> , n.d.)
biocrude	2.44	(Eicher, 2013)
gas (mostly CO <sub>2</sub> )	0.167	( <i>Carbon Dioxide Gas—Specific Heat</i> , n.d.)

### 3.2.3 Reactor

The heat of reaction for the production of biocrude from biomass was identified from PNNL’s study as 761 kJ/kg. Therefore, reactor duty was calculated using equation 4.

$$W = H_{rxn} * m * 0.277 \quad \text{Equation 4}$$

### 3.2.4 Calculating EROI

EROI is the ratio of energy produced to energy consumed for the production of biofuels. Using the boundaries in standard EROI, as explained in section 2.6.4, the energy produced was found by multiplying the heating value of biocrude, 39.5 MJ/kg, by the amount of biocrude produced. The energy consumed was found by summing all of the duties from heat exchangers, pumps, and reactors in the HTL processes. Dividing energy produced by energy consumed resulted in a value for EROI.

### 3.3 Sensitivity Analysis

A sensitivity analysis was performed for influential variables on EROI for the HTL process that was previously modeled. The variables that were chosen were the solids loading fraction of the feed, biocrude yield percent, heating value of the biocrude, heat exchanger duty, feed heat capacity, and pump efficiency. These variables were chosen because they had the largest predicted potential to impact EROI within the parameters of this study. Additionally, all of these variables were likely to have some variation depending on the details of the process. The solids loading fraction varies with every feedstock depending on the water content. The biocrude yield percent changes based on various process conditions. Similarly, the heating value of the biocrude is dependent on the exact composition of the product and has the potential to differ for each unique process. The variation in heat exchanger duty represents heat exchanger efficiency, as the duty changes depending on the efficiency of the heat exchangers. The feed heat capacity varies due to the composition of the feed, which can fluctuate between sewage sludge, wood, algae, and other biomasses. Lastly, pump efficiency is specific to each pump and is likely to vary from one process to another.

Once the variables included in the sensitivity analysis were determined, a minimum and maximum were set for each one. Table 7 provides the minimum and maximum values for each variable used in the analysis. The minimum and maximum values were approximated by completing a literature review of experimental trials on HTL. Xu, et al. performed a study that provided the minimum solids loading and biocrude yield for the sensitivity analysis (2019) while Obeid, et al. performed a study that used the maximum solids loading for the analysis (2020). The maximum biocrude yield is represented by a study published by Zhao et al (2013). Additionally, the minimum and maximum heating values for the sensitivity analysis were found in studies published by Xu, et al. (2018) and Koley et al. (2018), respectively. Using “Thermodynamic data for biomass conversion and waste incineration”, a range for specific heat was found through compiling different plausible feedstocks for HTL (Domalski, 1986). Regarding pump efficiency, according to Joe Evans of Pumps and Systems®, medium to large pumps operate in the range of 75 to 93 percent efficient while smaller pumps fall into the 50 to 70 percent range (Evans, 2012). Because a pump was not sized for this analysis, we chose to use a median conservative efficiency of 50%. Efficiency was then varied  $\pm 20\%$  for the sensitivity analysis. In the study performed by PNNL, no specific heat exchanger efficiency value was

noted. To represent variation in the heat exchanger efficiency, we chose to vary the heat exchanger duties. Heat exchangers typically range from 80% to almost 100% efficient (*Heat Exchangers*, n.d.)). To ensure that we covered the full range of efficiency, we chose to vary the heat exchanger duty  $\pm 20\%$  in either direction. After identifying minimum and maximum values for each variable, the middle value for each variable was determined from the PNNL process since that was the base case for this study. This value was also assumed to be the most likely value for each variable.

*Table 7. Variables' Minimum and Maximum Values for Sensitivity Analysis*

Variable	Minimum	Maximum	Source
Solids Loading (wt fraction)	0.10	0.30	(Xu, et al., 2019) (Obeid, et al., 2020)
Biocrude Yield (wt fraction)	0.20	0.60	(Xu, et al., 2019) (Zhao, et al., 2013)
HHV (MJ/kg)	33	41	(Xu, et al., 2018) (Koley, et al., 2018)
Heat Exchanger Duty (MJ)	1,677	2,514	(IPIECA, 2021)
Feed Heat Capacity (kJ/kg°C)	0.91	1.37	(Domalski, et al., 1986)
Pump Efficiency	30%	70%	(Evans, 2012)

Next, the EROI was determined at the minimum and maximum value while holding all other variables constant. Once EROI was determined, a tornado plot was created to display the minimum and maximum EROIs for each variable. This plot was used to demonstrate how drastically the EROI changed resulting from the fluctuation of several variables.

### 3.4 Analyzing Important Process Variables

Using the sensitivity analysis, we determined which variables had the largest impact on EROI. After identifying these variables, we continued to analyze how EROI would be impacted by the variables using graphs and plots. This also included incorporating the energy consumption of biocrude upgrading into our EROI analysis as a correction factor.

### *3.4.1 Upgrading*

While HTL is efficient in producing biocrude, this product must go through multiple stages of upgrading to be used as a viable fuel. PNNL's study provides a guide for upgrading biocrude into gasoline and diesel. For our analysis, we used data directly from PNNL's upgrading processes to calculate energy input. All upgrading equipment duties were found from the study. This includes all heat exchangers, pumps, and compressors in the hydrotreating and hydrocracking processes of upgrading, as well as the hydrogen plant, product cooling system, and steam system. These values take into account the upgrading energy required for the biocrude products of 10 HTL plants. We then calculated various EROIs that incorporated the energy used by the upgrading equipment and used the final gasoline and diesel heating values to represent energy output. The energy input and outputs of the upgrading process are detailed in Appendix B and C, respectively. This allowed us to make our EROI analysis more comprehensive with values that represent the production of a more useful biofuel.

### **3.5 Literature Projection**

Once the EROI analysis including upgrading was complete, we superimposed data from published HTL studies onto our EROI plot. The published data used in the analysis represented multiple categories of feedstock such as wood and algae. This analysis would allow someone conducting HTL to use our plot to project their EROI based on their process variables and/or feedstock composition.

## Chapter 4. Results and Discussion

### 4.1 Sensitivity Analysis

Figure 9 shows the effect of biocrude yield, feed solids loading, biocrude high heating value (HHV), heat exchanger duty, feed heat capacity, and pump efficiency on the EROI of HTL. As seen below, biocrude yield is the most influential process variable as EROI ranges from 5.5 to 16.6. After biocrude yield, in decreasing influence are solids loading, biocrude heating value, heat exchanger duty, feed heat capacity, and pump efficiency.

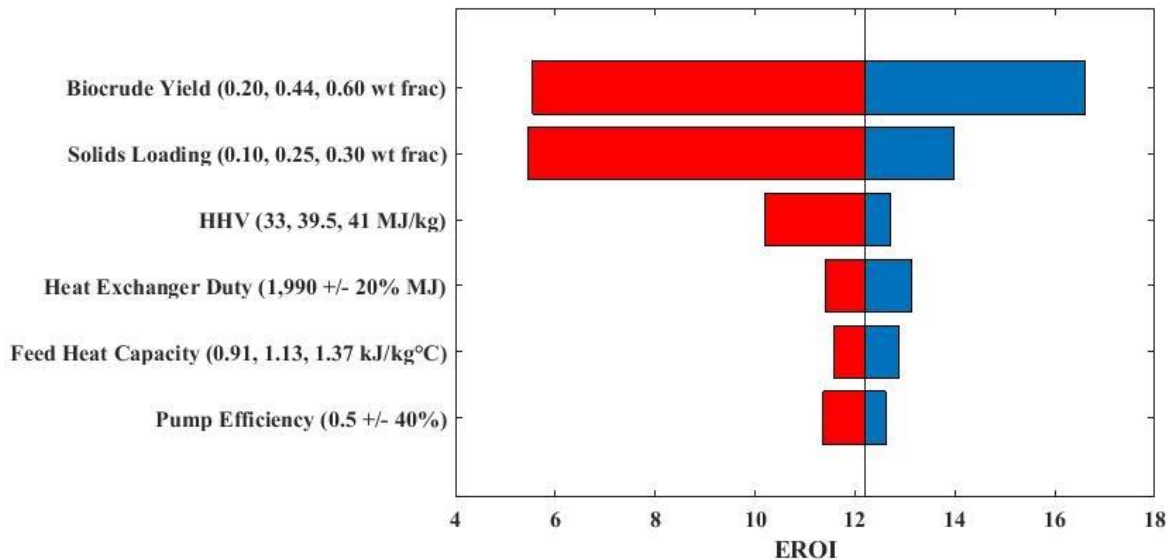


Figure 9. Sensitivity analysis of hydrothermal liquefaction

We chose to examine how the three most influential variables impacted EROI. This included evaluating the effect of solids loading and biocrude yield on EROI and the effect of solids loading and biocrude heating value on EROI. Solids loading was used in both analyses as it is a common independent variable for HTL studies, and provides a more in-depth analysis when combined with the other two variables.

### 4.2 The Effect of Yield with Solids Loading on EROI

After determining which variables should be further analyzed, Figure 10 was created using the values in Appendix D to demonstrate the effect of yield with solids loading on EROI. The first trend that can be observed is that EROI increases as solids loading increases. This correlation is a result of the fact that the process requires more energy when more water is present in the feed. The increase in water leads to higher flow rates throughout the process and

consequently larger duties for the pumps and heat exchangers. Additionally, it takes more energy to heat and cool the streams when they contain more water.

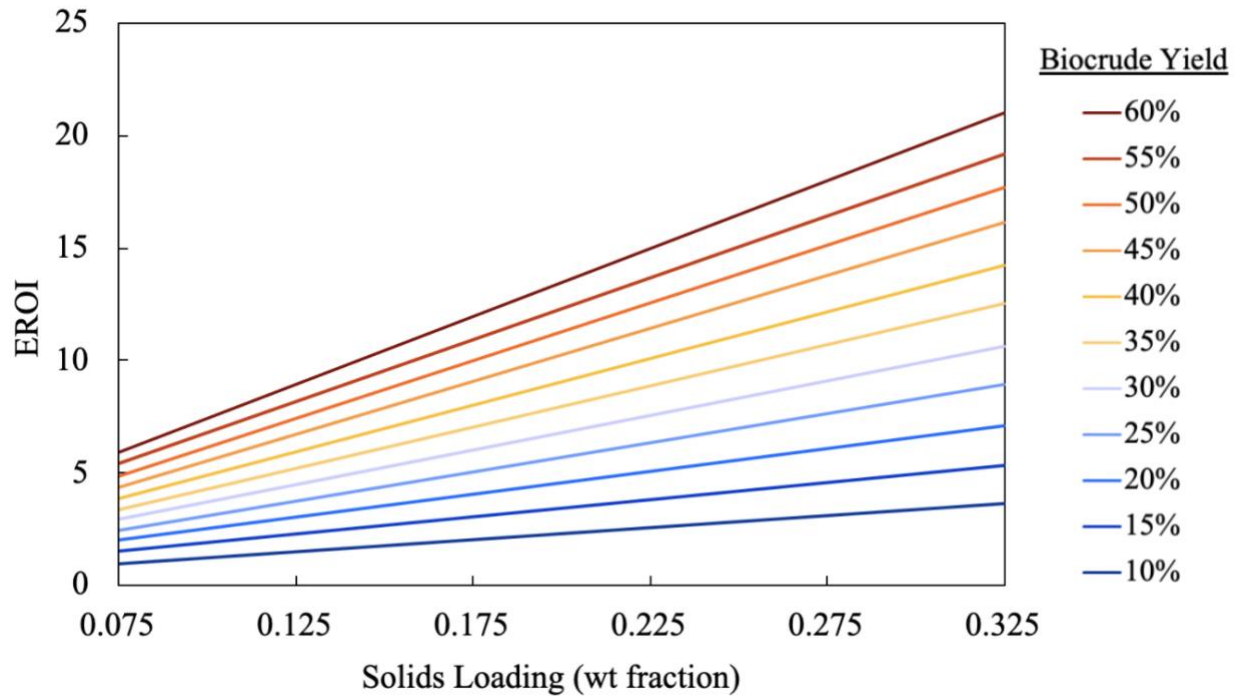


Figure 10. The effect of yield with solids loading on EROI

The second trend that can be observed is that at higher yields, solids loading has a greater impact on EROI. As demonstrated by Figure 10, the lines for the higher yield percents are steeper than lines for the lower yield percents. At 60% yield, the maximum EROI is 20.81 and the minimum EROI is 5.66, while at 10% yield the maximum EROI is 3.60 and the minimum is 0.91. The range for EROI at 60% yield is 15.15 compared to a range of 2.69 at 10% yield. This difference in the EROI range illustrates that the solids loading has a greater impact on EROI at higher yields. This is likely because at higher yields the potential for EROI to be high is much greater than at lower yields. A high solids loading combined with a high yield increases EROI more than a high solids loading with a low yield.

### 4.3 The Effect of Heating Value with Solids Loading on EROI

To analyze the effect of the heating value of the biocrude on EROI, Figure 11 was created in a similar manner to Figure 10. The data used to create Figure 11 is displayed in Appendix E. EROI was graphed compared to solids loading with various trendlines based on heating value. This figure follows similar trends to Figure 10, as EROI increases with solids

loading. EROI also increases with heating values, although the trendlines appear closer together than they do in the yield plot because EROI is less sensitive to heating value than it is to yield.

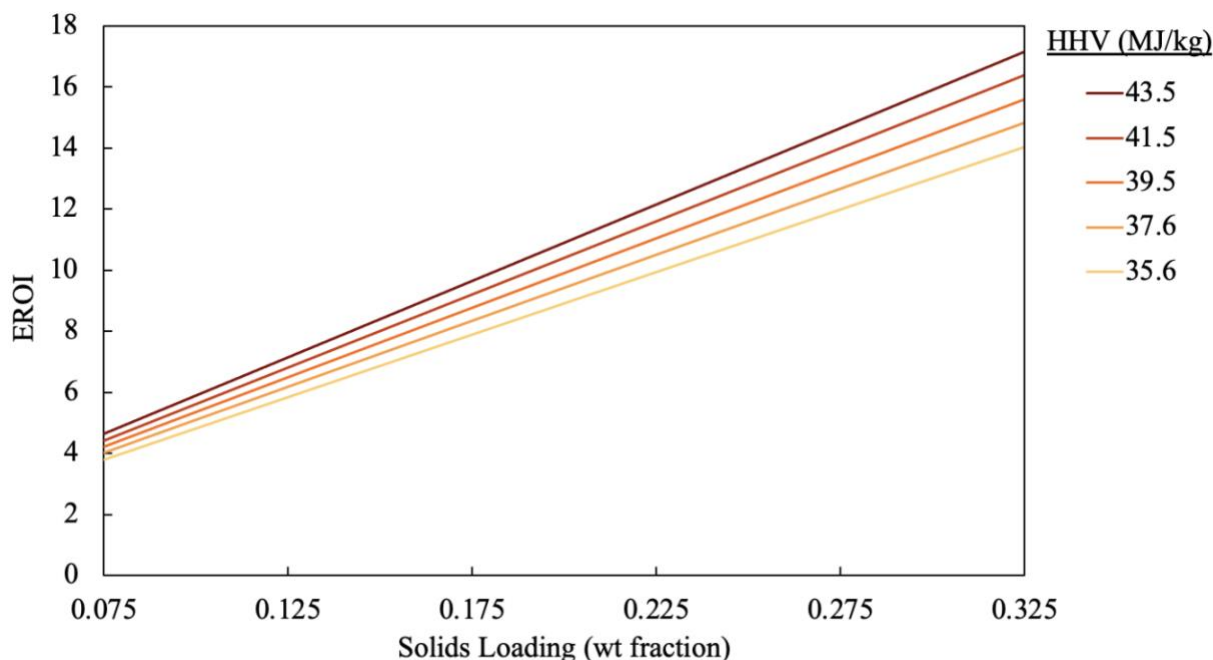


Figure 11. The effect of heating value with solids loading on EROI

Another important trend to note is that the trendlines are more compact at 0.075 solids loading and more spaced out at 0.325 solids loading, illustrating that HHV has more of an impact on EROI at high solids loading content. This is another trend that is similar to the trends observed in Figure 10. Consequently, the higher heating values have a slightly higher range of EROI values than the lower heating values. This could be because at higher solids content less energy is required for the process, so when that is combined with a higher heating value, the return on energy is much higher. Conversely, the need for more energy to process the added water in the feed at lower solids content offsets the additional energy produced from a higher heating value.

#### 4.4 The EROI of Upgraded Biocrude

To make the EROI values for HTL more comprehensive, the biocrude upgrading process was incorporated into the analysis as a correction factor. Figure 12 displays the results of analyzing the effect of yield and solids loading on EROI for the combination of the HTL and upgrading processes. The data for solids loading, yield, and EROI used to create Figure 12 is displayed in Appendix F. We chose to incorporate upgrading into the analysis that included

solids loading and yield since those were the two most impactful variables, as opposed to biocrude heating value which was less impactful according to the sensitivity analysis. The trends of this plot follow very similar trends to the plot in Figure 10. It can be observed that EROI increases with both increasing solids loading and yield. The difference in this plot, compared to the plot in Figure 10, is that the EROI values are much lower and the range of EROI for each yield is much smaller. This is because the upgrading process requires much more energy (up to 4 times more) than the HTL process. In other words, compared to the upgrading process, the HTL process has a smaller impact on EROI.

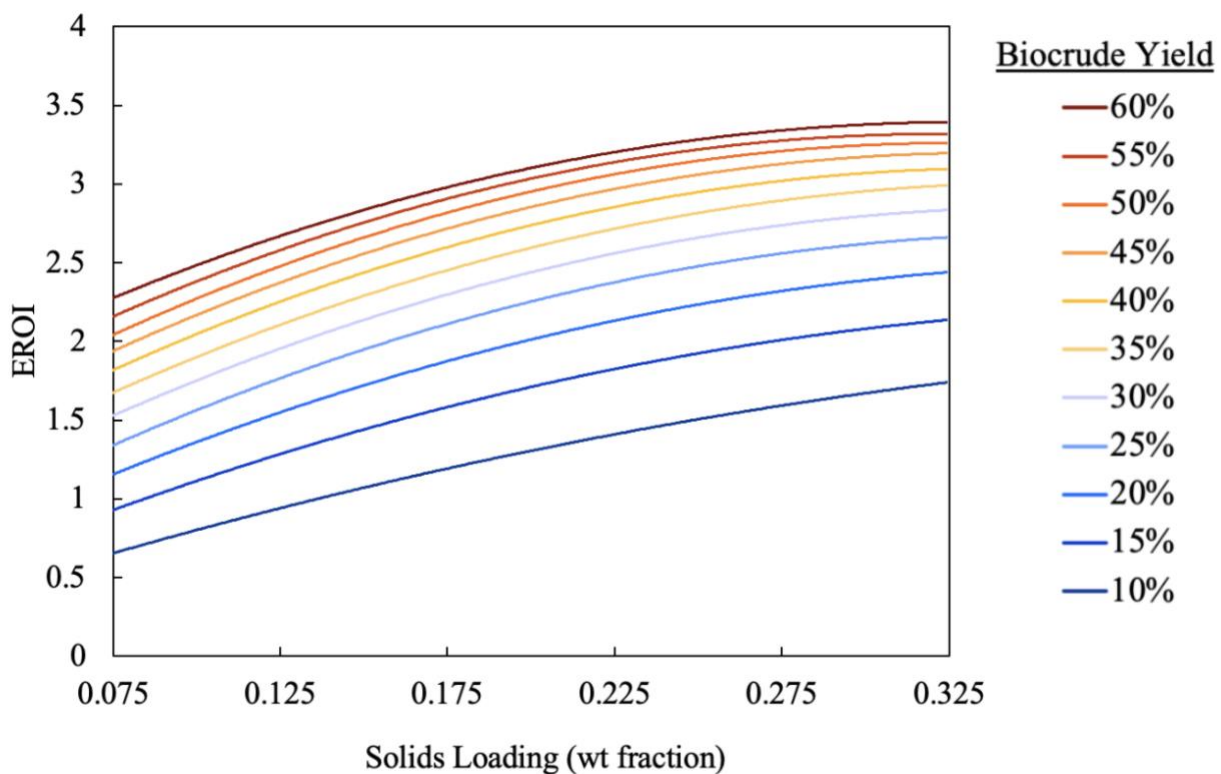


Figure 12. The effect of yield with solids loading on the EROI of upgraded biocrude

It can also be observed on this plot that at higher solids loading and yields the EROI begins to plateau. This suggests that a maximum conversion of biocrude to bio-oil is reached when continuing to increase solids loading and yield. This can be attributed to the HTL process requiring a wet feedstock, so increasing the solids loading too much can make the process less efficient. For example, if the feed becomes too thick with solids, its pumpability will decrease, requiring more energy to move the feed through the system. Lastly, this plot suggests that the best tradeoff between energy efficiency and biomass usage is in the middle of the solids loading



range. This is especially true at higher yields since at a solids loading of approximately 0.225 and above there is very little change in the EROI.

#### 4.5 Literature Projection

To contextualize the results of the HTL and upgrading processes, data points from multiple HTL studies were superimposed on the plot in Figure 12 to create Figure 13. Appendix G details the values used and the projected EROI for each data point. Using the solids loading and yield data from each study, the EROI was projected using our HTL model and upgrading correction factor. The plot that included upgrading was chosen since it most accurately represented the processes in the literature studies. The data points were grouped by type of feedstock: algae (spirulina and chlorella), biomass (wood, rice husk, and cornstalk), and sewage sludge.

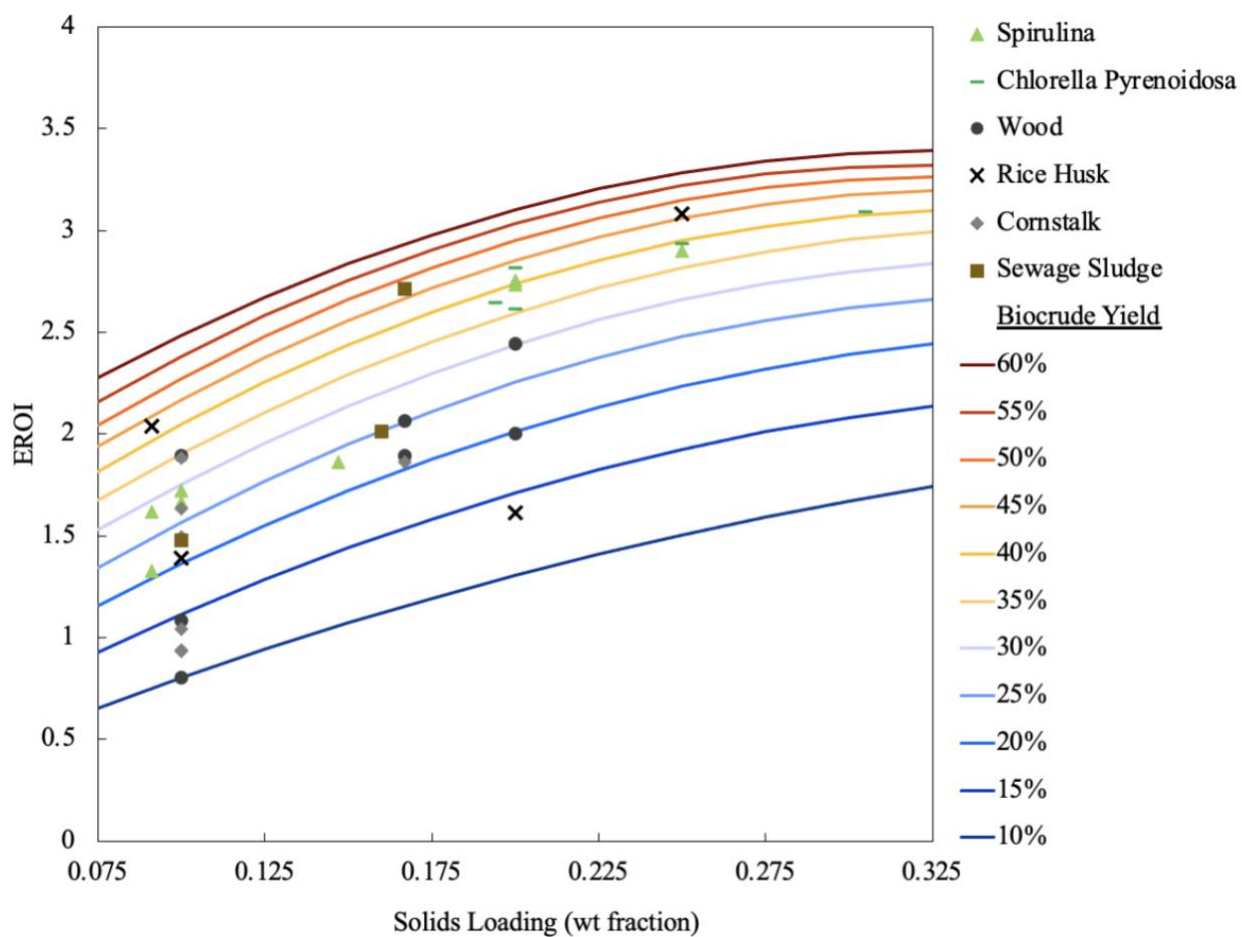


Figure 13. EROI vs solids loading with yield for the upgraded biocrude with data from literature

The first observable trend from the data is that algae tend to have a greater yield and EROI than wood at the same solids loading. For example, Jena et al. performed a study to determine the optimum HTL process conditions for the production of biocrude from the algae spirulina (2011). The study determined that the optimum process conditions were 350°C, 60 minute holding time, and 0.20 solids loading. These optimum conditions resulted in a biocrude yield of 39.9%. Using our model, we were able to predict the EROI of this process as 2.73. Chlorella is another common algae for HTL. Gai et al. conducted an experiment testing the co-liquefaction of chlorella and rice husk (2015). The process conditions in this study were a solids loading of 0.20 conducted at 300°C and a holding time of 60 minutes. The experiment included a run of only chlorella with no rice husk that resulted in a biocrude yield of 43.6%. For this chlorella study our model predicted an EROI of 2.81. In comparison, de Caprariis et al. conducted a study to determine the influence of temperature and feed composition on the production of biocrude by HTL (2017). One of the feedstocks tested in this experiment was oak wood with a solids loading of 0.20. This process was run at 280°C with a 30 minute holding time and resulted in a yield of 19.9%. With this solids loading and yield, our model predicted an EROI of 2.00 for the oak wood. All three of these studies used 0.20 for solids loading although the two algae had a significantly higher EROI and yield. This exemplifies the trend that using algae as a feedstock for HTL results in a greater biocrude yield and EROI than using wood as a feedstock.

The second trend that can be observed in the plot in Figure 13 is that sewage sludge tends to have a slightly greater yield and therefore greater EROI compared to biomass (wood and cornstalk) at the same solids loading. Malins et al. conducted an experiment to determine the effects of influential process variables such as solids loading, temperature, pressure, holding time, and catalysts on the HTL of sewage sludge (2015). This study was able to achieve a biocrude yield of 47% using a solids loading of 0.167 at a temperature of 300°C with a  $\text{FeSO}_4$  catalyst. This solids loading and yield results in an EROI of 2.71 using our HTL model. In comparison, Liu and Zhang studied the HTL of pinewood under various solvents (2008). In this study, using a solids loading of 0.167 at 350°C with a 20 minute holding time and ethanol as a solvent, a biocrude yield of 21.5% and an EROI of 1.89 were achieved. This yield is lower than the yield that sewage sludge produced using the same solids loading in the previous study. Yang et al. conducted an experiment that also used a solids loading of 0.167 for the co-liquefaction of

coffee grounds and lignocellulosic feedstocks (2017). This study ran a trial with pure cornstalk at 250°C and resulted in a yield of 20.8% without the use of a catalyst, which is also lower than the yield in the previous sewage sludge study. This process's solids loading and yield give an EROI of 1.86 using our HTL EROI model. Although all of these processes utilize the same solids loading, they were run at different process conditions such as temperature, pressure, and use of a catalyst. The trends we have described are suggested by Figure 13, but it is hard to draw definitive conclusions due to the variation in different processes.

#### **4.6 EROI Comparison with Other Processes**

After our EROI analysis was complete, we compared our values to EROI values for various other processes, including pyrolysis, anaerobic digestion, gasification, and combustion. The EROI values for these processes as well as other process information are displayed in Table 8. The EROI values for these processes vary from less than 1 to 6.8. HTL can be most closely compared with pyrolysis because the processes are the most similar, where the other methods follow significantly different conversion processes. When examining the data in Table 8, the EROI values for our modeled HTL process are significantly greater than other processes. The EROI values for our modeled HTL process with the upgrading process correction factor are within an average range or slightly lower. There is variation between the other processes, but many were able to achieve an EROI of at least 3-4, illustrating that to be competitive, an HTL process might need to achieve something similar.

Table 8. EROI Comparison with various conversion methods

Source	Feedstock	Process	Energy Input	EROI
Lo et al., 2017	Lignocellulosic Biomass	Pyrolysis	Main energy consuming units of pyrolysis by using microwave heating	3.56
Zaimes et al., 2015	Miscanthus and Switchgrass	Pyrolysis	Energy required to produce miscanthus and switchgrass, main energy consuming units of fast pyrolysis, catalytic upgrading of bio-oil to transportation fuels	1.52-2.56
Marques et al., 2019	Microalgae	Anaerobic Digestion	Energy input from various pretreatment methods, main energy consuming units of anaerobic digestion	$\leq 1$
Marques et al., 2019	“	Anaerobic Digestion (Thermal Pretreatment)	Energy input from thermal pretreatment, main energy consuming units of anaerobic digestion	6.8
Briones-Hidrovo et al., 2021	Residual Forest Biomass	Gasification	Energy input for forest management, biomass collection, processing and transportation, and electricity generation using a fluidized bed reactor	3.634
Briones-Hidrovo et al., 2021	“	Combustion	“	4.238

When looking at pyrolysis as an alternative conversion method, Table 8 illustrates two examples in which the EROI is 3.56 in the first study and ranges between 1.52-2.56 in the second study. The first study by Lo et al. uses microwave heating to perform pyrolysis on lignocellulosic biomass, which is a combination of various biomass sources such as rice husk, rice straw, coffee grounds, and other wastes. The bio-oil yield for this study ranged between 40-48 wt% and all

feeds were air-dried before they were used. Since there was no water in the feed for the study by Lo et al. it cannot be directly compared to the HTL process used in this study. However, when looking at the EROI including upgrading for HTL with a yield of 40-50 wt%, the EROI ranges from 1.77 to 3.29. This is slightly less than the EROI for the pyrolysis process with a similar yield. Although the EROI including upgrading is slightly less than the EROI for this pyrolysis process, the EROI of the HTL process alone is much higher and ranges from 3.66 to 17.33 for the same yield range. For the second pyrolysis study by Zaines et al., fast pyrolysis was used to convert miscanthus and switchgrass first to bio-oil, then to transportation fuels through catalytic upgrading. This pyrolysis study produced EROI values of 1.52-2.56 using a feed that was dried to a solids loading of 0.93 and resulted in a 44.56-53.1% bio-oil yield. The solids loading for the study by Zaines et al. is outside of the parameters of this HTL study, but the EROI can be compared to that of the HTL model including upgrading for a yield between 45-55%. These EROI values range between 1.87 to 3.35 depending on solids loading content and exact yield. This range is slightly greater than the pyrolysis study, indicating that the HTL process is more energy efficient with a favorable solids loading and yield within the given range.

The next conversion process that was researched for comparison is anaerobic digestion. Marques et al. performed a study in which various pretreatment methods were tested to evaluate the energy efficiency of anaerobic digestion on microalgae. Most EROI values for the different pretreatment methods were found to be less than or equal to 1, with the exception of a thermal pretreatment method that led to an EROI of 6.8. The thermal pretreatment has a greater EROI than all of the modeled HTL processes that include upgrading, making it more competitive in the energy market than HTL when upgrading is included.

Lastly, a study by Briones-Hidrovo et al. analyzed the EROI of gasification and combustion of residual forest biomass. This combustion/gasification study considers an average moisture content to be 40%, making the solids loading 0.60 which is outside of the range that this HTL study investigated. A carbon conversion efficiency of 80% was assumed in the gasifier and a combustion efficiency of 99% was assumed in the gas turbine. The gasification process obtained an EROI of 3.634 while the combustion process obtained an EROI of 4.238. Both of these values are higher than the EROI values of HTL with upgrading, where at the greatest yield and solids loading the EROI only reaches 3.43. On the other hand, they are significantly lower than the EROI values of HTL alone.

## Chapter 5. Conclusion

Nonrenewable energy sources such as fossil fuels are harmful to the environment and are running out as society continues to deplete our supply of coal, oil, and natural gas. Hydrothermal Liquefaction (HTL) is a potentially viable renewable energy process that converts biomass into biocrude. HTL is especially promising because it uses a wet feedstock, making it useful for sewage sludge which is an abundant and cheap waste product. HTL must have a high energy efficiency to make it both energetically and economically competitive with nonrenewable energy sources. Energy efficiency can be measured using Energy Return on Investment (EROI) in which the energy produced is divided by the energy consumed during the process.

Very few studies currently exist that evaluate the energy efficiency of HTL. The studies that do exist tend to evaluate the EROI of HTL at a specific set of process conditions, and therefore more information is needed on general EROI trends. This study determined the most influential factors that impact the EROI of HTL and analyzed the EROI based on these factors. This information allowed us to project the EROI for an HTL process based on specific process conditions.

Biocrude yield, feed solids loading, and higher heating value of biocrude were identified as the three most impactful variables on the EROI of HTL, in that respective order. Various plots were constructed to display the effect of varying these factors on the EROI. These plots suggested that EROI increases with solids loading, biocrude yield, and biocrude higher heating value. Additionally, yield and HHV have a greater impact on EROI at higher solids loading.

After analyzing the EROI trends of HTL, biocrude upgrading was included as a correction factor on the plot evaluating yield and solids loading. With the addition of upgrading, the EROI values dropped significantly as this process requires a very large amount of energy. The drastic change in EROI values indicates that it is essential to optimize the upgrading process to make it more energy efficient. The EROI trends with upgrading included were similar to those of HTL alone, with EROI increasing as yield and solids loading increased. However, the observation that yield had a greater impact on EROI at higher solids loading was no longer applicable. Additionally, the plot began to plateau, and the margins began to narrow at higher yields and solids loading, suggesting that a maximum conversion of biomass was reached. These trends illustrate that the middle range of solids loading (0.175-0.225) gives the best tradeoff between energy efficiency and biomass usage.

After analyzing EROI trends for HTL and HTL with upgrading, data from published literature was superimposed onto the plot that included upgrading. The process conditions from these HTL studies were used to project EROIs for the given data based on our model. No extensive, clear trends could be distinguished, although it was clear that algae compared to wood tended to have greater yields for the same solids loading, which consequently resulted in a greater EROI. Additionally, sewage sludge had a slightly greater yield and therefore greater EROI compared to biomass (wood and cornstalk) at the same solids loading. Since there were no obvious large-scale trends, we suggest that more data points are superimposed to support the identified trends and determine any additional trends.

Lastly, the EROI values found in this study were compared with the EROIs of various thermal conversion methods including pyrolysis, anaerobic digestion, gasification, and combustion. A literature review was completed to obtain the EROIs for studies representing these processes. When comparing the values from our study, the EROI values of HTL alone were significantly greater than the EROIs of other conversion methods. Conversely, the EROI values for HTL with upgrading were within an average range of the other processes or slightly lower. Again, this demonstrates that for HTL to be a competitive energy conversion process, the upgrading method needs to be made more efficient.

## Chapter 6. Recommendations for Future Work

As previously discussed, the scope of this study only included modeling the HTL process and using the upgrading process as a correction factor for the EROI values. Because it was not modeled, manipulation of the upgrading process conditions could not be performed. We recommend that the upgrading process is modeled in a similar manner to the HTL process model so that the study can be extended to determine the most sensitive process variables for upgrading and their impact on the EROI of upgraded biocrude. This information could be very useful since the upgraded biocrude is a more advantageous fuel than biocrude that has not been upgraded. Modeling the upgrading process could also help determine opportunities for improved efficiency, therefore resulting in increased EROI values.

In this study, the EROI values for numerous HTL studies from the literature were projected using our model. The EROI data points were superimposed onto our results plot to observe the EROI trends for HTL of numerous feedstocks. This plot included points from 35 sources that each represented a certain type of feedstock and various process conditions. There were no clear, extensive trends that could be identified. For this reason, we recommend that the EROIs of even more literature studies are projected using the model and plotted on the graph by feedstock type. The goal of this work would be to establish more distinguished trends and determine if certain feedstocks result in greater EROIs than others.

Another detail that we recommend is investigated further are additional factors that can impact the energy efficiency of the entire HTL and upgrading process. For this study, we used standard EROI with defined parameters for which energy consuming tasks were included, but other operations could factor into a more comprehensive EROI. For example, it would be beneficial to determine how much energy would be used to transport the biocrude from the HTL plant to the upgrading plant. This study assumed that the upgrading plant would be fed by 10 HTL plants. Because of the amount of space these plants would require, it is likely they would be in different locations than the upgrading plant and the biocrude from the HTL plants would need to be transported. If the energy consumed during transportation has a significant negative impact on EROI, it may be necessary to investigate options such as collocating the HTL and upgrading plants.

The EROI values found in this study also did not take into account the energy potential of the HTL byproducts (char and fuel gas). Char and fuel gas both have the potential to be energy



sources, and their heating values could be included in the energy output of the process in the EROI calculation. We recommend that these values are obtained and included in the EROI analysis of HTL to increase the energy efficiency and make HTL a more competitive biomass conversion process.

Lastly, we recommend that future work reintroduces the simplifications that we made back into the HTL process. For simplicity and ease of calculations, modifications were made to the HTL process in this study. This involved removing some heat exchangers and pumps and not including recycled hot oil for the heat exchangers and the reactors. Reintroducing these simplifications most likely would not change the EROI trends, however, it would change the EROI values since more energy would be required for the increase in heat exchangers and heat recovery would be accounted for.

## References

- Akalin, M. K., Das, P., Alper, K., Tekin, K., Ragauskas, A. J., & Karagöz, S. (2017). Deconstruction of lignocellulosic biomass with hydrated cerium (III) chloride in water and ethanol. *Applied Catalysis A: General*, 546, 67–78. <https://doi.org/10.1016/j.apcata.2017.08.010>
- Akhtar, J., & Amin, N. A. S. (2011). A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews*, 15(3), 1615–1624. <https://doi.org/10.1016/j.rser.2010.11.054>
- Anastasakis, K., Biller, P., Madsen, R. B., Glasius, M., & Johannsen, I. (2018). Continuous Hydrothermal Liquefaction of Biomass in a Novel Pilot Plant with Heat Recovery and Hydraulic Oscillation. *Energies*, 11(10), 2695. <https://doi.org/10.3390/en11102695>
- Arango-Miranda, R., Hausler, R., Romero-López, R., Glaus, M., & Ibarra-Zavaleta, S. P. (2018). An Overview of Energy and Exergy Analysis to the Industrial Sector, a Contribution to Sustainability. *Sustainability*, 10(1), 1–19.
- Asdrubali, F., & Desideri, U. (Eds.). (2019). Chapter 7—High Efficiency Plants and Building Integrated Renewable Energy Systems. In *Handbook of Energy Efficiency in Buildings* (pp. 441–595). Butterworth-Heinemann. <https://doi.org/10.1016/B978-0-12-812817-6.00040-1>
- Beal, C., Hebner, R., Webber, M., Ruoff, R., & Seibert, A. (2012). The Energy Return on Investment for Algal Biocrude: Results for a Research Production Facility. *Bioenergy Research*, 5, 1–22. <https://doi.org/10.1007/s12155-011-9128-4>
- Beims, R. F., Hu, Y., Shui, H., & Xu, C. (Charles). (2020). Hydrothermal liquefaction of biomass to fuels and value-added chemicals: Products applications and challenges to develop large-scale operations. *Biomass and Bioenergy*, 135, 105510. <https://doi.org/10.1016/j.biombioe.2020.105510>
- Biller, P., & Ross, A. B. (2011). Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. *Bioresource Technology*, 102(1), 215–225. <https://doi.org/10.1016/j.biortech.2010.06.028>
- Bioenergy Technologies Office. (2017). *Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities*. 127.
- Bora, A. P., Gupta, D. P., & Durbha, K. S. (2020). Sewage sludge to bio-fuel: A review on the sustainable approach of transforming sewage waste to alternative fuel. *Fuel*, 259, 116262. <https://doi.org/10.1016/j.fuel.2019.116262>
- Briones-Hidrovo, A., Copa, J., Tarelho, L. A. C., Gonçalves, C., Pacheco da Costa, T., & Dias, A. C. (2021). Environmental and energy performance of residual forest biomass for electricity generation: Gasification vs. combustion. *Journal of Cleaner Production*, 289, 125680. <https://doi.org/10.1016/j.jclepro.2020.125680>
- Carbon Dioxide Gas—Specific Heat. (n.d.). Retrieved March 5, 2021, from [https://www.engineeringtoolbox.com/carbon-dioxide-d\\_974.html](https://www.engineeringtoolbox.com/carbon-dioxide-d_974.html)
- Charm Industrial. (n.d.). Charm Industrial. Retrieved February 8, 2021, from <https://charmindustrial.com>
- Chen, G. Q., Jiang, M. M., Chen, B., Yang, Z. F., & Lin, C. (2006). Emergy analysis of Chinese agriculture. *Agriculture, Ecosystems & Environment*, 115(1), 161–173. <https://doi.org/10.1016/j.agee.2006.01.005>

- Coal and the environment—U.S. Energy Information Administration (EIA)*. (2020, December 1). U.S Energy Information Administration. <https://www.eia.gov/energyexplained/coal/coal-and-the-environment.php>
- Davis, P. D., Parbrook, G. D., & Kenny, G. N. C. (1995). CHAPTER 10—Heat Capacity and Latent Heat. In P. D. Davis, G. D. Parbrook, & G. N. C. Kenny (Eds.), *Basic Physics and Measurement in Anaesthesia (Fourth Edition)* (pp. 125–133). Butterworth-Heinemann. <https://doi.org/10.1016/B978-0-7506-1713-0.50015-9>
- de Caprariis, B., De Filippis, P., Petruccio, A., & Scarsella, M. (2017). Hydrothermal liquefaction of biomass: Influence of temperature and biomass composition on the bio-oil production. *Fuel*, 208, 618–625. <https://doi.org/10.1016/j.fuel.2017.07.054>
- Dokuz Eylül University. (n.d.). *Wastewater Engineering*. Retrieved March 5, 2021, from <http://web.deu.edu.tr/atiksu/ana52/wdesign06.html>
- Domalski, E. S., Jobe, J., & Milne, T. A. (1986). *Thermodynamic data for biomass conversion and waste incineration (SERI/SP-271-2839)*. National Bureau of Standards, Washington, DC (US); Solar Energy Research Inst., Golden, CO (US). <https://doi.org/10.2172/7038865>
- Duan, P., Bai, X., Xu, Y., Zhang, A., Wang, F., Zhang, L., & Miao, J. (2013). Catalytic upgrading of crude algal oil using platinum/gamma alumina in supercritical water. *Fuel*, 109, 225–233. <https://doi.org/10.1016/j.fuel.2012.12.074>
- Eicher, A. (2013). Comparison of Biomass to Bio-oils Reactor Systems: Direct Conversion vs. Companion Coal Gasification. *Honors Theses and Capstones*. <https://scholars.unh.edu/honors/106>
- Elliott, D., Biller, P., Ross, A., Schmidt, A., & Jones, S. (2014). *Hydrothermal liquefaction of biomass: Developments from batch to continuous process / Elsevier Enhanced Reader*. <https://doi.org/10.1016/j.biortech.2014.09.132>
- Evans, J. (2012, January 20). *Pump Efficiency—What Is Efficiency?* Pumps and Systems Magazine. <https://www.pumpsandsystems.com/pump-efficiency-what-efficiency>
- Feng, H., He, Z., Zhang, B., Chen, H., Wang, Q., & Kandasamy, S. (2019). Synergistic bio-oil production from hydrothermal co-liquefaction of *Spirulina platensis* and  $\alpha$ -Cellulose. *Energy*, 174, 1283–1291. <https://doi.org/10.1016/j.energy.2019.02.079>
- Fossil*. (n.d.). Department of Energy. Retrieved February 8, 2021, from <https://www.energy.gov/science-innovation/energy-sources/fossil>
- Fossil fuels account for the largest share of U.S. energy production and consumption*. (2020, September 14). U.S Energy Information Administration. <https://www.eia.gov/todayinenergy/detail.php?id=45096>
- Freise, J. (2011). The EROI of Conventional Canadian Natural Gas Production. *Sustainability*, 3(11), 2080–2104. <https://doi.org/10.3390/su3112080>
- Gai, C., Li, Y., Peng, N., Fan, A., & Liu, Z. (2015). Co-liquefaction of microalgae and lignocellulosic biomass in subcritical water. *Bioresource Technology*, 185, 240–245. <https://doi.org/10.1016/j.biortech.2015.03.015>
- Gai, C., Zhang, Y., Chen, W.-T., Zhang, P., & Dong, Y. (2014). Energy and nutrient recovery efficiencies in biocrude oil produced via hydrothermal liquefaction of *Chlorella pyrenoidosa*. *RSC Advances*, 4(33), 16958–16967. <https://doi.org/10.1039/C3RA46607H>
- Hall, C., Lambert, J., & Balogh, S. (2013). EROI of Different Fuels and the Implications for Society. *Energy Policy*, 64, 141–152. <https://doi.org/10.1016/j.enpol.2013.05.049>

- Heat Capacity and Water*. (n.d.). Retrieved February 8, 2021, from [https://www.usgs.gov/special-topic/water-science-school/science/heat-capacity-and-water?qt-science\\_center\\_objects=0#qt-science\\_center\\_objects](https://www.usgs.gov/special-topic/water-science-school/science/heat-capacity-and-water?qt-science_center_objects=0#qt-science_center_objects)
- Heat Exchangers*. (2014, February 1). IPIECA. <https://www.ipieca.org/resources/energy-efficiency-solutions/efficient-use-of-heat/heat-exchangers/>
- Hu, Y., Wang, S., Li, J., Wang, Q., He, Z., Feng, Y., Abomohra, A. E.-F., Afonaa-Mensah, S., & Hui, C. (2018). Co-pyrolysis and co-hydrothermal liquefaction of seaweeds and rice husk: Comparative study towards enhanced biofuel production. *Journal of Analytical and Applied Pyrolysis*, *129*, 162–170. <https://doi.org/10.1016/j.jaap.2017.11.016>
- Hydrofaction® – Steeper Energy*. (n.d.). Retrieved February 8, 2021, from <https://steeperenergy.com/hydrofaction/>
- Jena, U., & Das, K. C. (2011). Comparative Evaluation of Thermochemical Liquefaction and Pyrolysis for Bio-Oil Production from Microalgae. *Energy & Fuels*, *25*(11), 5472–5482. <https://doi.org/10.1021/ef201373m>
- Jena, U., Das, K. C., & Kastner, J. R. (2011). Effect of operating conditions of thermochemical liquefaction on biocrude production from *Spirulina platensis*. *Bioresource Technology*, *102*(10), 6221–6229. <https://doi.org/10.1016/j.biortech.2011.02.057>
- Jin, B., Duan, P., Xu, Y., Wang, F., & Fan, Y. (2013). Co-liquefaction of micro- and macroalgae in subcritical water. *Bioresource Technology*, *149*, 103–110. <https://doi.org/10.1016/j.biortech.2013.09.045>
- Karagöz, S., Bhaskar, T., Muto, A., & Sakata, Y. (2004). Effect of Rb and Cs carbonates for production of phenols from liquefaction of wood biomass. *Fuel*, *83*(17), 2293–2299. <https://doi.org/10.1016/j.fuel.2004.06.023>
- Koley, S., Khadase, M. S., Mathimani, T., Raheman, H., & Mallick, N. (2018). Catalytic and non-catalytic hydrothermal processing of *Scenedesmus obliquus* biomass for bio-crude production – A sustainable energy perspective. *Energy Conversion and Management*, *163*, 111–121. <https://doi.org/10.1016/j.enconman.2018.02.052>
- Kumar, S., Lange, J.-P., Van Rossum, G., & Kersten, S. R. A. (2015). Liquefaction of lignocellulose: Do basic and acidic additives help out? *Chemical Engineering Journal*, *278*, 99–104. <https://doi.org/10.1016/j.cej.2014.12.026>
- Lam, M. K., Loy, A. C. M., Yusup, S., & Lee, K. T. (2019). Chapter 9—Biohydrogen Production From Algae. In A. Pandey, S. V. Mohan, J.-S. Chang, P. C. Hallenbeck, & C. Larroche (Eds.), *Biohydrogen (Second Edition)* (pp. 219–245). Elsevier. <https://doi.org/10.1016/B978-0-444-64203-5.00009-5>
- Liquid Water—Properties at various Temperature and Pressure*. (n.d.). Retrieved March 5, 2021, from [https://www.engineeringtoolbox.com/water-properties-d\\_1258.html](https://www.engineeringtoolbox.com/water-properties-d_1258.html)
- Liu, H., Li, M., Cao, X., & Sun, R. (2013). Influence of Alkali Pretreatment on Cypress Characters for Bio-oil from Liquefaction in Ethanol. *Energy Technology*, *1*(1), 70–76. <https://doi.org/10.1002/ente.201200035>
- Liu, H.-M., Feng, B., & Sun, R.-C. (2011a). Enhanced Bio-oil Yield from Liquefaction of Cornstalk in Sub- and Supercritical Ethanol by Acid–Chlorite Pretreatment. *Industrial & Engineering Chemistry Research*, *50*(19), 10928–10935. <https://doi.org/10.1021/ie2014197>
- Liu, H.-M., Feng, B., & Sun, R.-C. (2011b). Acid–Chlorite Pretreatment and Liquefaction of Cornstalk in Hot-Compressed Water for Bio-oil Production. *Journal of Agricultural and Food Chemistry*, *59*(19), 10524–10531. <https://doi.org/10.1021/jf2025902>

- Liu, H.-M., Li, M.-F., & Sun, R.-C. (2013). Hydrothermal liquefaction of cornstalk: 7-Lump distribution and characterization of products. *Bioresource Technology*, *128*, 58–64. <https://doi.org/10.1016/j.biortech.2012.09.125>
- Liu, H.-M., Xie, X.-A., Li, M.-F., & Sun, R.-C. (2012). Hydrothermal liquefaction of cypress: Effects of reaction conditions on 5-lump distribution and composition. *Journal of Analytical and Applied Pyrolysis*, *94*, 177–183. <https://doi.org/10.1016/j.jaap.2011.12.007>
- Liu, H.-M., Xie, X.-A., Ren, J.-L., & Sun, R.-C. (2012). 8-Lump reaction pathways of cornstalk liquefaction in sub- and super-critical ethanol. *Industrial Crops and Products*, *35*(1), 250–256. <https://doi.org/10.1016/j.indcrop.2011.07.004>
- Liu, X., Saydah, B., Eranki, P., Colosi, L. M., Greg Mitchell, B., Rhodes, J., & Clarens, A. F. (2013). Pilot-scale data provide enhanced estimates of the life cycle energy and emissions profile of algae biofuels produced via hydrothermal liquefaction. *Bioresource Technology*, *148*, 163–171. <https://doi.org/10.1016/j.biortech.2013.08.112>
- Liu, Z., & Zhang, F.-S. (2008). Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks. *Energy Conversion and Management*, *49*(12), 3498–3504. <https://doi.org/10.1016/j.enconman.2008.08.009>
- Lo, S.-L., Huang, Y.-F., Chiueh, P.-T., & Kuan, W.-H. (2017). Microwave Pyrolysis of Lignocellulosic Biomass. *Energy Procedia*, *105*, 41–46. <https://doi.org/10.1016/j.egypro.2017.03.277>
- Malins, K., Kampars, V., Brinks, J., Neibolte, I., Murnieks, R., & Kampare, R. (2015). Bio-oil from thermo-chemical hydro-liquefaction of wet sewage sludge. *Bioresource Technology*, *187*, 23–29. <https://doi.org/10.1016/j.biortech.2015.03.093>
- Marques, A. de L., Araújo, O. de Q. F., & Cammarota, M. C. (2019). Biogas from microalgae: An overview emphasizing pretreatment methods and their energy return on investment (EROI). *Biotechnology Letters*, *41*(2), 193–201. <https://doi.org/10.1007/s10529-018-2629-x>
- McKendry, P. (2002). Energy production from biomass (part 2): Conversion technologies. *Bioresource Technology*, *83*(1), 47–54. [https://doi.org/10.1016/S0960-8524\(01\)00119-5](https://doi.org/10.1016/S0960-8524(01)00119-5)
- Midgett, Jason. S., Stevens, B. E., Dassey, A. J., Spivey, J. J., & Theegala, Chandra. S. (2012). Assessing Feedstocks and Catalysts for Production of Bio-Oils from Hydrothermal Liquefaction. *Waste and Biomass Valorization*, *3*(3), 259–268. <https://doi.org/10.1007/s12649-012-9129-3>
- Natural gas and the environment—U.S. Energy Information Administration (EIA)*. (2020, September 24). U.S Energy Information Administration. <https://www.eia.gov/energyexplained/natural-gas/natural-gas-and-the-environment.php>
- Obeid, R., Lewis, D. M., Smith, N., Hall, T., & van Eyk, P. (2020). Reaction Kinetics and Characterization of Species in Renewable Crude from Hydrothermal Liquefaction of Mixtures of Polymer Compounds To Represent Organic Fractions of Biomass Feedstocks. *Energy & Fuels*, *34*(1), 419–429. <https://doi.org/10.1021/acs.energyfuels.9b02936>
- Oil and the environment—U.S. Energy Information Administration (EIA)*. (2020, August 25). U.S Energy Information Administration. <https://www.eia.gov/energyexplained/oil-and-petroleum-products/oil-and-the-environment.php>



- Pimentel, D., & Patzek, T. (2005). Ethanol Production Using Corn, Switchgrass, and Wood; Biodiesel Production Using Soybean and Sunflower. *Natural Resources Research*, 14, 65–76. <https://doi.org/10.1007/s11053-005-4679-8>
- Qian, L., Wang, S., & Savage, P. E. (2017). Hydrothermal liquefaction of sewage sludge under isothermal and fast conditions. *Bioresource Technology*, 232, 27–34. <https://doi.org/10.1016/j.biortech.2017.02.017>
- Ramirez, J., Brown, R., & Rainey, T. (2015). A Review of Hydrothermal Liquefaction Bio-Crude Properties and Prospects for Upgrading to Transportation Fuels. *Energies*, 2015, 6765–6794. <https://doi.org/10.3390/en8076765>
- Sawayama, S., Minowa, T., & Yokoyama, S.-Y. (1999). Possibility of renewable energy production and CO<sub>2</sub> mitigation by thermochemical liquefaction of microalgae. *Biomass and Bioenergy*, 17(1), 33–39. [https://doi.org/10.1016/S0961-9534\(99\)00019-7](https://doi.org/10.1016/S0961-9534(99)00019-7)
- Sciubba, E., & Ulgiati, S. (2005). Emery and exergy analyses: Complementary methods or irreducible ideological options? *Energy*, 30(10), 1953–1988. <https://doi.org/10.1016/j.energy.2004.08.003>
- Seiple, T. E., Coleman, A. M., & Skaggs, R. L. (2017a). Conceptual Biorefinery Design and Research Targeted for 2022: Hydrothermal Liquefaction Processing of Wet Waste to Fuels. *Journal of Environmental Management*, 197, 673–680. <https://doi.org/10.1016/j.jenvman.2017.04.032>
- Seiple, T. E., Coleman, A. M., & Skaggs, R. L. (2017b). Municipal wastewater sludge as a sustainable bioresource in the United States. *Journal of Environmental Management*, 197, 673–680. <https://doi.org/10.1016/j.jenvman.2017.04.032>
- Shafiee, S., & Topal, E. (2009). When will fossil fuel reserves be diminished? *Energy Policy*, 37(1), 181–189. <https://doi.org/10.1016/j.enpol.2008.08.016>
- Shi, W., Jia, J., Gao, Y., & Zhao, Y. (2013). Influence of ultrasonic pretreatment on the yield of bio-oil prepared by thermo-chemical conversion of rice husk in hot-compressed water. *Bioresource Technology*, 146, 355–362. <https://doi.org/10.1016/j.biortech.2013.07.094>
- Snowden-Swan, L. J., Zhu, Y., Jones, S. B., Elliott, D. C., Schmidt, A. J., Hallen, R. T., Billing, J. M., Hart, T. R., Fox, S. P., & Maupin, G. D. (2016). *Hydrothermal Liquefaction and Upgrading of Municipal Wastewater Treatment Plant Sludge: A Preliminary Techno-Economic Analysis, Rev.1* (PNNL-25464-Rev.1). Pacific Northwest National Lab. (PNNL), Richland, WA (United States). <https://doi.org/10.2172/1327165>
- Terzi, R. (2018). Application of Exergy Analysis to Energy Systems. *Application of Exergy*. <https://doi.org/10.5772/intechopen.74433>
- Toor, S. S., Reddy, H., Deng, S., Hoffmann, J., Spangsmark, D., Madsen, L. B., Holm-Nielsen, J. B., & Rosendahl, L. A. (2013). Hydrothermal liquefaction of Spirulina and Nannochloropsis salina under subcritical and supercritical water conditions. *Bioresource Technology*, 131, 413–419. <https://doi.org/10.1016/j.biortech.2012.12.144>
- Tsatsaronis, G. (1999). Strengths and Limitations of Exergy Analysis. In A. Bejan & E. Mamut (Eds.), *Thermodynamic Optimization of Complex Energy Systems* (pp. 93–100). Springer Netherlands. [https://doi.org/10.1007/978-94-011-4685-2\\_6](https://doi.org/10.1007/978-94-011-4685-2_6)
- Verma, M., Godbout, S., Brar, S. K., Solomatnikova, O., Lemay, S. P., & Larouche, J. P. (2012, April 8). *Biofuels Production from Biomass by Thermochemical Conversion Technologies* [Review Article]. *International Journal of Chemical Engineering*; Hindawi. <https://doi.org/10.1155/2012/542426>

- Wang, J., Peng, X., Chen, X., & Ma, X. (2019). Co-liquefaction of low-lipid microalgae and starch-rich biomass waste: The interaction effect on product distribution and composition. *Journal of Analytical and Applied Pyrolysis*, *139*, 250–257. <https://doi.org/10.1016/j.jaap.2019.02.013>
- World Population Prospects: The 2017 Revision | Multimedia Library - United Nations Department of Economic and Social Affairs. (2017, June 21). <https://www.un.org/development/desa/publications/world-population-prospects-the-2017-revision.html>
- Xiu, S., & Shahbazi, A. (2012). Bio-oil production and upgrading research: A review. *Renewable and Sustainable Energy Reviews*, *16*(7), 4406–4414. <https://doi.org/10.1016/j.rser.2012.04.028>
- Xu, D., Lin, G., Liu, L., Wang, Y., Jing, Z., & Wang, S. (2018). Comprehensive evaluation on product characteristics of fast hydrothermal liquefaction of sewage sludge at different temperatures. *Energy*, *159*, 686–695. <https://doi.org/10.1016/j.energy.2018.06.191>
- Xu, D., Wang, Y., Lin, G., Guo, S., Wang, S., & Wu, Z. (2019). Co-hydrothermal liquefaction of microalgae and sewage sludge in subcritical water: Ash effects on bio-oil production. *Renewable Energy*, *138*, 1143–1151. <https://doi.org/10.1016/j.renene.2019.02.020>
- Yang, L., He, Q. (Sophia), Havard, P., Corscadden, K., Xu, C. (Charles), & Wang, X. (2017). Co-liquefaction of spent coffee grounds and lignocellulosic feedstocks. *Bioresource Technology*, *237*, 108–121. <https://doi.org/10.1016/j.biortech.2017.02.087>
- Yu, G., Zhang, Y., Guo, B., Funk, T., & Schideman, L. (2014). Nutrient Flows and Quality of Bio-crude Oil Produced via Catalytic Hydrothermal Liquefaction of Low-Lipid Microalgae. *BioEnergy Research*, *7*(4), 1317–1328. <https://doi.org/10.1007/s12155-014-9471-3>
- Yuan, C., Wang, S., Cao, B., Hu, Y., Abomohra, A. E.-F., Wang, Q., Qian, L., Liu, L., Liu, X., He, Z., Sun, C., Feng, Y., & Zhang, B. (2019). Optimization of hydrothermal co-liquefaction of seaweeds with lignocellulosic biomass: Merging 2nd and 3rd generation feedstocks for enhanced bio-oil production. *Energy*, *173*, 413–422. <https://doi.org/10.1016/j.energy.2019.02.091>
- Zaimes, G. G., Soratana, K., Harden, C. L., Landis, A. E., & Khanna, V. (2015). Biofuels via Fast Pyrolysis of Perennial Grasses: A Life Cycle Evaluation of Energy Consumption and Greenhouse Gas Emissions. *Environmental Science & Technology*, *49*(16), 10007–10018. <https://doi.org/10.1021/acs.est.5b00129>
- Zhang, B., Chen, J., Kandasamy, S., & He, Z. (2020). Hydrothermal liquefaction of fresh lemon-peel and *Spirulina platensis* blending -operation parameter and biocrude chemistry investigation. *Energy*, *193*, 116645. <https://doi.org/10.1016/j.energy.2019.116645>
- Zhang, C., Tang, X., Sheng, L., & Yang, X. (2016). Enhancing the performance of Co-hydrothermal liquefaction for mixed algae strains by the Maillard reaction. *Green Chemistry*, *18*(8), 2542–2553. <https://doi.org/10.1039/C5GC02953H>
- Zhang, J., & Zhang, X. (2019). 15—The thermochemical conversion of biomass into biofuels. In D. Verma, E. Fortunati, S. Jain, & X. Zhang (Eds.), *Biomass, Biopolymer-Based Materials, and Bioenergy* (pp. 327–368). Woodhead Publishing. <https://doi.org/10.1016/B978-0-08-102426-3.00015-1>
- Zhao, Y.-P., Zhu, W.-W., Wei, X.-Y., Fan, X., Cao, J.-P., Dou, Y.-Q., Zong, Z.-M., & Zhao, W. (2013). Synergic effect of methanol and water on pine liquefaction. *Bioresource Technology*, *142*, 504–509. <https://doi.org/10.1016/j.biortech.2013.05.028>

Zhu, Z., Si, B., Lu, J., Watson, J., Zhang, Y., & Liu, Z. (2017). Elemental migration and characterization of products during hydrothermal liquefaction of cornstalk. *Bioresource Technology*, 243, 9–16. <https://doi.org/10.1016/j.biortech.2017.06.085>



# Appendices

## Appendix A. Base Case Calculations

### Appendix A.1 Basic Flow Information

											lb/day (dry)	lb/hr (dry)	lb/day sludge	lb/hr (sludge)	
<b>Equipment</b>	<b>Duty (BTU/hr)</b>	<b>Biomass Fraction 0.25</b>									110 dry tons/day from PNNL	219999.8182	9166.659091	879999.2727	36666.63636
Pump	630,004														
Feed Heater	1,927,791														
Reactor	3,000,000														
Biocrude Cooler	58,080														
SUM	2,615,875														

<b>product yield (PNNL experimental) wt% - dry sludge</b>		<b>product yield (PNNL experimental) wt% - wet sludge</b>	
oil	44	oil	4033.33
aqueous	31	aqueous	30341.64159
solids	9	solids	824.9993182
gas	16	gas	1466.665455

Stream #	1	2	3	4	5	6	7	8	9	10	11	12	13
<b>Description</b>	Feed	Pressurized Feed	Product Heated Feed	Heated Feed	Reactor Outlet	Solids Product	Filtered Product	Depressurized Product	Feed Cooled Product	Separated Bio-oil	Cooled Bio-oil	Separated Flue Gas	Separated Aqueous Phase
<b>Flow Rate (lb/hr)</b>	36,667	36,667	36,667	36,667	36,667	2,357	34,309	34,309	34,309	4,033	4,033	1,467	28,810
<b>Temperature (F)</b>	60	60	595	656	656	656	656	656	140	140	110	140	140
<b>Pressure (psia)</b>	15	3,000	3,000	3,000	3,000	3,000	3,000	30	30	30	30	30	30
<b>Composition (mass frac)</b>													
<b>Biomass</b>	0.25	0.25	0.25										
<b>Water</b>	0.75	0.75	0.75			0.65							
<b>Oil</b>							0.12	0.12	0.12	1	1		
<b>Aqueous</b>							0.84	0.84	0.84				1
<b>Solids</b>						0.35							
<b>Gas</b>							0.04	0.04	0.04			1	

### Appendix A.2 Feedstock Cp Data

Material	Description	Cp temp range (F)	Cp (Btu/lbm*F)
Filter Paper	pure cellulose	77-167	0.217
Cucumbers	96.1% water	40	0.92
Rice (Italian)	0.009% moisture		0.282
Wheat	0.004% moisture		0.307
Beech Wood	air dried solid	32-223	0.326
Chestnut Wood	air dried solid	32-223	0.317
Elm Wood	air dried solid	32-223	0.325
Fir Wood	air dried solid	32-223	0.327
Hemlock Wood	air dried solid	32-223	0.322
White Oak Wood	air dried solid	32-223	0.325

Appendix A.3 Pump Calculations

$W=qhsg/(3690\text{eff})$		$h = 2.31 \cdot P / SG$	
q = flow (GPM)	66.58568585	flow (lb/hr)	36,667
p = density (lb/ft <sup>3</sup> )	68.65	flow (lb/min)	611.1106061
g = gravity (ft/s <sup>2</sup> )	32.174	flow (ft <sup>3</sup> /min)	8.901829659
h = head (ft)	6236.091479	flow (gal/min)	66.58568585
efficiency	0.5		
specific gravity	1.100160256		
P = pressure (psi)	2970		
		density (lb/ft <sup>3</sup> )	water 62.4 biomass 87.4
W(hp)	247.6013089		
W(BTU/hr)	630,004		

Appendix A.4 Feed/Product Heat Exchanger Calculations

Product			
Temp In (F)	656	components	wt% Cp (BTU/lbm°F)
Temp Out (F)	140	oil	0.12 0.582
Flow (lb/hr)	34,309	aqueous	0.84 1
Pressure (psia)	30	gas	0.04 1.102
Cp (BTU/lbm°F)	0.95392		
Q (BTU/hr)	-16,887,913		
Feed			
Temp In (F)	60		
Temp Out (F)	594.9359188		
Flow (lb/hr)	36,667		
Pressure (psia)	3000		
Cp (BTU/lbm°F)	0.861		
Q (BTU/hr)	16,887,913		

*Appendix A.5 Feed Heater Calculations*

Sludge		
<b>Temp In (F)</b>	594.9359188	
<b>Temp Out (F)</b>	656	
<b>Flow (lb/hr)</b>	36,667	
<b>Pressure (psia)</b>	3,000	
<b>Cp (BTU/lbm*F)</b>	0.861	
<b>Q (BTU/hr)</b>	1,927,791	
Cp Calculations		
(BTU/lbm*F)		
water in	0.986	interolated
water out	1.13	
biomass	0.27	

*Appendix A.6 Reactor Calculations*

<b>Hrxn (BTU/lb)</b>	327.3
<b>Biomass Feed (lb/hr)</b>	9,167
<b>Duty (BTU/hr)</b>	3,000,248

*Appendix A.7 Biocrude Cooler Calculations*

<b>Temp In (F)</b>	140
<b>Temp Out (F)</b>	110
<b>Flow (lb/hr)</b>	4,033
<b>Pressure (psia)</b>	30
<b>Cp (BTU/lbm*F)</b>	0.48
<b>Q (BTU/hr)</b>	-58,080

*Appendix A.8 EROI Calculations*

<b>Heating Value of Bio Crude (MJ/kg oil)</b>	39.5		<b>Equip Duty</b>	<b>BTU/hr</b>
BTU/lb	16,997		Pump	630,004
			Feed Heater	1,927,791
Avg (BTU/lb)	16,997		Reactor	3,000,248
			Biocrude Cooler	58,080
Biocrude Produced (lb/hr)	4,033		<b>Energy Input (BTU/hr)</b>	<b>5,616,123</b>
<b>Energy Output (BTU/hr)</b>	<b>68,555,382</b>			
<b>EROI</b>	<b>12.20688836</b>			

**Appendix B. Upgrading energy inputs from PNNL used as correction factor**

<b>Equipment</b>	<b>Duty (mmBTU/hr)</b>
Hydrotreating	
H-311	7.25
HX-318A	2.31
H-316	4.84
E-310	1.36
T-310 Condenser	0.64
T-310 Reboiler	4.34
T-320 Condenser	4.55
T-320 Reboiler	6.26
T-336 Condenser	2.64
T-336 Reboiler	2.87
P-310	0.2711599051
K-311	1.489992764
K-310	3.810334814
Hydrocracking	
H-351	1.36
H-352	0.53
H-371	1.36
T-350 Condenser	0.24
T-350 Reboiler	2.98
P-350	0.0904035979
K-350	0.1371702213
K-355	0.0089309493
Hydrogen Plant	
H-414	6.07
H-415	1.64
H-420	18.63
H-425	12.24
H-430	10.3
K-400	2.140857958
K-461	1.215041658
K-462	0.7065627667
Product Cooling	
H-360	0.23
HX-385	3.18
H-365	2.08
Steam	
HX-600	18.29
E-601	6.504835295
	132.5652899
<b>Total</b>	<b>mmBTU/hr</b>

**Appendix C. Energy output of upgrading process used as a correction factor**

<b>Products</b>	<b>Flow (lb/hr)</b>
Hydrotreating	
Naphtha	6423
Diesel	12,262
Hydrocracking	
Naphtha	716
Diesel	10944
Total	
Naphtha	7139
Diesel	23,206
Total Energy (mmBTU/hr)	566.905273

**Appendix D. Data for the effect of yield with solids loading graph**

<b>Solids Loading</b>	<b>EROI</b>					
	<b>10% Yield</b>	<b>15% Yield</b>	<b>20% Yield</b>	<b>25% Yield</b>	<b>30% Yield</b>	<b>35% Yield</b>
0.325	3.604673833	5.232800611	6.832445839	8.770977552	10.46987517	12.55031261
0.3	3.296961175	4.915338681	6.728728923	7.97117605	9.809140832	11.35720597
0.275	3.045286308	4.530299768	6.082692568	7.794438315	9.101798325	10.6865639
0.25	2.789489273	4.206860472	5.549002908	6.970588522	8.124815496	9.819874632
0.225	2.48477662	3.807384643	5.093303566	6.366158146	7.662317989	8.657373198
0.2	2.303203717	3.341366735	4.605024784	5.763680093	6.682954002	8.059572302
0.175	2.03105151	3.148445256	4.044208345	5.051623959	6.263924486	6.903041652
0.15	1.75444374	2.662100922	3.540187409	4.398041049	5.262828996	6.209927795
0.125	1.444820555	2.231433523	2.961253114	3.737426447	4.463136387	5.163158068
0.1	1.209504013	1.8673719	2.412794464	2.995214787	3.622350596	4.196495449
0.075	0.9143876203	1.379822082	1.890972977	2.292491994	2.767491802	3.187356229

<b>Solids Loading</b>	<b>EROI</b>				
	<b>40% Yield</b>	<b>45% Yield</b>	<b>50% Yield</b>	<b>55% Yield</b>	<b>60% Yield</b>
0.325	14.00965859	16.19112748	17.33166457	18.6014069	20.81276721
0.3	13.07979147	14.59249153	16.33071997	17.8017009	19.54997786
0.275	12.0923839	13.68411693	15.04455019	16.63839558	17.62713943
0.25	11.48613065	12.52758682	13.97559406	14.90213134	16.61660827
0.225	10.10274255	11.77263676	12.64646752	13.9407478	15.23829954
0.2	9.218914247	10.01211334	11.49976997	12.65538638	13.31632289
0.175	7.880200219	9.15271604	10.15676666	11.11848568	12.11092239
0.15	7.075866574	7.908134901	8.75892791	9.603360433	10.59288771
0.125	5.957125851	6.667840465	7.479483415	8.184534571	8.849799878
0.1	4.833339079	5.597578155	5.815428856	6.577841406	7.230990128
0.075	3.66426966	4.000472275	4.564881108	5.051052953	5.664589721

**Appendix E. Data for the effect of HHV with solids loading graph**

<b>Solids Loading</b>	<b>EROI</b>				
	<b>HHV=35.55</b>	<b>HHV=37.525</b>	<b>HHV=39.5</b>	<b>HHV=41.475</b>	<b>HHV=43.45</b>
0.325	14.18578864	14.97388801	15.76198738	16.55008675	17.33818612
0.3	12.57039172	13.26874682	13.96710192	14.66545701	15.36381211
0.275	11.9973419	12.6638609	13.33037989	13.99689889	14.66341788
0.25	10.98668374	11.59705506	12.20742638	12.8177977	13.42816902
0.225	10.32618147	10.89985822	11.47353497	12.04721171	12.62088846
0.2	8.786590384	9.274734294	9.762878204	10.25102211	10.73916602
0.175	8.033947327	8.480277734	8.926608141	9.372938548	9.819268956
0.15	6.943838602	7.329607413	7.715376224	8.101145035	8.486913847
0.125	5.856754464	6.182129712	6.50750496	6.832880208	7.158255456
0.1	4.918031823	5.191255813	5.464479804	5.737703794	6.010927784
0.075	3.516466242	3.711825478	3.907184713	4.102543949	4.297903185

**Appendix F. Data for the effect of yield with solids loading on EROI with upgrading**

<b>Solids Loading</b>	<b>EROI</b>					
	<b>10% Yield</b>	<b>15% Yield</b>	<b>20% Yield</b>	<b>25% Yield</b>	<b>30% Yield</b>	<b>35% Yield</b>
0.325	1.756484227	2.150821405	2.434080335	2.690236715	2.862521961	3.028506248
0.3	1.66491832	2.083922204	2.418023246	2.593708444	2.800160369	2.938426415
0.275	1.584929055	1.996907097	2.311343004	2.570771385	2.727000854	2.881841946
0.25	1.498447197	1.918291058	2.213516573	2.455041092	2.613152361	2.801217375
0.225	1.387885526	1.813375715	2.121934656	2.359622761	2.553212131	2.677206121
0.2	1.317717639	1.678540771	2.014330248	2.254015338	2.410847165	2.60495064
0.175	1.205920505	1.618301102	1.87667108	2.113150772	2.342486319	2.444851949
0.15	1.083290013	1.453272014	1.73783079	1.965402172	2.156938592	2.333311133
0.125	0.9338600421	1.289033266	1.557118494	1.794034276	1.981016418	2.136497455
0.1	0.8105930096	1.134519468	1.360470355	1.568426931	1.761549659	1.915681936
0.075	0.6425266653	0.9006967528	1.145019035	1.31347151	1.490749886	1.630674903

<b>Solids Loading</b>	<b>EROI</b>				
	<b>40% Yield</b>	<b>45% Yield</b>	<b>50% Yield</b>	<b>55% Yield</b>	<b>60% Yield</b>
0.325	3.123450873	3.241188256	3.293657622	3.346148551	3.425318643
0.3	3.064709038	3.157451705	3.247909023	3.313765253	3.381843565
0.275	2.99540484	3.103544782	3.182473515	3.26241847	3.306394489
0.25	2.948782113	3.026903906	3.121399618	3.174712115	3.2614045
0.225	2.82853722	2.971231091	3.035240671	3.119293724	3.192858361
0.2	2.739610827	2.819894926	2.949868304	3.035861641	3.080211639
0.175	2.581979165	2.732508545	2.833640278	2.918818781	2.996778966
0.15	2.470697719	2.58559807	2.688864678	2.779599287	2.873554943
0.125	2.289170462	2.408465649	2.528307824	2.620589406	2.699153678
0.1	2.065952377	2.222821616	2.263540989	2.394157167	2.493282848
0.075	1.773480915	1.865227917	2.005003451	2.113029936	2.235521379



## Appendix G. Literature projection data

<b>Feedstock</b>	<b>Solids Loading</b>	<b>Biocrude Yield</b>	<b>Projected EROI</b>
Chlorella Pyrenoidosa	0.2	35.4	2.6154
Chlorella Pyrenoidosa	0.25	39.6	2.93574
Chlorella Pyrenoidosa	0.305	41	3.093708
Chlorella Pyrenoidosa	0.194	37.7	2.643366328
Chlorella Pyrenoidosa	0.2	43.5	2.8183
Cornstalk	0.167	20.8	1.861043324
Cornstalk	0.1	12.1	0.933098
Cornstalk	0.1	12.2	0.939336
Cornstalk	0.1	13.8	1.039144
Cornstalk	0.1	23.3	1.491
Cornstalk	0.1	27	1.6354
Cornstalk	0.1	34.2	1.88104
Beech wood	0.1	34.6	1.89352
Cypress	0.1	10	0.8021
Cypress	0.1	14.5	1.08281
Oak wood	0.2	19.9	2.00206
Pine sawdust	0.167	25.2	2.062508876
Pine wood	0.2	30.3	2.4452
Pine wood	0.167	21.5	1.89335062
Rice husk	0.1	20.8	1.391
Rice husk	0.091	43.1	2.040130312
Rice husk	0.25	46	3.07875
Rice husk	0.2	13.8	1.613656
Spirulina	0.1	27.7	1.66214
Spirulina	0.1	29.2	1.71944
Spirulina	0.091	28.6	1.618742972
Spirulina	0.25	38	2.8987
Spirulina	0.2	39.9	2.7324
Spirulina	0.2	40.7	2.75166
Spirulina	0.091	21	1.32599542
Spirulina	0.147	23.7	1.863797116
Sewage sludge	0.1	23.5	1.499
Sewage sludge	0.167	47	2.71096236
Sewage sludge	0.1	22.9	1.475
Sewage sludge	0.16	25	2.00984