ABSTRACT

Title of Thesis: IMPROVING THE PROCESS OF SUPERCRITICAL CARBON-DIOXIDE-ASSISTED LIQUEFACTION OF BIOMASS FOR THE PRODUCTION OF BIOFUELS

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The United States has been looking for alternative energy sources to combat energy dependence and carbon emissions. There exists a multitude of methods attempting to achieve this effort while making use of existing infrastructure. One such novel method is the supercritical carbon-dioxide-assisted liquefaction of biomass. This method seeks to exploit a large supply of biomass waste in the US through the use of carbon dioxide, a readily available and nontoxic gas. This paper investigated two potential improvements for liquid yields in the supercritical carbon-dioxide-assisted liquefaction system. Those improvements were the effects of heating on the solid and liquid yields and the efficacy of supercritical carbon dioxide extraction of liquid products.

Three specific aspects of heating were investigated: resident time, heating rate, and total time. Resident times of 10 minutes 20 minutes and 60 minutes were tested. High heating rates

were achieved via the use of induction heating. Heating rates of 6, 12, and 250 °C/min were tested. The effects of total reaction time were also investigated; however, this was dependent on the heating rate and resident time, thus it could not be independently controlled. The investigation found that neither resident time nor total reaction time has a significant impact on the solid or liquid yields. The heating rate, on the other hand, showed a good correlation with a proposed relationship of $L = 13.01 \cdot H^{0.1687}$ and $S = 58.57 \cdot H^{-0.08348}$, where L is the liquid yield in wt%, S is the solids yield in wt%, and H is the heating rate in °C/min.

This investigation had a stated goal of achieving a liquid yield of over 30% in under 45 minutes while maintaining a solids yield of less than 50%. It achieved this goal with a particular test having a liquid yield of 32% and a solids yield of 40% in under 12 minutes.

Supercritical carbon dioxide extraction was proven to be effective at recovering liquid yields. It was not as successful as acetone-aided extraction; however, it shows promise, especially given its potential for overall process integration in the future. sCO_2 extraction was seen to be most effective when conducted in conjunction with sCO_2 liquefaction.

IMPROVING THE PROCESS OF SUPERCRITICAL CARBON-DIOXIDE-ASSISTED LIQUEFACTION OF BIOMASS FOR THE PRODUCTION OF BIOFUELS

By

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Thesis Submitted to the Faculty of the Graduate School of the University of Maryland, College Park in partial fulfillment of the requirements for the degree of Master of Science
2024

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Acknowledgments

"This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Bioenergy Technologies Office Award Number DE-EE0009757."

I owe a significant thanks to Professor Ashwani Gupta who helped turn this aspiration into a reality. I certainly would not have been able to make it this far without his continued support. This work could not have been completed without the assistance Dr. Kiran Burra who assisted in the experimentation.

I also owe my gratitude to the United States Marine Corps for allowing me to delay my reporting to Quantico, Virginia for the basic officer course so that I would be able to pursue graduate education. Specifically, I owe my place here to Colonel Micheal Styskal USMC retired and Vice Admiral Sean Buck USN retired for selecting and permitting me to pursue graduate education after commissioning.

There is a litany of professors and instructors who have mentored me up to this point, and there are a few who deserve special recognition for going beyond the standard. Those include Professor Joshua Radice who, despite not always agreeing, was able to challenge me and push the envelope of what I thought could be done, and Professor Jim Cowart who I had as an instructor more times than anyone else in my baccalaureate and whose support encouraged me to dig deeper into assignments to try and find better and more elegant solutions.

Table of Contents

List of Figures

Chapter 1: Introduction

1.1 Justification

The U.S. currently has approximately 692 million tons of biomass available annually with only 342 million tons being used for energy-related enterprises. The U.S. Department of Energy believes that annual biomass yields could increase to as high as 1.238 billion tons of biomass with "purpose growth" high-yield energy crops on pre-existing cropland. Investment in the development of new forms of biomass including algae could improve availability to as much as 1.750 billion tons annually.[1] Biomass will need to be exploited to achieve sustainability goals in the future.

The International Energy Agency estimated emissions of more than 36.8 billion tons of carbon dioxide in 2022.[2] Fossil fuels account for over 77% of US energy production with petroleum making up 28%.[3] The problem with fossil fuels is that they introduce "new" carbon dioxide into the atmosphere. In the crude oil, natural gas, or coal forms, carbon is effectively being stored in a way that does not adversely impact the environment. When those fuels are used, that CO_2 is then released into the atmosphere. Carbon dioxide is a greenhouse gas that contributes to global warming which has negative long-term effects including sea level rise and erratic or extreme weather events.[4,5] Excess CO_2 in the atmosphere will diffuse into the ocean forming carbonic acid which is harmful to marine life.[6] As an alternative, biomass only releases the amount of CO_2 that it had previously captured from the atmosphere. To simplify, a tree's structure is made of complex carbohydrates known as cellulose and starch. These structures are produced by cellular processes that retain atmospheric carbon dioxide. This tree can then be made into a biofuel which will release no more carbon dioxide than it had already taken out of the atmosphere, creating a net zero carbon emission. While the use of carbon-based fuels is necessary, it can be done in such a way that does not introduce excessive amounts of carbon dioxide into the atmosphere.

The transportation industry alone contributes 27% to the total US energy usage with 89% being from petroleum-based fuels.[1] This led to the transportation sector being responsible for a 28% share of US greenhouse gas emissions in 2022.[7] The U.S. liquid fuel infrastructure system includes over one million barrels worth of storage capacity, over 60,000 miles of oil pipelines, more than 100 oil rail terminals with an upload capacity of 2 million barrels per day, and more than 300 oil ports.[8] This is all to express that a viable fossil fuel alternative would need to make use of existing liquid fuel infrastructure if it is to be realistically employed. This leaves open the door for liquid biofuels; however, it also limits the applicability of certain solid and gaseous fuels that may not be as useful in the transportation sector.

There are socioeconomic drawbacks to the use of biofuels as well as some negative environmental impacts that need to be considered. The cultivation of land to produce energy crops could have potentially negative impacts on the availability of arable land for food production, thus increasing the price and decreasing the availability of food. Other drawbacks include biofuels generally having lower energy yields than fossil fuels, unsuitable power grids or infrastructure for biofuel production, and the harmful environmental effects of the pesticides, fertilizers, and carbon emissions required for the cultivation of the energy crops.[9,10] All of these must be appropriately balanced for biofuels to be an effective fossil fuel alternative. These problems are mainly in reference to biomass produced from energy crops; there are already large amounts, over 300 million tons, of unused biomass that would have far less significant drawbacks.

1.2 Background

While there are a variety of ways to use biomass for energy, this paper will focus on the production of biofuels. Biofuels are defined as "combustible fuels derived from recently produced biomass, as opposed to ancient biomass… typically referring to liquid fuels.[17]" This definition is suitable as it acknowledges the fact that fossil fuels and biofuels originate from carbon-based biomass, the difference being that fossil fuels occur naturally over a long period of time while biofuels are synthesized rapidly.

1.2.1 Bioethanol

The most common biofuel available today is bioethanol.[11] Feedstock includes starches and simple sugars with approximately 40% of global production coming from sugar cane and sugar beet and an estimated 60% coming from starches such as corn.[12] The process for producing ethanol is known as alcohol fermentation and is conducted by yeast in an anaerobic environment. This process leads to the production of hydrated ethanol. The water is then extracted from the mixture to produce usable anhydrous ethanol.[13] Bioethanol is currently mixed with gasoline as a method of lowering emissions. The precise effects of these blends are dependent on the engine characteristics as well as the operating conditions such as speed and torque.[14] The general trend is that a higher ethanol percentage will decrease harmful emissions such as carbon monoxide, NOx, and total hydrocarbons at the cost of energy efficiency.[15] Newly manufactured vehicles are being designed with ethanol mixtures in mind; however, there are already over 270.1 million light-duty vehicles being operated in the US alone as of 2019.[16] The average light-duty vehicle can safely use 10% ethanol and 90% gasoline blended fuel; however, mixtures with larger ratios of ethanol can be harmful to older vehicles and accelerate engine deterioration.[17]

1.2.2 Biodiesel

Biodiesel is the second most common fossil fuel alternative.[18] Biodiesel can be synthesized from a variety of oils and fats.[19] The feedstock for biodiesel is vegetable oil with soybean oil specifically having the largest share. Waste oils, fats, and greases also compose a large quantity of the feedstock.[20]

Table 1: Biodiesel feedstocks for 2024 in millions of pounds.[20]

2024	Tallow	White Grease	Yellow Grease
January	631	45	616
February	715	55	586
March	586	68	635
2024	Canola Oil	Corn Oil	Soybean Oil
January	376	335	960
February	296	314	888
March	356	322	1026

The process for producing biodiesel is known as transesterification and requires alcohol and a catalyst (typically a base). The resulting mixture must then be purified to yield usable biodiesel. Unique advantages of biodiesel include no sulfur dioxide emissions, a high flash point, and the ability to be used in diesel engines without modification. Disadvantages include higher NOx emissions than regular diesel, a higher freezing point, and the degradation of rubber or plastic products; it is also not stable and therefore not suitable for long-term storage.[21] Engine modifications are not required for blends of 20% biodiesel or less but are required for higher percentages.[19]

1.2.3 Green Biodiesel

An alternative to biodiesel is green diesel, which is also known as renewable diesel. The process uses the same feedstocks as biodiesel with the main difference being hydrogenation. The typical biodiesel process uses esterification while green diesel requires catalytic hydrotreating. [22] The hydrotreating process is already well established and would not require significant investment or conversion to be used in the production of renewable diesel. Green diesel also requires a subsequent isomerization step. Green diesel does not contain aromatics, oxygen, or sulfur and therefore has a higher heating value than biodiesel. It even exceeds that of conventional diesel from fossil fuels. The renewable diesel process does not yield any byproducts, unlike esterification which produces glycerin.[GB2]

1.2.4 Other biodiesels

The success of biodiesel has led to the development of a variety of biofuel-diesel production methods. These methods are numerous and constantly expanding. The work *Comparison between different types of renewable diesel* by Stella Bezergianni covers this topic extensively and should be referenced for further interest in sustainable diesel alternatives.[23]

1.2.5 Pyrolysis

Pyrolysis is a method of thermochemical biofuel production that involves heating in an anaerobic environment. The products of pyrolysis include biochar, gas, and bio-oil; the proportions of which are largely dependent on the temperatures and the heating rates.[24] The fundamental principle behind pyrolysis is the thermal decomposition of biomass in the absence of oxygen. The absence of oxygen allows heating beyond the thermal stability of the biomass which then produces more stable products.[25] Slow pyrolysis uses heating rates of less than 10 ℃ / min and is typically used with larger particles that have a diameter greater than 2mm. The process yields a relatively high ratio of biochar and can take multiple days to complete. The resident temperature is 400 ℃.[26] Intermediate pyrolysis operates between 500 ℃ and 650 ℃ with a heating rate between 0.1 and 10 ℃ / min and resident times of 300 - 1000 seconds. Product composition includes 40-60% liquid, 20-30% gas, and 15-25% biochar.[27] An advantage of intermediate pyrolysis is that it can use a variety of particle sizes, unlike fast pyrolysis which can only use small particles.[28] Fast pyrolysis, as its name would imply, uses a short resident time and high heating rates. The temperature is typically over 500 ℃, and resident time is only a few seconds. Maximum liquid yields are obtained in the range of 500 - 550 ℃.[24] The process yields 70 - 75% bio-oil from dry wood.[29] One drawback of fast pyrolysis is the need to use small particles of biomass; research into ablative reactors has produced similar results with much larger particles.[30] Flash pyrolysis uses extremely high temperatures and high heating rates. The resident temperature is 700 - 1000 ℃, and the heating rate is anywhere from 500 to 1000 ℃ / minute with resident times of less than 1 second. Flash pyrolysis can only be achieved with extremely small particles and is not yet considered feasible for large-scale use despite bio-oil yields of over 75% [28,31] Hydro pyrolysis differs from fast pyrolysis in the way that it uses hydrogen as the inert gas and is conducted at pressures ranging from 5 - 20 MPa. The presence of hydrogen prevents the formation of unsaturated hydrocarbons, thus yielding a higher-quality bio-oil.[32] While pyrolysis achieves high yields, it is important to consider the quality of the liquid products. Bio-oil produced from pyrolysis has high oxygen content which leads to a lower energy density and a substantial amount of carboxylic acids. This combination makes the bio-oil acidic. The presence of ash within bio-oil can lead to erosion, corrosion, or deterioration in engines if it is in a large enough concentration.[33] The key takeaway from pyrolysis is the importance of temperature and heating rate on the outcome of the process.

1.2.6 Gasification:

Gasification is the process of converting biomass into syngas, hydrogen, and methane. The process has three stages: drying, pyrolysis, and partial oxidation. The process characteristics such as heating rate, resident time, and max temperature depend on the form of pyrolysis being used. Following oxidation, the product must undergo gasification for liquid products to transition to the gaseous state. Gasification is under continued study with constant developments being made. The precise process for gasification is also dependent on the feedstock being used. There are a variety of systems for gasification including fixed-bed, fluidized-bed, and entrained flow gasifiers.[34] Output yields depend on the gasifying agent which can be air, pure oxygen, steam, carbon dioxide, or other mixtures.[35] The primary use for syngas, the main product, is electricity generation; further processing can yield other usable products. The Fischer-Tropsch method can produce gasoline and diesel from syngas.[36] Syngas can also be used to synthesize methanol, DME, hydrogen gas, and natural gas.[37] Gasification has a variety of drawbacks associated with it. The primary drawback is the formation of tar which causes catalyst deactivation and can lead to engine fouling. The removal of tar requires further processing which adds cost and complication to the system. Other contaminants include ammonia, hydrogen cyanide, sulfur-containing compounds, halogens, and some metals.[38] Gasification is limited by moisture in the feedstock that it can use. Gasification efficiency is reduced based on moisture content and becomes uneconomical. This prevents the use of gasification on municipal sludge, algae, or other biomass with a high moisture content. It also means that available biomass must be dried before use which consumes additional energy and resources.[39] The transportation industry does not yet have the infrastructure to support non-liquid fuels on a large scale which limits the applicability of gasification products.

1.2.7 Hydrothermal Liquefaction

Hydrothermal liquefaction is a process that uses near-critical to supercritical water at moderately high temperatures and high pressures to produce bio-crude from feedstocks with a high moisture content. The method operates in conditions ranging between 250 to 450 °C with optimum liquid yields typically around 300 °C. Pressure conditions range from 100 - 300 bar.[35] Yields from the hydrothermal liquefaction process are largely dependent on a variety of operating conditions including reaction temperature, feedstock composition, resident time, H_2O to biomass ratio, reaction pressure, reaction catalyst, and heating rate.[40] The process produces bio-oil with a better energy density (30-37 MJ/kg) and a lower oxygen content (10-20%) than other biofuel production methods like pyrolysis.[41] The oxygen content, despite being relatively low, is still high enough that the bio-crude becomes acidic and lacks stability for extended storage.[42] This becomes more problematic as oxygenation can lead to catalyst degradation which coke formation and costs.[40] The major advantage of hydrothermal liquefaction is the ability to process materials that other methods cannot efficiently process such as wet algae, municipal sludge, or any other high moisture content biomass. The drawbacks involve the high energy input costs, significant economic costs, and the significant amount of post-processing required for the product to be usable.

1.2.8 Supercritical Carbon-Dioxide-Assisted liquefaction

Supercritical Carbon-Dioxide-Assist Liquefaction is a process with similar operating conditions as hydrothermal liquefaction; however, it makes use of carbon dioxide as the assisting agent rather than water. An advantage of CO_2 over water is that it has a much lower critical point, 31.1 °C at 73.8 bar versus 374 °C at 221 bar, which uses significantly less energy to achieve.[43] Operating pressures for sCO_2-assisted liquefaction range from 100 to 300 bar with temperatures at 150 to 400 °C.[44]

sCO_2 also acts as a suitable solvent. It is nonpolar, yet still soluble with hydroxides, carbonyls, and fluoride groups as a result of its quadrupole moment. Water does not dissolve in sCO_2 but can form water-in-CO_2 emulsions. The solubility of reactants can be increased through the addition of co-solvents such as alcohols, acetone, hexane, formic acid, and acetic acid.[45] In the supercritical regime, small changes in temperature cause large changes in density which directly impacts the solubility.[46]

These traits, compounded with the fact that CO_2 is a safe and readily available gas, make it ideal for use in biofuel production. The use of sCO_2 in biomass pretreatment, as well as bio-oil extraction, makes it ideal for an integrated system that could further increase efficiency.[44]

Studies have already been conducted on the use of cosolvents including water, ethanol, and acetone as well as mixtures of these liquids. Certain yields were as high as 65% liquid yield.[47] Studies were also conducted using supercritical methanol and ethanol as solvents producing yields between 43% and 45% liquid yield.[48]

Alkali salts including Na_2CO_3, K_2CO_3, and $KHCO_3$ have shown promise as catalysts. They reduce the formation of biochar which improves desired yields.[49] Amongst these catalysts, potassium salts are the best for oil yield. Salts are better catalysts than hydroxide compounds possibly as a result of the formation of bases and bicarbonates with the bicarbonates also acting as catalysts.[50] The elevated pH is conducive to the formation of more stable products.[51]

Supercritical carbon-dioxide-assisted liquefaction is an improvement to the hydrothermal liquefaction process that eliminates the need for additional water thus reducing energy costs. The suitability of CO_2 with a wide range of catalysts and cosolvents means that the process can be further manipulated to improve the already relatively high yields from HTL. When used with appropriate co-solvents and catalysts, the sCO_2 system produces a slightly basic environment that is suitable for the production of more stable yields. The process can be readily integrated with supercritical carbon dioxide extraction to further reduce yield losses in the extraction process as well as increase the economic and energy efficiency of the overall biomass to biofuel procoss.

1.3 Areas of Improvement

Supercritical Carbon Dioxide Assisted Liquefaction (sCO_2L) is being researched extensively at the University of Maryland College Park and has proven to be a viable technology for carbon emission reduction. The process must still be proven to be feasible on a large scale. To do this, the system must be refined by decreasing the batch time and increasing liquid yields. Essentially, sCO_2L must be so advantageous that there is no option but to adopt it. On a trivial level, liquefaction is a chemical reaction composed of the decomposition of the biomass feedstock and the synthesis of alkanes, alkenes, alcohols, aromatics, and other organic compounds that compose bio-oil. The factors that generally affect chemical reactions are catalysts, pH, particle size, reactant concentration, and temperature.

Catalysts have already been extensively researched in bio-oil production. While most of this research has been done with the hydrothermal process, there is still some existing research on the subject in relation to sCO_2L. pH, on the other hand, has not been widely explored directly, but its indirect effects are fairly well established. The general trend is that acidic solutions yield less stable bio-oils, and basic solutions yield more stable bio-oils. Additionally, the pH is largely dependent on the catalysts and solvents. This makes it difficult to vary without affecting some other aspects of the reaction.

Particle size or, more specifically, reaction surface area, will also impact the specimen's ability to react. Generally, a smaller particle size will increase the reaction surface area and in turn, increase the rate of the reaction. For biomass, reducing particle size correlates to increased energy and economic. Therefore, the particle size must be optimized with respect to yields, reaction rate, and costs.

Typically, as reactant concentrations increase, so does the reaction rate. This is particularly important when liquid solvents are being used. The precise effects of this have not been greatly studied; however, current focus is not on this concept.

Temperature is the last mechanism that significantly impacts a reaction. In the sCO_2L process, temperature directly affects the pressure, and solubility of the CO_2. The focus of this paper will be on the manipulation of temperature / heating in an attempt to improve the batch time and liquid bio-oil yield. This will be measured by two metrics: liquid yield (wt%) and total reaction time or batch process time.

An increase in temperature generally increases the reaction rate. In this particular system, the desired product is liquid bio-oil; however, the formation of biochar and gasses also occurs. The key is to find a heating profile that promotes the rapid and abundant synthesis of bio-oil but delays or fully inhibits the formation of biochar.

1.4 Goals and Objectives

The investigation will focus on the impacts of heating as well as the feasibility of sCO_2 extraction. The goal is to improve liquid yields while decreasing or maintaining solid yields. The objectives of this investigation are to:

1. Find conditions that will improve liquid oil yields above 30% by mass. The existing system makes use of K_2CO_3 and produces liquid yields in excess of 30% from 10 grams of biomass in a 100 mL reactor. This 30% mark is the baseline for the process to be considered improving.
2. Lower the batch process time to less than 45 total minutes. The existing process uses a 120-minute resident time. The usefulness of this 120 minutes is questionable and makes the testing process time-intensive. Reducing this time while maintaining yields will allow for further testing. Additionally, a long resident time requires more energy to maintain high temperatures. Reducing the overall process time will reduce the required energy input, further demonstrating the benefits of supercritical liquefaction.
3. Prevent Biochar yields from exceeding 50% by mass. Biochar production is overall an ancillary concern except for in how it relates to liquid yield production. The existing process can achieve yields well below 40%. 50% is for a cap on solid by-products.

Chapter 2: Heating

2.1 Introduction

As seen from pyrolysis and hydrothermal liquefaction, resident temperature, resident time, and heating rate all play key roles in determining bio-oil yields. The totality of these aspects can be called the heating profile. A clear distinction needs to be made between the heating profile and the temperature profile. The heating profile relates to the input of energy as an effort to achieve certain temperatures in a certain amount of time, for example, the object will be heated at 10 °C per minute until it reaches 100 °C and then that temperature will be maintained for 30 minutes. A temperature profile, on the other hand, is the achieved temperature distribution throughout the pressure vessel at any given time. For example, at time 30 minutes, the outer wall of the pressure vessel may be at a temperature of 120 °C, the inner wall at 110 °C, and the center of the specimen at 90 °C. The temperature profile is directly related to the heating profile but is also affected by other factors such as particulate matter flow, thermal conductivity, and the mass fraction of the co-solvents, catalysts, and biomass itself. In essence, a heating profile is an attempt to achieve a certain desired temperature profile. The ideal temperature profile would be uniformity throughout the biomass. To properly investigate heating, the system needs to achieve a relatively wide range of temperatures and heating rates. The standard practice for CO_2-assisted liquefaction is furnace heating. While furnace heating achieves high enough temperatures, it does not allow for high heating rates.

2.2 Goals and Objectives

This chapter will investigate the effects of heating rate and resident time on liquid and solid yields from supercritical liquefaction. To achieve this, improvements must be made to the existing heating system. The 100 mL and 1200 mL reactors can achieve a 20 and 6.7 ℃ per minute heating rate respectively. Therefore, this chapter will also include a preliminary investigation into heating solutions with the goal of achieving higher heating rates. The objectives of this chapter are:

1. Achieve a heating rate in excess of 100 ℃ per minute while being able to reach a minimum temperature of 300 ℃. Literature shows that heating rates in excess of 100 ℃ per minute are able to increase the liquid yield by several percent while decreasing the gas and solid yields by significant margins.[51]
2. Lower the batch process time to less than 45 total minutes. This is in fulfillment of investigation Objective Two. To be considered successful, the tests should take less than 45 minutes including heating and resident time, and should have liquid yields in excess of 20% and solid yields less than 50% by mass.

2.3 Background

Heating is certainly important and the method of heating is just as relevant. The basic system is a 316 stainless steel pressure vessel. There are currently two options available with one being 100mL and the other being 1200mL. The 100mL vessel is suitable for experimentation; however, the 1200mL would be optimal for further development in the integrated liquefaction extraction process. The conditions inside of the pressure vessel are corrosive and can range anywhere from moderately acidic to very basic depending on the catalyst and co-solvents.

Additionally, despite being low relative to pyrolysis, the high temperatures over 300 °C must be considered. This paired with the high pressure of 300 bar makes modifications to the inside of the system a challenge.

Figures 2.1 and 2.2: Parr 4590 series microreactor (left).[53] Parr 1200mL pressure vessel (right).[54]

Please note that the photos are not to scale with each other. A table of dimensions was also provided to assist in grasping the dimensions:

Table 2.3: Pressure Vessel Dimensions.[55,56]

	100 mL	1200 mL
Inner Diameter	1.3 inches	3.25 inches
Outer Diameter	2 inches	4.5 inches
Depth	4.6 inches	9.8 inches
Height	5.5 inches	11.65 inches
Heater Power	700 Watts	1300 Watts

2.3.1 Existing System

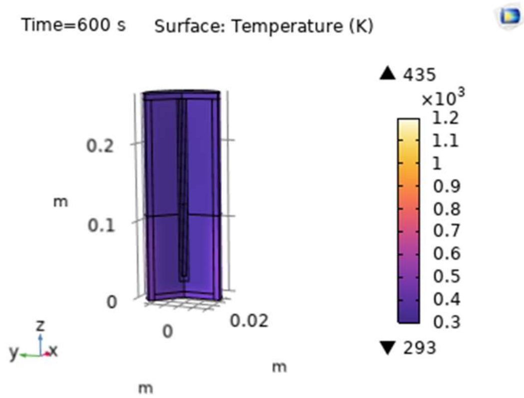
Both systems were originally heated via an external furnace. The shortcoming of the external method is the requirement to heat the pressure vessel itself. This requires a significant amount of power and results in much longer heating times. The metal shell also acts as a thermal store making precise temperature manipulation difficult.

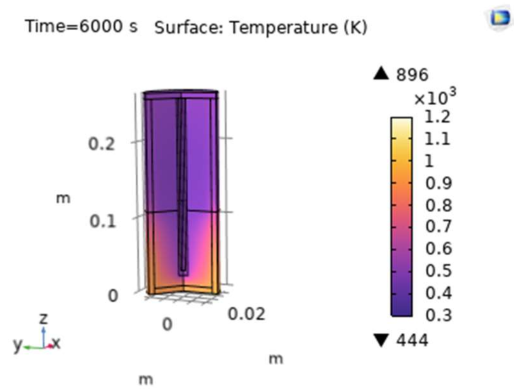
Figure 2.4: Standard 1300-watt furnace heater for 1200 mL pressure vessel.

The 1200 mL pressure vessel has 316 stainless steel (SS316) walls that are 0.3 inches thick. The specific heat capacity of 316 stainless steel averages 535 J/kg/K for the temperatures used[57] and the mass of the pressure vessel is approximately 13.63 kg. To get the biomass to 300 °C, for the external system, the pressure vessel would need to be at a temperature greater than 300 °C at least locally. The thermal conductivity of stainless steel, 16.3 W/m/K[58] is relatively high compared to 0.090 W/m/K for pine wood[59] and 0.12 W/m/K as the maximum conductivity for supercritical CO_2[60]. Based on this and an insulated external boundary condition, it can reasonably be assumed that the temperature of the pressure vessel is nearly uniform along the vertical axis. This means that, at a minimum, the entire mass of the pressure vessel would need to increase by approximately 280 °C which comes out to over 2 million joules. A 1300-watt heater would need 25 minutes to get the pressure vessel up to temperature assuming that none of the heat is being transferred out. Thus, the absolute shortest amount of time that this external heater could achieve the desired operating conditions for this system would be 25 minutes assuming perfect conditions. In reality, the 1200mL vessel takes closer to 45 minutes to achieve the desired operating conditions. This makes it impossible to achieve a 45-minute batch time. This is also well below the desired heating rate of 100 °C/min.

Using the same procedure as above and a calculated mass of 1.46 kg, the 100mL pressure vessel requires a minimum of 4.85 minutes to get to the temperature. In reality, the imperfect system takes over three times as long with actual heat-up times ranging from 15 to 20 minutes. Again, it is well below the 100 °C/min desired heating rate.

COMSOL simulation software was used to compare various heating options. The simulated vessel is composed of 0.3-inch thick 316 Stainless walls with a 316 stainless steel thermowell in the middle for a heater to be inserted into. The lower volume of the pressure vessel is simulated as western white oven-dried pine wood. The actual material used in the experimentation is particulate soft pine. For comparison purposes, these materials share similar thermodynamic properties and therefore are good approximations for each other. This similarity only holds when there is no stirring as the flow characteristics of particulate matter would affect the heat transfer. Flow characteristics for particulates not suspended in a fluid are extremely difficult to predict given their non-conformity to traditional models. This is beyond the scope of this research and therefore will be neglected. The upper volume is simulated as gaseous carbon dioxide. The entirety of the external wall was treated as insulated for comparison with the ideal conditions.





Figures 2.5 and 2.6: Results for external heating COMSOL simulation

The vertical part of the external wall was also given a heat rate of 750 watts. 750 watts was used because this is the actual operating heating rate for the external heater. Figures 2.4 and 2.5 illustrate the simulated temperature distribution at times 600 s and 6000 s respectively. At 600 s, the biomass had only achieved an average temperature of 61.85 °C, and at 6,000 s the biomass was at 311 °C. These numbers are known to be inaccurate to empirical data; however, they can be used for comparison purposes later.

2.3.2 Joule Heating

The seemingly obvious solution would be simply to move the heater from outside to inside of the pressure vessel. This would theoretically reduce heat loss to the pressure vessel itself thus transferring more heat to the biomass and increasing the heating rate. Joule or resistance heating is a simple and yet a very efficient way to transfer electrical energy to thermal energy. Joule heating works by passing a current through a material with high resistance which produces a power loss in the form of heat. The typical material used in joule heating is nichrome. The heat generation is equal to the current times the voltage which is also equivalent to the voltage squared divided by the resistance. Joule heating is highly efficiency with essentially a 100% electrical to thermal energy conversion efficiency.[61]

As previously mentioned, the conditions within the pressure vessel are not well-suited for typical materials. This was a major consideration in determining an acceptable joule heating solution. Commercially available heaters are simply not made to withstand these conditions. The critical weak point is the wires. The wires would require a highly durable, thermally resistant coating for insulation as well as interface sealants with the same properties. A wire feedthrough would also have to be obtained which could handle the pressure and temperature as well as the current requirements for the heaters. This all adds complexity to joule heating which makes a theoretically simple solution far more complex in practice. For practical purposes, options were limited to those that would not directly expose the heater or heater wires to the conditions. This of course will lower the achievable heating rate but is a balance between achieving the goal and doing so at an acceptable cost.

The primary option for joule heating was to insert a small yet powerful cartridge heater into the already existing thermowell. This option attempts to capitalize on the existing pressure vessel design and would have a very low cost.

The 1200 mL reactor has a removable thermowell with a half-inch outer and quarter-inch inner diameter. The thermowell is used in conjunction with a thermocouple to obtain an approximate temperature for the biomass during the reaction.

Figure 2.7: Thermowell for 1200 mL pressure vessel.[62]

A relatively simple solution would be to purchase a quarter-inch cartridge heater and place it inside the thermowell. This solves the aforementioned problem of exposing the wire leads to the reaction. The main advantages of this system are that it is simple, non-intrusive, and does not affect the dead volume. Disadvantages include a relatively low power output, and potentially high local temperatures contributing to nonuniform heating. COMSOL was used to analyze the potential improvement from a cartridge heater.

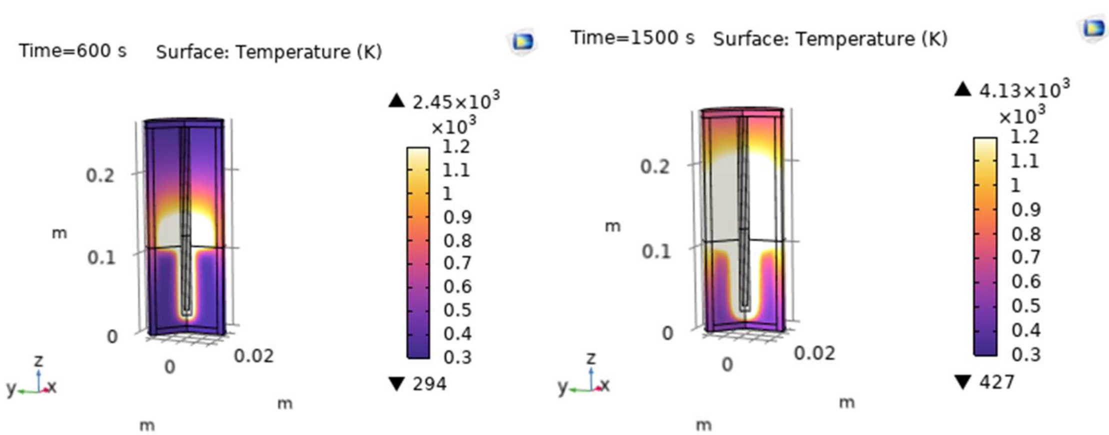


Figure 2.8 and 2.9: Results for internal cartridge heating COMSOL simulation

The conditions for this simulation are almost identical to the existing setup, but there are a few key differences. First, the external wall is no longer acting as a heater and is now strictly simulated as insulated. Second, a heater was placed inside the aforementioned thermowell and simulated to produce 400 watts of heat. This heat rate was chosen based on standard operating conditions for commercially available cartridge heaters of this size. Figures 2.7 and 2.8 illustrate the simulated temperature distribution at times 600 s and 1500 s respectively. At 600 s, the average temperature of the biomass was 338 °C, and at 1500 s, the average temperature was 947 °C. In the simulation, the cartridge heater achieves a higher average temperature, 338°C vs 311°C, with a smaller heat input, 400 watts vs 750 watts, in a tenth of the time, 600 seconds vs. 6000 seconds. The range of temperatures is extremely large, and the difference between the maximum and minimum temperature is over 700 degrees Celsius. This temperature differential would prevent proper testing as the goal is for the system to have a uniform temperature profile at all times.

Thermowell joule heating provides a possible solution, with little to no modification to the existing system. While the thermowell provides a technically easy solution, the walls of the thermowell inhibit the ability to achieve the desired temperature profile and risk damaging the heater itself.

2.3.3 Induction heating

Induction heating is based on the principles of eddy current loss. Simply put, any electrically conductive material can generate heat via a magnetic field-induced current. The exact characteristics of this heating method are fairly complex and could constitute an investigation by themselves. For the sake of brevity, this paper will only address the variables that affect heating without dwelling too much on the physics of the phenomenon.

The first and arguably most important variable to consider is electrical current through the induction coil. The coil itself should be composed of a highly conductive material with low resistance. This is to increase the current through the coil while reducing losses to heating the coil itself. Induction coils typically operate with high currents of hundreds of Amps.

The second most important variable is the frequency of the alternating current. The alternating current from the coil is what produces the magnetic field and in turn, produces the induced current in the pressure vessel. That induced and constantly shifting current produces a phenomenon known as eddy currents which then produce heat due to the resistance of the workpiece. In essence, the pressure vessel is becoming a joule heater. Another impact of the AC frequency is the skin depth. The skin depth can be understood as the depth at which the current density has decreased by a factor of $1/e$; This is critical as the current density directly relates to the heat generation and thus the AC frequency determines the heat generation distribution throughout the workpiece.

Another important variable is the coil geometry. The coil itself is often oversimplified as a solenoid. This simplification, while not entirely accurate, does well to explain the importance of geometry. The geometry of the coil impacts two key aspects, the magnetic field and the inductance. The magnetic field is dependent on the radius of the coil, and as mentioned before, the strength of the magnetic field determines the heat generation; thus, the radius indirectly impacts the heat generation. A similar correlation can be made between the length of the solenoid and the magnetic field; however, the relationships are different. The exact characterization of these relationships is beyond the scope of this investigation. The other impact of the coil's geometry comes in the form of its inductance. The inductance is dependent on the coil's length, radius, and number of turns. Inductance contributes to impedance which reduces the amount of current that can be put through the coil. Paradoxically, the conditions that optimize the magnetic field also increase the inductance and thus reduce the current. Therefore, a balance must be established for the geometry of the coil. The coil radius and length are already determined based on the geometry of the pressure vessel which means the number of turns was the method used for optimizing heat transfer.

The workpiece geometry is equally as important as the coil geometry. This investigation used pre-existing pressure vessels, so the geometry could not be adjusted; however, it is still important to understand the impact this played on the system. The workpiece itself also has an inductance that depends strictly on the geometry and will reduce current. It also has further implications on the heat transfer characteristics of the heat generated.

The final major characteristic affecting the induction heating process is the material of the workpiece. The material properties are responsible for things such as the electrical resistivity and the thermal conductivity. Both of these characteristics are key to understanding why a workpiece heats the way it does.

One drawback of induction heating is its theoretical complexity which makes optimization efforts difficult and expensive. As thoroughly discussed, the characteristics of the induction heater have critical impacts on its heat generation capabilities. The only way to have complete control of these characteristics is to manufacture the system independently which would require professional expertise.

2.4 Experimental

By taking a holistic approach, it was determined that induction heating would be the primary option. Induction heating can theoretically accomplish the goal without requiring any pressure vessel modifications. The non-intrusive nature of induction heating makes it highly compatible with the system.

2.4.1 Materials

As previously mentioned, the process has a multitude of factors limiting material selection. The reactor is a Series 4590 Micro Stirred Reactor, 100mL produced by Parr Instruments. The pressure vessel is rated for 500 °C and pressures as high as 5000 PSI with proper fittings and gaskets. A flexible graphite gasket, also produced by Parr, is used in this investigation to reach the 500 °C rating. This particular reactor was constructed out of 316 Stainless Steel because of its strength and corrosion resistance.

Figure 2.10: Parr 4590 Series Micro Reactor with Stand.[53]

The pressure vessel is fitted with inlet and outlet valves, a built-in thermocouple, a pressure gauge, and a magnetic stirring drive. An internal stirring rod is attached to the magnetic drive inside the pressure vessel. The reaction itself uses approximately 10 grams of biomass and 1 gram of K_2CO_3. Literature shows that a 10% K_2CO_3 to biomass ratio improves bio-oil yields.[2] The biomass is kiln dry pine wood. Liquid carbon dioxide was used in this investigation in conjunction with a Core Separations CL series pump.

Figure 2.11: Core Separations high-pressure liquid pump.[63]

The CL series pump can handle subcritical and supercritical CO_2. The dual piston design also reduces pulsation allowing for more precise CO_2 loading into the pressure vessel.

A U.S. Solid 15KW 30-80 kHz Frequency Induction Heater Furnace, Single Phase 220 V, 16:1 Turns Ratio was used for rapid heating.

Figure 2.12: US Solid 220V 16:1 Turns ratio high-frequency induction heater.[64]

The induction heater allows for heating rates well in excess of 100 °C in the 100 mL reactor allowing for sufficient analysis of the effects of heating rate. The induction heater produces high enough heating rates in the 1200 mL reactor that it can be compared for scalability with using the existing furnace heater on the 100 mL reactor. The existing Parr ceramic heating furnace was also used for cases requiring lower heating rates. Acetone is used as a solvent in the filtration process. Its ability to dissolve most compounds in bio-oil, as well as water, makes it suitable for this purpose.

Figure 2.13 Eyela Rotary Evaporator.[65]

The filter paper used for filtration is VWR Filter Paper, 413 which has a particle retention of 5µm. The Eyela Rotary Evaporator N-1200BS series is used for acetone removal and recovery.

2.4.2: Procedure:

A sample is prepared in the 100mL pressure vessel with 10g of biomass and 1g K_2CO_3. The pressure vessel is sealed and supercritical CO_2 is pumped into the pressure vessel until the pressure and temperature indicate a density of 0.2g/mL. For high heating rates, the apparatus is then placed in a four-turn copper induction coil which is connected to the U.S. solid induction power supply. The current is set to 600 amps until the pressure vessel reaches 300 °C at which point the current is reduced to maintain temperature. This is done manually because there is no controller for the induction heater. The temperature is then maintained for the desired resident time. At the end of the resident time, the pressure vessel is placed in a water bath and cooled to room temperature. For low heating rates, the apparatus is placed in the Parr furnace instead of the induction heating system. The rest of the process is the same except that a PID controller regulates temperature at 300 °C.

Once the pressure vessel has cooled, the outlet valve is opened so that the gasses can leave the system and the pressure can return to atmospheric. The valve may only be opened slightly as too fast of a flow rate will result in liquid and biochar exiting the system. The system is now unsealed and acetone is used to wash biochar and oil from the interior of the apparatus into a beaker.

The solid particles are then filtered out of the acetone solution using filter paper. The all-liquid solution is heated at 75 °C using the Eyela rotary evaporator to separate acetone from the liquid products. The liquid products are then placed in a vial and heated again to remove all remaining acetone. At this point, the aqueous products separate from the bio-oil and can be removed using a standard syringe. The remaining liquid is considered the liquid yield of the process. The residual solid particles in the filter are placed in an oven and heated at 105 ℃ overnight to evaporate any liquids. The remaining particles are weighed.

2.4.3 Analysis:

Yields will be measured by weight percentage (wt%). The weight percentage is calculated by dividing by the initial quantity of biomass:

Liquid Yield (wt%) = (Recovered Liquid) / (Initial Weight of Biomass) x 100%

Solid Yield (wt%) = (Recovered Solids - Catalyst Weight) / (Initial Weight of Biomass) x 100%

An important note is that since liquid yields are not exclusively bio-oil, there are additional aqueous products that are inseparable. The same is true for the solid yields. The solid yield is not necessarily exclusively biochar.

The internal temperature of the pressure vessel was recorded via a thermocouple. These plots of temperature versus time were then used to determine the achieved heating rates, resident temperature, and total reaction time. Figure 2.13 is provided as an example. The average resident temperature was calculated by taking the average of all temperatures starting and ending at designated temperatures (Marker A). The stop temperature was determined as the last temperature reading prior to cooling. This point can easily be identified by the steep decrease in temperature (Marker B). The start temperature (Marker C) was iteratively changed until it was within ± 0.5 ℃ of the average resident temperature. In this example, the resident temperature is 298 ℃ (Marker D), and the start temperature is 298.4 ℃. The standard deviation of the resident temperature was also taken for comparison purposes, in this instance, it is 9.58459°C (Marker E). The resident time is the difference in time between the first time the plot reaches the start temperature and the last time that the plot is greater than the stop temperature; in this example, the resident time starts at about 920 and ends at about 1570 (Marker F). The precisely calculated resident time in this example was 10 minutes and 44 seconds (Marker G).

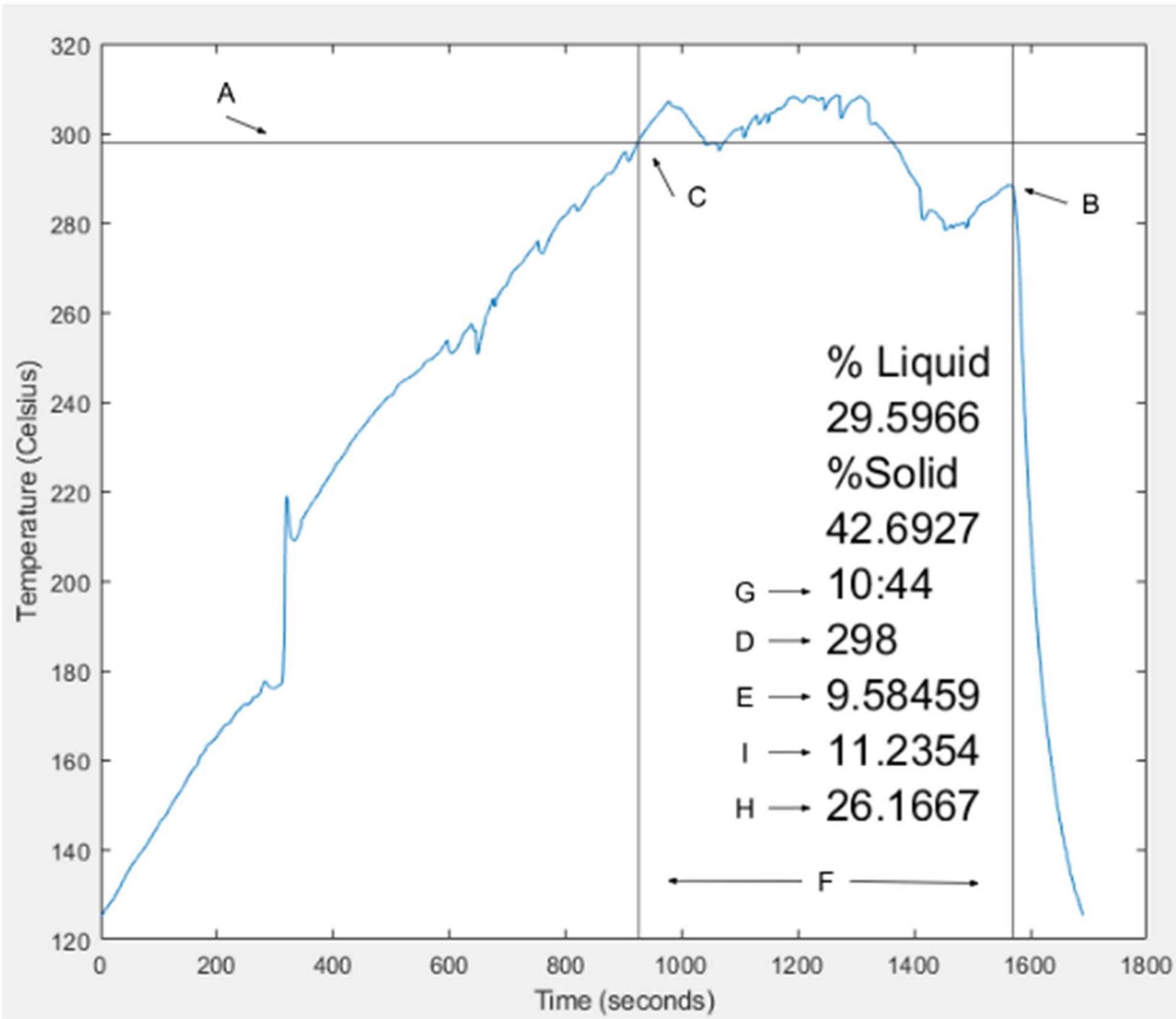


Figure 2.14: Temperature versus Time plot analysis example

The total time is the difference between the first time at which the temperature exceeded 125 °C and the stop temperature, 26.1667 minutes for this example (Marker H). 125 °C was chosen because biomass decomposition begins around 150 °C, thus there is sufficient interval prior to biomass decomposition. The heating rate was calculated by dividing the change in temperature from the first point where the temperature exceeded 125 °C until the stop temperature by the elapsed time between those two points:

(Stop Temperature - 125 °C) / (Elapsed Time)

In this example, the change in temperature is (297 - 125) °C and the elapsed time is approximately 920 seconds. When converted into °C per minute it comes out to be 11.2354 °C/min (Marker I).

2.5: Results

A series of tests were conducted with the aforementioned procedure were heating rate and resident time varied. An attempt was made to keep the resident temperatures constant throughout the experiment.

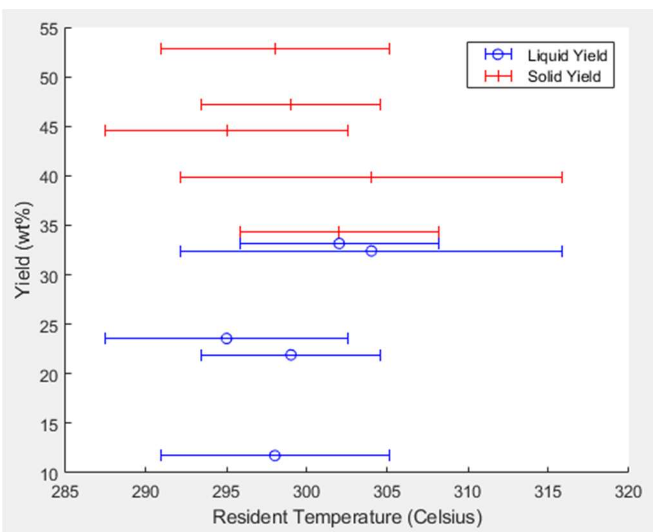


Figure 2.15: Yield versus Resident Temperature plot for all tested cases.

The intent of the experimentation was to maintain all of the tests at the same resident temperature 300 °C. Due to variations in control, it was difficult to achieve a specified resident temperature; however, 300 °C does fall within one standard deviation of the mean for every test.

This certifies that the achieved resident temperatures were not significantly different from 300 °C or from each other.

Resident times were deliberately varied to investigate their effect on the yields. Again, due to control limitations, the exact desired resident times were not achieved; however, they were still accurately measured and provided a more than sufficient range of data for comparison.

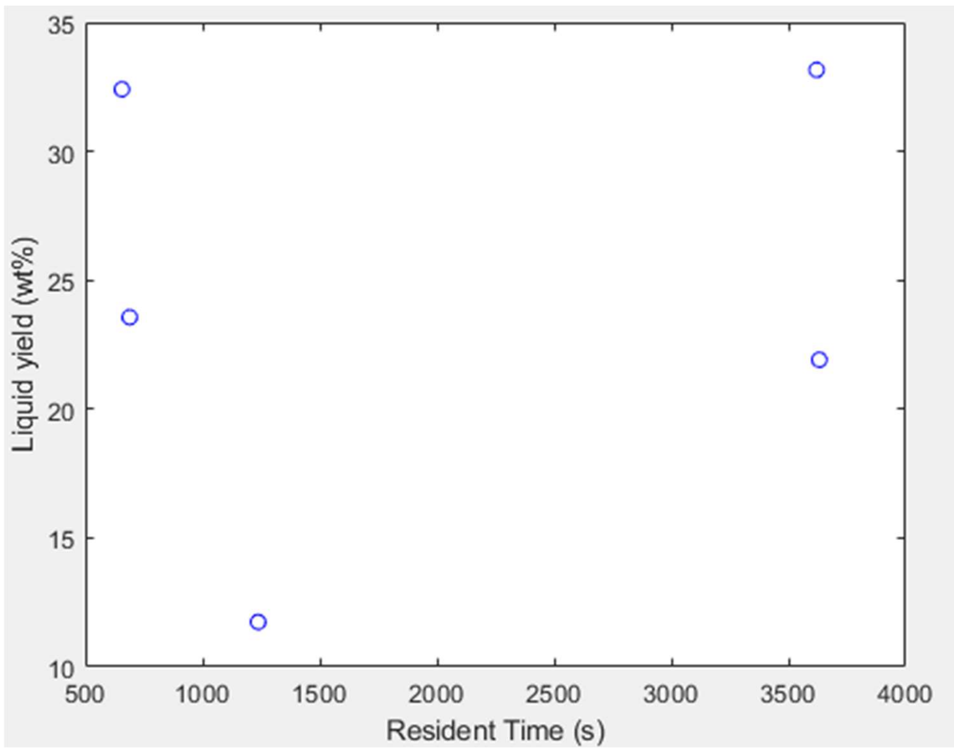


Figure 2.16: Liquid Yield versus Resident Time.

Three desired resident times were attempted and five were achieved. The spread of the liquid yields indicates that the resident time did not significantly impact the liquid yields. It should be noted that the resident times were deliberately limited to just 60 minutes. A more robust testing would include significantly longer resident times such as 2 hours or 4 hours. Those tests were not conducted in this investigation as data for 2 hours already exists and re-evaluation would not be beneficial.

Solid yields were also compared in relation to residence times. While there is a dependency between the liquid and solid yield (as they come from the same reactants), it is possible to shift the relationship to favor the formation of liquids. It also needs to be acknowledged that gaseous products are still produced, thus it is entirely possible for the liquids and solids yields to increase to an extent.

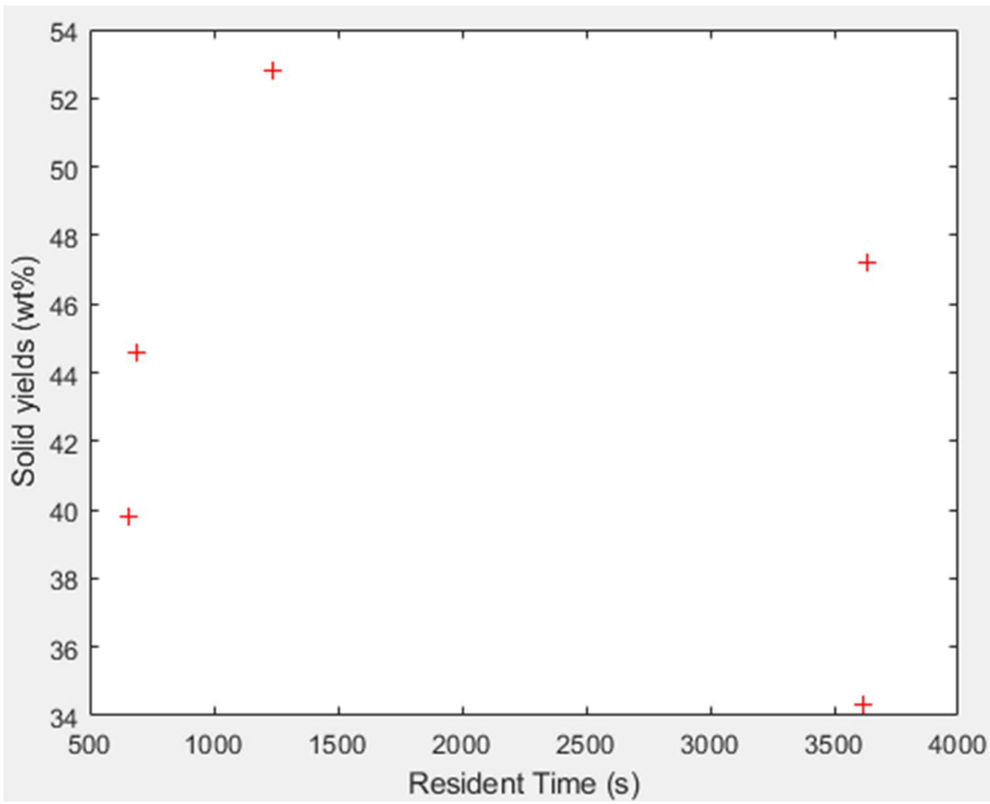


Figure 2.17: Solids Yield versus Resident Time.

Similar to the liquid yield, the solid yield does not demonstrate dependence on the resident time up to one hour. Significantly longer resident times are known to decompose the solids further in favor of gaseous products. This investigation did not go beyond one hour in an effort to fulfill investigation Objective Two: a batch time of 45 minutes or less.

Closely related to resident time is the total reaction time. The total reaction time is a metric that takes into account the amount of time required to reach the resident temperature. This is important as the reaction begins prior to achieving the resident temperature. The precise temperature where the reaction begins is debatable; however, for the sake of comparison, it will be considered 125 °C.

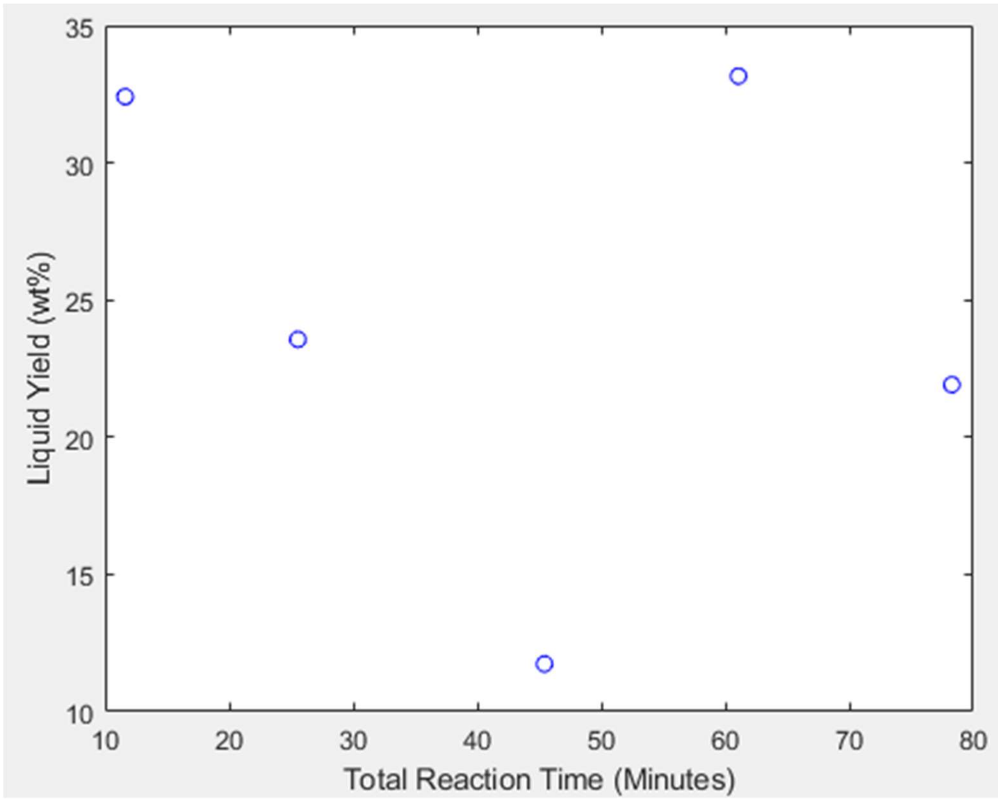


Figure 2.18: Liquid Yield versus Total Reaction Time.

Figure E shows that there is no discernable relationship between the liquid yields for tests held for varying total reaction times. This makes logical sense given that the data was also independent of the resident time which is the major factor in the total reaction time.

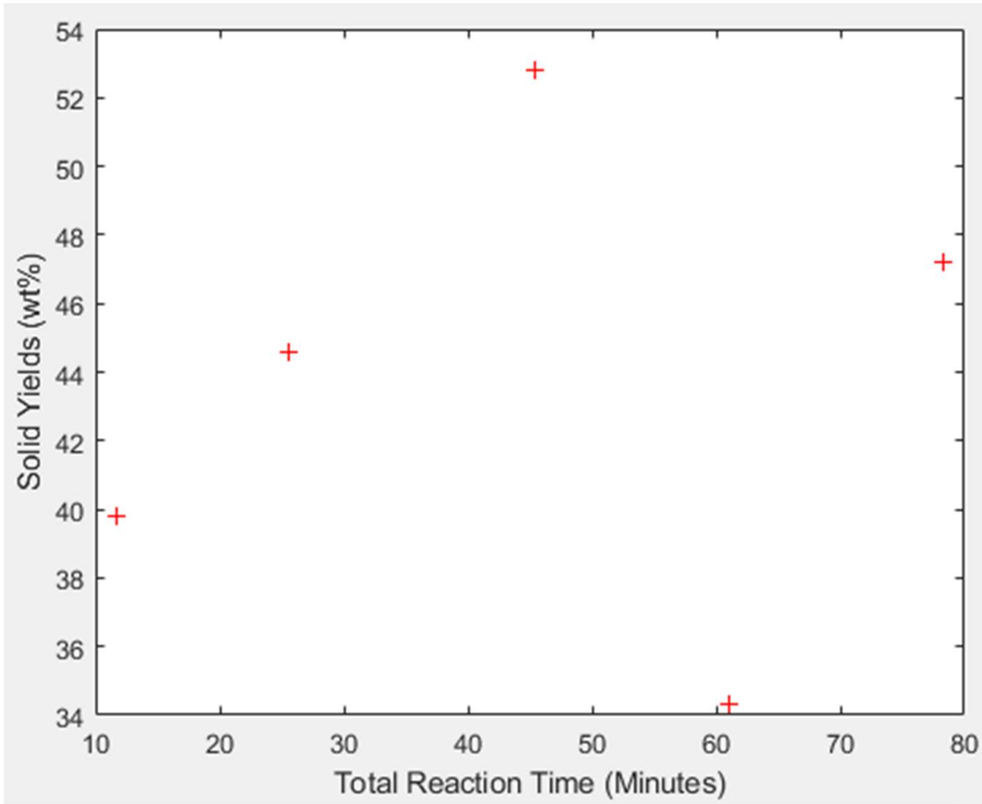


Figure 2.19: Solid Yields versus Total Reaction Time.

Figure E shows the solid yields as a function of total reaction time. Again, the data is randomly distributed with no significant relationship.

The final metric being investigated is the heating rate. The heating rate is characterized by the time the system takes to reach the resident temperature. In practice, the existing furnace was used to achieve the lower heating rates while the induction heater was used to achieve the higher heating rates.

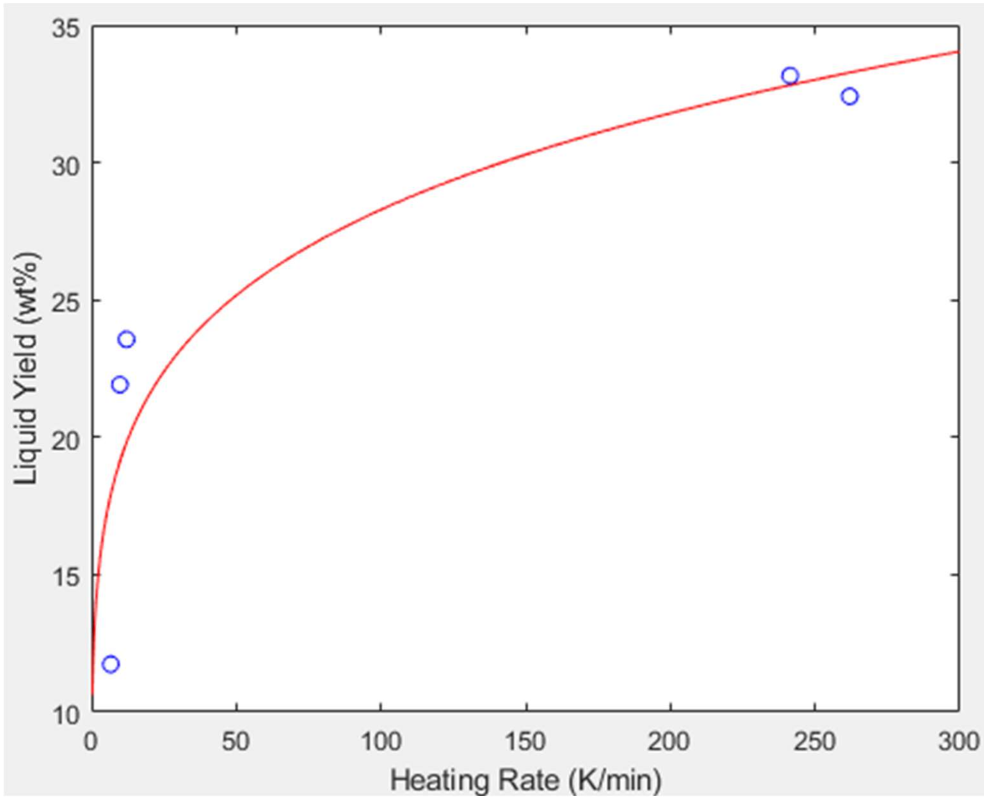


Figure 2.20: Liquid Yield versus Heating Rate.

Figure G is a plot of the liquid yield as a function of heating rate with the red line serving as a proposed relationship. This plot provides significant evidence that liquid yield is dependent on heating rate in the range of 0 K/min to 300 K/min. The relationship resembles that of a power function of the form:

$$A \cdot H^{B} \qquad \text{Eq. (2.1)}$$

Where A is a coefficient equal to 13.01, B is a coefficient equal to 0.1687, and H is the heating rate of K/min or °C/min. The R^2 value was 0.8024. This is high given the relatively high amount of post-processing variability. It can be said that the proposed function is a good fit given the data obtained in this investigation.

$$13.01 \cdot H^{0.1687} \qquad \text{Eq. (2.2)}$$

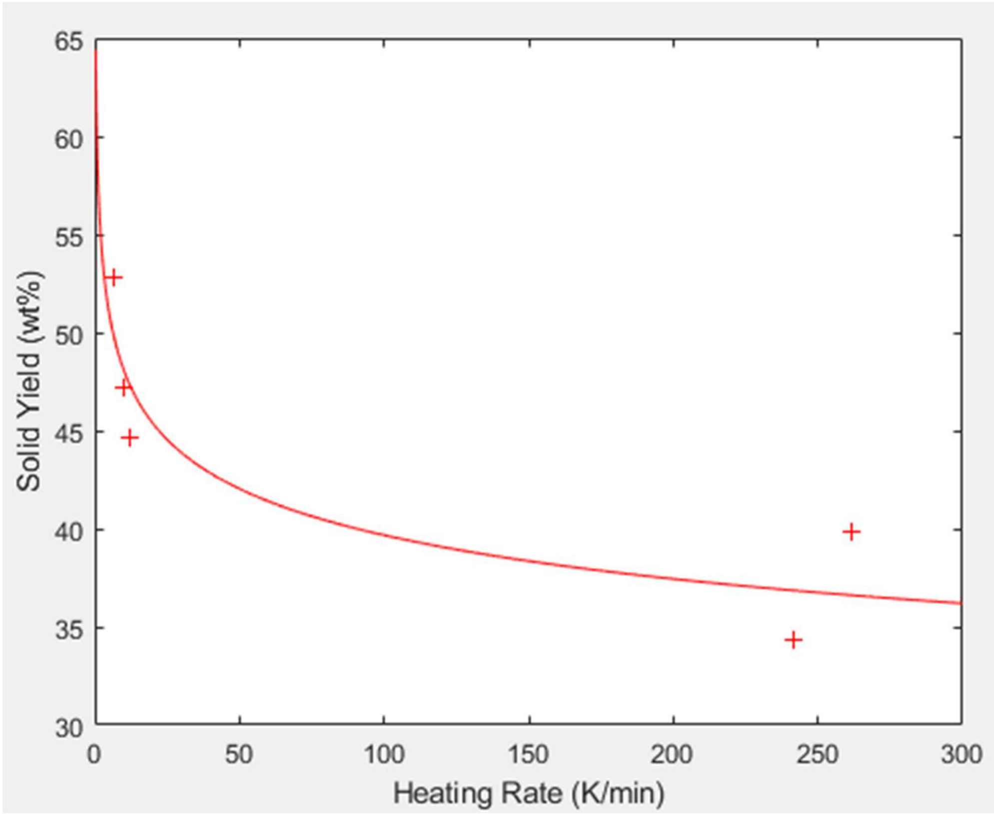


Figure 2.21: Solid Yield versus Heating Rate.

Figure H is a plot of the solid yield as a function of the heating rate. The plot demonstrates that a relationship exists between the solid yields and the heating rate. A power function of the same form as equation (2.1) was used; however, this time the coefficients were A = 58.27 and B = -0.08348.

$$58.27 \cdot H^{-0.08348} \qquad \text{Eq. (2.3)}$$

The R^2 value is 0.8273, slightly higher than the R^2 value for the liquid-to-heating rate relationship. Again, this is an indicator that the proposed function is a good fit.

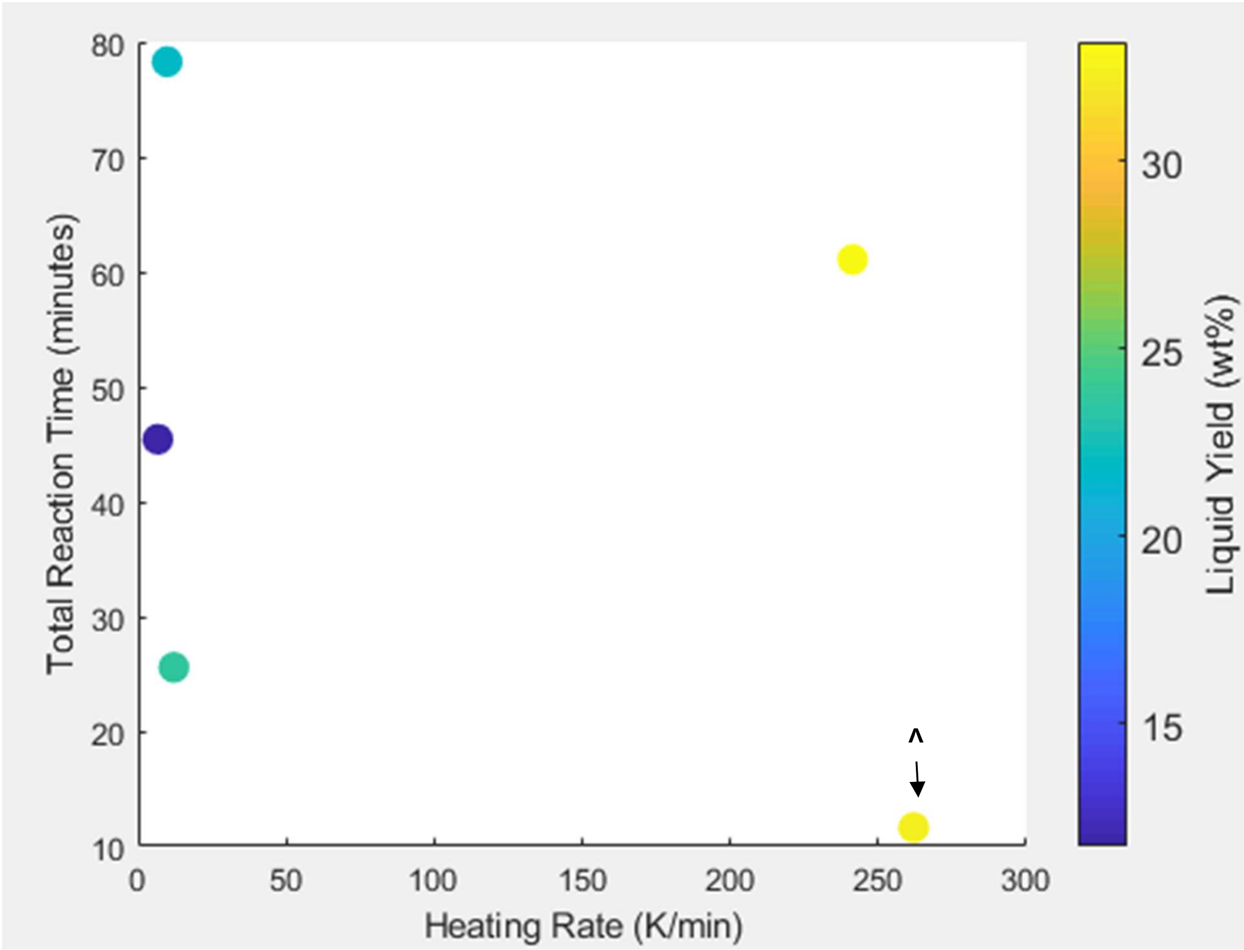


Figure 2.22: Liquid Yields versus Total Reaction Time and Heating Rate.

Figure 2.22 does not introduce any new information; however, it provides an additional view of the data which helps show that liquid yield depends strictly on the heating rate and that that relationship is not significantly impacted by the total reaction time. Point A exists to demonstrate that a yield in excess of 30% was achieved in significantly less than 45 minutes. This is in satisfaction of two investigation goals.

2.6 Discussion:

Chapter Objective One was achieved. The goal was to reach a heating rate of 100 °C per minute; experimentation achieved heating rates consistently over 200 °C per minute. This ability allowed for a robust investigation of the effects of heating rate.

Chapter Objective Two was also proven to be possible and demonstrated. It was found that resident time and total reaction time do not significantly impact either the liquid or solid yields of supercritical CO_2-assisted liquefaction within a time span of 10 to 80 minutes. Longer or shorter intervals may not agree with this result. This is a promising result as it shows that so long as there is sufficient resident time, approximately ten minutes, the results will not significantly change. This corresponds to the ability to reduce overall batch times without sacrificing yields thus confirming that Objective Two can be achieved. This was demonstrated experimentally and can be seen via point A in figure 2.22 which achieved a liquid yield of over 32% with a total reaction time of less than 12 minutes. That same test also had a solids yield of 39.8% thus also achieving the investigation Objective Three.

The heating rate does have an impact on the liquids and solids yields. Both relationships can be characterized by power functions as displayed in equations 2.2 and 2.3. The post-processing of the experiments adds a decent amount of variability. Despite this, both proposed relationships had high R^2 values, suggesting that the function is a good fit. There are limitations to this data as it can only be confirmed within the tested boundaries. Thus, it can only be confidently stated that the relationship holds between the intervals of 5 and 300 °C/min.

Chapter 3: Supercritical Carbon Dioxide Extraction

3.1 Introduction

The US Energy Information Administration conducts a monthly review of the energy used and produced in the United States. Since January 2024, the United States produced more energy than it consumes. In June 2024 the US produced 8.557 quadrillion BTU of energy while only consuming 7.585 quadrillion BTU. Despite this, the US still imported 1.815 quadrillion BTU. From January to June of 2024, the United States used 46.599 quadrillion BTU of energy with 17.392 quadrillion BTU coming from petroleum, which is over 35% of US consumption. In the same time period, the US produced only 13.541 quadrillion BTU from crude oil. Not surprisingly, petroleum makes up over 84% of total US energy imports.[3] The US imports so much petroleum, despite producing a surplus of other forms of energy, because of the vast oil infrastructure that already exists. In essence, the oil infrastructure in the United States is so robust that fully transitioning away from it would be impractical. A better solution is to figure out how to use the existing infrastructure in a way that reduces net carbon dioxide emissions, such as converting biomass into bio-oil.

There are several well-researched methods for biomass conversion including pyrolysis, transesterification, gasification, and hydrothermal liquefaction. The interest of this investigation is with a derivative of hydrothermal liquefaction that uses alternative solvents for bio-oil production and extraction. The process is based on the Near-critical Integrated Liquefaction Extraction system or NILE for short.

The NILE process includes dewatering, liquefaction, and extraction. The dewatering characteristics have shown promise; however, this paper intends to focus on the liquefaction and extraction aspects of the system. The process is designed to use supercritical Carbon Dioxide. sCO_2 acts as a suitable solvent as previously discussed in Chapter 1 Section 1.2.8.

The process operates at pressures between 10-30 MPa and at temperatures between 150 and 400 °C. The reaction occurs in a batch reactor with biomass, catalysts, and CO_2. This investigation is looking into the use of acetone as a co-solvent thus the reactor will also contain acetone. Supercritical carbon dioxide has several advantages over water which is typically used in the liquefaction process. These advantages include having a controllable solubility and reduced energy cost due to a lower specific heat and critical point.[46]

Acetone was deliberately selected as a co-solvent based on research conducted by Yun Wang. The research found that liquefaction using Acetone without water increased the bio-oil yields from below 20% to almost 30% by weight.[66] Ethanol was also examined in the aforementioned study; however, the relatively high boiling point of ethanol makes it unsuitable for extraction by evaporation as the temperature required would cause a greater loss in liquid yields.

Another paper by Zhengang Liu and Fu-Shen Zhang investigated various co-solvents including acetone. The solvent can dilute the reaction products which prevents further reactions or reverse reactions. The study found that the highest conversion rate was achieved when acetone was used. For example, oil-yields for acetone were 20% at best while oil-yields for ethanol were 26.5%.[67] Despite this, acetone is still considered a better co-solvent for this investigation because of its lower boiling point. Another important note from Liu and Zhang is that the chemical composition of the oil produced varies significantly with the choice of co-solvent.[67]

3.2 Goals and Objectives

This chapter will investigate the efficacy of the extraction component of the Near-critical Integrated Liquefaction and Extraction system. The investigation will also use acetone as a solvent and cosolvent, theoretically increasing liquid yields and thus allowing for a more effective extraction process. For this, a preliminary investigation will be conducted into the use of acetone as a solvent and co-solvent. The objectives of this chapter are:

1. Increase liquid yields to above 40%. This will allow for there to be more product for the extraction process thus reducing potential system losses. Literature indicates that the use of acetone as either a solvent or cosolvent may boost current liquid yields beyond this threshold.
2. Obtain at least 20% liquid products from the supercritical carbon dioxide extraction process. It is assumed that the sCO_2 extraction will not be able to obtain the same yields as acetone extraction due to the difference in their solubility properties. Despite this, sCO_2 extraction can recover a higher quality product and has potential for future development.

3.3 Background

A preliminary investigation into the effects of acetone as a solvent and cosolvent was conducted to verify that yields in excess of 40% could be obtained. For the sake of brevity, in depth analysis of this investigation will not be conducted. The relevant data and figures can be found in Appendix (B). This investigation obtained a liquid yield of over 42% in the 100 mL reactor and 46% in the 1200 mL reactor. These tests took advantage of the relationships developed in Chapter 2. Tests were all conducted with the highest possible heating rates with only a few exceptions. The total reaction time was also maintained at no greater than 45 minutes for every test. The exceptions to the highest possible heating rate were done to determine if tests are scalable between the 1200mL and 100mL reactor. The 1200 mL reactor has a maximum improved heating rate of approximately 15 °C per minute; therefore, the heating rate of the 100 mL reactor had to be reduced to match this. It was proven that within a range of error, tests from the 100 mL reactor can be scaled to the 1200 mL reactor and achieve the same results. This is promising for the future development of sCO_2 liquefaction as it demonstrates the scalability of the system and the potential for future employment on an industrial scale.

To gain a robust understanding of the NILE process with respect to acetone co-solvent, four experiments were conducted with varying methods. Several conditions remained constant including the heating rates, the total reaction time, the resident temperature, and the ratio of reactants and catalysts.

The first experiment was conducted with nitrogen as the gas rather than carbon dioxide. Nitrogen is inert and is a poor solvent meaning that it would have little to no impact on the production of bio-oil. The purpose of adding nitrogen as a filler gas is to try and maintain the appropriate pressure. The purpose of conducting a test with nitrogen is to have a reference point to evaluate the impact of supercritical CO_2 on the liquefaction process. Standard extraction was then used for this experiment, again to form a reference point to compare against supercritical CO_2 extraction.

The second experiment used the same liquefaction process with nitrogen but used supercritical CO_2 extraction as a primary extraction method and standard extraction as a secondary method to recover residual liquid products. The purpose of this two-step extraction is to determine not just how much liquid yield can be recovered from the supercritical process, but also what kind of effect the supercritical process has on the overall liquid yield.

The third and fourth experiments are the same as the first and second experiments the only difference is that the gas used is CO_2 instead of Nitrogen. Theoretically, the solvent properties of CO_2 should impact the liquid yields of the process.

3.4 Experimental

The experimental section in this chapter is deliberately shorter especially in terms of materials as most of the equipment was already covered in Chapter 2 Section 2.4.

3.4.1 Materials:

The reactor being used is a Parr series 4540 High Pressure, 1200 mL reactor. The vessel is rated for 345 bar and 350 °C which is well in excess of the operating conditions. The vessel is constructed of 316 stainless steel because of its corrosive-resistant properties. The pressure vessel head has a pressure gauge, a thermo-couple inside of a thermowell, and a stirring rod rotated by an external magnetic driver. Heating was conducted with an induction heater. This allowed for the achievement of faster heating rates.

Every test used 50 grams of biomass, 5 grams of K_2CO_3, and 100 grams of acetone. The biomass is kiln-dried pine wood. K_2CO_3 is acting as a catalyst based on data from other literature.[66] Acetone is being used as a co-solvent based on previous successes in existing research.[66,67] Compressed CO_2 and Nitrogen were also used over the course of this investigation.

Filter paper with a retention size of 5 μm was used for the separation of solids and liquid particles. Evaporation and condensation extraction, henceforth referred to as standard extraction, used an Eyela Rotary Evaporator N-1200BS series for acetone removal. Supercritical CO_2 extraction requires high-pressure supercritical pumps and an additional condensation chamber.

3.4.2 Procedures

3.4.2A Liquefaction Procedure

50g biomass, 5g K_2CO_3, and 100g acetone are placed in the 1200 mL pressure vessel. The pressure vessel is then completely sealed. The gas is added until the pressure is 500 psi at room temperature. The induction heater is used to raise the temperature to 300 °C. The reaction is allowed to occur for 45 minutes starting from when the heating element is powered on. At the end of 45 minutes, the pressure vessel is quenched in a large water bath.

3.4.2B Standard Extraction Procedure

After the pressure vessel cools completely, the vessel is opened and the inside is washed with acetone. Acetone is used on the stirring rod, thermowell, and all other exposed surfaces until it runs clear. All products are then collected and filtered to separate the solids from the liquids. Acetone is again used to wash the solid residue for the filtration process until the flow is clear. The solid residue is then placed in an oven and left to dry overnight. The liquid products are heated to 75 °C to evaporate out the acetone. While not necessary, the acetone is condensed to prevent additional waste. The remaining liquid is then poured into a pre-weighed vial. The boiling flask is washed with acetone to ensure that all bio-oil goes into the vial. The vial is then heated to 75 °C until acetone can no longer be seen to condense. At this point, there is a clear separation between the bio-oil and the aqueous products. The aqueous products are separated using a syringe and the mass of the remaining bio-oil is measured.

2.4.2C Supercritical CO_2 Extraction Procedure

After the pressure vessel cools to room temperature, the vessel is opened and all exposed surfaces are washed with acetone. All solid residue and liquid products are placed in a beaker. The beaker is allowed to sit exposed to the air so that the acetone will naturally evaporate. The remaining residues are placed in a 500 mL pressure vessel. The pressure vessel is heated to 100 °C and the pressure is increased to 330 bar. Supercritical CO_2 flows through the system with a mass flow rate of 40 grams/minute. Vaporized products are carried to another 500 mL pressure vessel that is maintained at 40 °C.

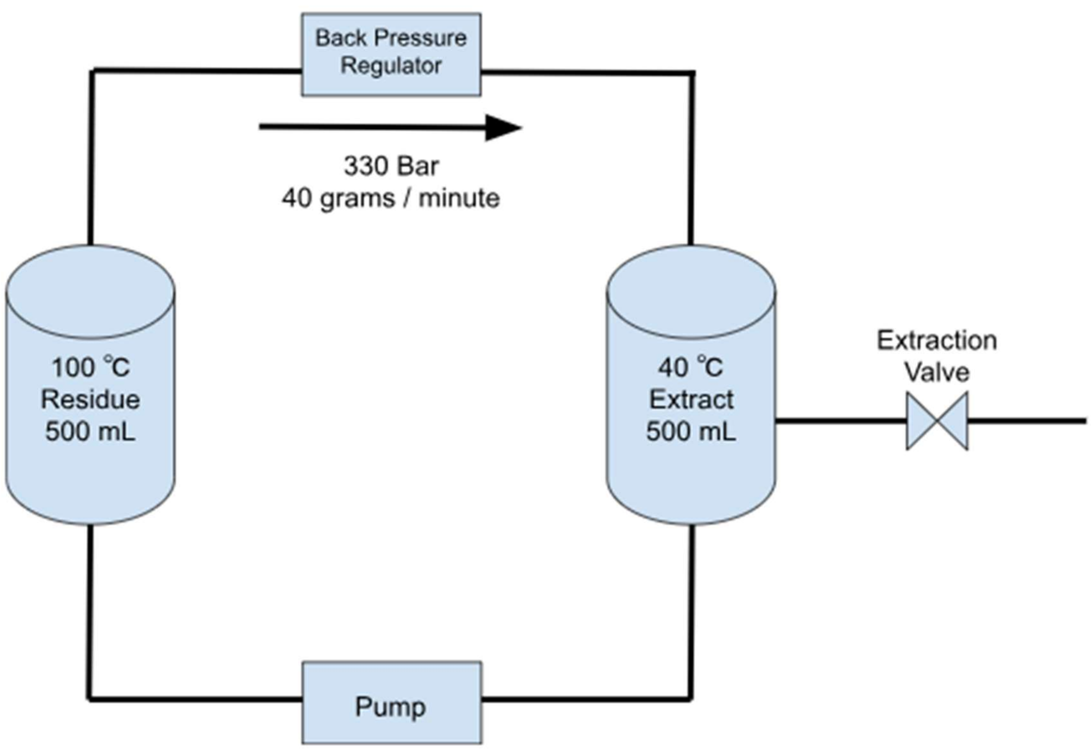


Figure 3.1: Supercritical CO_2 Extraction Diagram.

The vaporized products condense at the lower temperature and remain in the second pressure vessel while the supercritical CO_2 is recycled back to the first pressure vessel. Recycling carbon dioxide is not obligatory; however, it further helps to reduce waste. The extract is collected from the 2nd pressure vessel approximately every 30 minutes. The process runs continuously for at least 4 to 7 hours until the extract stops collecting.

3.4.3 Analysis

Bio-oil and solid residues were weighed to obtain the yield by % weight of biomass. The bio-oil was then analyzed using gas chromatography-mass spectroscopy (GC-MS). This GC-MS used Helium as the carrier gas with a flow rate of 1 mL/min (constant flow). The injection port temperature was 250 °C and the transfer line temperatures were maintained at 280 °C. The oven has an initial temperature of 45 °C for 10 minutes and a final temperature of 250 °C for 5 minutes with a ramp rate of 3 °C/min. The system has an injection volume of 1 μL with a split ratio of 30:1. The mass-selective detection scan range is m/z 29-600 and the EI ion source was 70eV.[68]

3.5 Results

3.5.1 Percentage Yields by Weight Analysis

Figure 3.2 shows the solid residues and liquid products obtained. The data has been normalized as a percentage of the biomass. The nitrogen and acetone liquefaction standard extraction case had a yield of 51.2% solid residue and a liquid yield of 46%. The solid residue in this instance is larger than typical liquefaction yields which typically range in the high 30% to low 40%. Additionally, the liquid yields were exceptionally high. The testing conditions used have historically produced liquid yields in the range of 20% to 30%; however, this test achieved a liquid yield in excess of 45%. While some aqueous products were separated from this oil, it is reasonable to assume that some of the aqueous products remained as emulsions in the bio-oil. Further analysis of the composition of the oil will be discussed in the subsequent section.

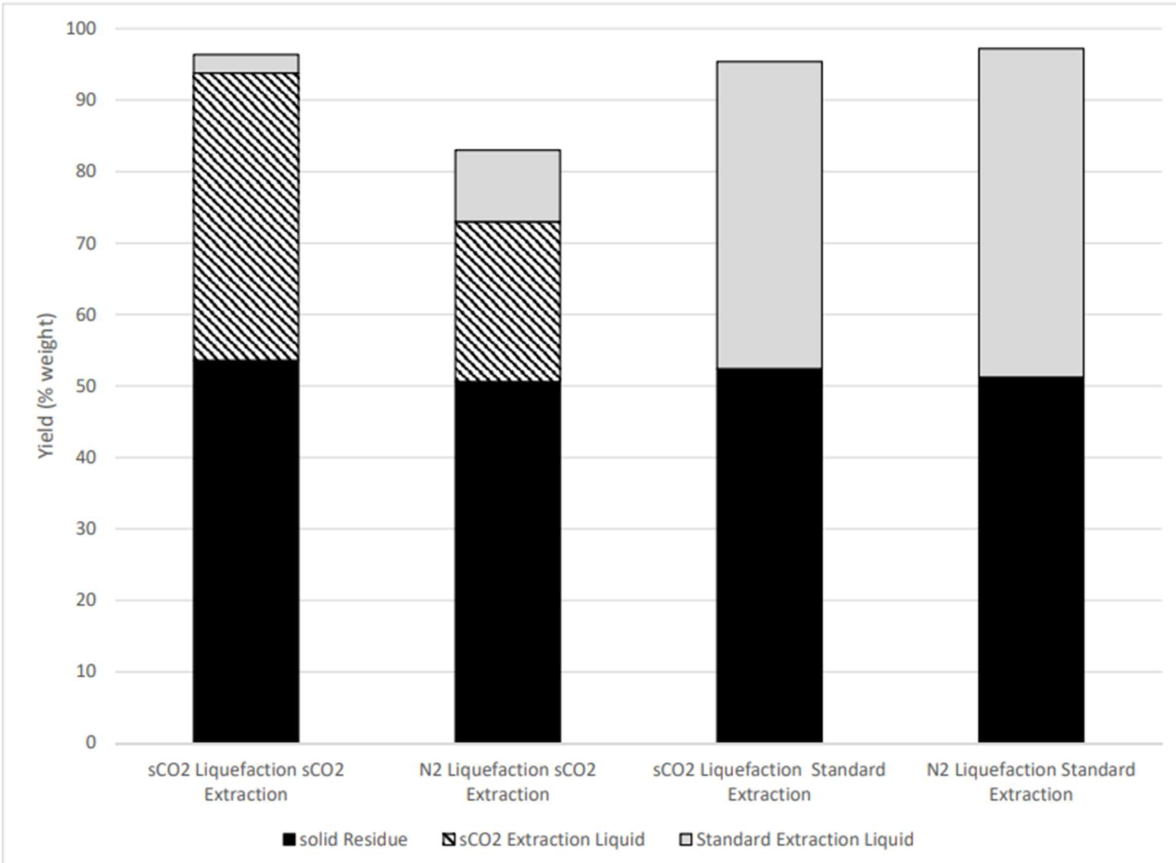


Figure 3.2: Solid and liquid yields from the investigation.

The nitrogen with supercritical CO_2 extraction case displayed a much lower solid and liquid conversion rate than any other case. While the solid yields were nearly identical across the board, the extracted liquid was severely diminished yielding only 22.4% from sCO_2 extraction and 10% from the following standard extraction. A potential explanation is that the nitrogen-acetone liquefaction process did not produce as many compounds that can dissolve in sCO_2. The reason that this would produce different results between standard and sCO_2 extraction is because of the differences in solubility between acetone and supercritical carbon dioxide. The standard extraction method is dependent on the solubility of acetone. Acetone is extremely soluble and can dissolve a large range of organic compounds due to it being polar and aprotic. Supercritical carbon dioxide on the other hand has a much narrower range of soluble compounds and does not have the ability to dissolve polar compounds without a co-solvent. The combination of these two factors would explain why standard extraction was more successful in this case. It should be noted that even with the reduced oil yield relative to the other cases, the yield still totals 32.4 % which would be considered a high yield.

The third case was for sCO_2-acetone liquefaction and standard extraction. This case yielded almost identical yields to the nitrogen-acetone liquefaction case. Note the verbiage is identical yields and not results. While the quantities of solid residues and liquid products may be similar, the composition for the different cases could be drastically different.

The fourth case was for sCO_2-acetone liquefaction and sCO_2 extraction. This case mirrored the two standard extraction cases with a nearly identical solid yield of 53.6% and a total liquid yield of 42.8%. This only further supports that the nitrogen and CO_2 cases produce a significantly different product. It would also make sense that the CO_2 liquefaction case would produce products that are more favorable for CO_2 extraction because sCO_2 soluble products would dissolve in the sCO_2. As Liu and Zhang noted, the products dissolving lowers the concentration of those products thus reducing the probability of further conversion or reverse reaction. GC/MS data will provide further insight.

3.5.2 Gas Chromatography Mass-Spectroscopy Comparison to Base Cases

GC-MS was conducted on the samples to gain an understanding of the major chemical compounds produced from the liquefaction reaction and obtained via the extraction methods. These results were compared against previous tests that did not use acetone as a co-solvent.

Table: 3.3GC-MS summary for base cases.[69]

	Average	Maximum	Occurance
1-Octanol	1.05	1.05	10%
2-Isopropyl-10-methylphenanthrene	1.39	1.66	50%
2-Methoxy-5-methylphenol	1.62	1.87	20%
2-pentanone, 4-hydroxy-4-methyl-	2.60	4.19	20%
Acetic Acid	3.72	5.18	40%
Cresol	1.44	1.81	30%
Cyclopropane, pentyl-	1.00	1.00	10%
Diisoamyl ether	1.24	1.32	50%
Dodecanoic acid, methyl ester	1.62	2.06	100%
Naphthalene, 1,2,3,4-tetrahydro-	3.17	6.15	30%
Phenol, 2,3-dimethyl	1.70	1.96	40%
Phenol, 2,5-dimethyl-	2.33	2.33	10%
Phenol, 2,6-dimethyl	1.67	2.06	20%
Phenol, 2-methoxy-	3.52	4.87	90%
Phenol, 2-methoxy-4-propyl	2.05	3.08	70%
Phenol, 2-methyl-	1.72	2.40	30%
Phenol, 3-methyl	1.67	2.33	20%
Phenol, 4-ethyl-2-methoxy-	2.07	2.70	90%

Table 3.3 contains a summary of the results obtained by GC-MS conducted on ten samples under varying conditions. Those conditions include CO_2 to biomass ratio, catalyst ratio, and particle size. These tests all had a resident time of 1 hour. Using a compilation of all of this data produces a wider range of what could be considered standard products. Thus, if the acetone case produces different products then the acetone itself, it can be credited with causing the change through its properties as a catalyst or potentially as a reactant. The listed compounds and functional groups have a relative peak area (RPA) greater than 1 and a similarity index of at least 850. The “Average” column is the average RPA for the cases that had an RPA of at least 1; cases with an RPA below 1 were excluded from the average. The “Maximum” column is the largest RPA exhibited by all of the base cases. The “Occurrence” column is the percentage of cases that had an RPA of at least 1 for each compound or functional group.

Table 3.4: GC-MS summary for investigation cases.

	sCO_2 Liquefaction sCO_2 Extraction	N_2 Liquefaction sCO_2 Extraction	sCO_2 Liquefaction Standard Extraction	N_2 Liquefaction Standard Extraction
Acetic Acid	-	1.40	-	-
2-Cyclohexen-1-one, 3 methyl-	2.18	1.1	1.24	-
2-Cyclohexen-1-one, 3,5-dimethyl-	-	1.56	-	-
2-Cylcopenten-1-one, 2,3-dimethyl-	1.21	1.27	-	1.02
2-Cylcopenten-1-one, 3-methyl-	1.48	1.18	1.21	1.61
3-Penten-2-one, 4-methyl-	11.81	10.05	14.93	15.89
4-Penten-2-one, 4-methyl-	-	-	2.23	-
Dodecanoic acid, methyl ester	-	1.00	1.09	1.17
Isophorone	3.43	-	2.65	4.66
isopropylidene-	-	7.46	-	-
Methyl Isobutyl Ketone	1.02	-	1.42	-
Phenol, 2,3-dimethyl-	1.48	1.37	1.40	-
Phenol, 2,5-dimethyl-	1.50	-	1.08	-
Phenol, 2-methoxy	1.46	1.86	1.1	1.64
Phenol, 3-methyl-	4.21	2.33	3.29	1.26
Phenol, 4-ethyl-2-methoxy	-	1.02	-	-

Table 3.4 contains GC-MS results for the cases under investigation. Of the 16 major components found in the acetone cases, only six are standard products (i.e. products also found in the non-acetone / base cases). Of the standard products dodecanoic acid, methyl-ester; and phenol 2,3-dimethyl appear with similar RPA values as the average RPAs for the base cases. This indicates that acetone as a solvent does not significantly impact the production of those two compounds. Phenol 2,5-dimethyl does have a significantly larger RPA in the base cases than in the investigation cases, but it has an occurrence of 10% indicating that it is not common. This compound appears in low quantities in only two out of the four investigation cases indicating that it is not common; therefore, it can be concluded that Phenol 2,5-dimethyl is also not significantly impacted by the presence of acetone during the reaction.

Acetic acid was only found in the N_2 Liquefaction sCO_2 extraction case and had an RPA of 1.40. It was found in 40% of the base cases with an average RPA of 3.72. Phenol 2-methoxy production is also reduced in the presence of acetone. The compound appears in every case except for one (base and investigation). The average for the base cases was an RPA of 3.52. The investigation cases had a maximum of 1.86, just above half that of the base cases. Phenol, 4-ethyl-2-methoxy appeared in 90% of the base cases with an average RPA of 2.07. The same compound only appeared in one of the investigation cases just barely reaching significance with an RPA of 1.02. Based on the comparisons, it can be said that acetic acid, phenol 2-methoxy-; and phenol 4-ethyl-2-methoxy relative production frequency is reduced when acetone is used as a solvent or co-solvent.

The last standard product obtained in the investigation cases is phenol 3-methyl. Phenol 3-methyl occurred in only 20% of the base cases and had an average RPA of 1.67. The investigation cases all had significant amounts of the compound with RPAs ranging from 4.21 to 1.26. The proportion of phenol 3-methyl increased with acetone as a solvent or co-solvent.

3.5.3 Gas Chromatography-Mass Spectroscopy Comparison Between Investigation Cases

The assumption must be made that each liquefaction technique produces the same products every time. For example, sCO_2 liquefaction will always have the same products, and N_2 liquefaction will always have the same products, but they may not be the same as each other. For the majority of components, the RPA for the sCO_2 extraction cases is higher than that of the standard extraction cases indicating that a wider range of products was obtained from the standard extraction. This was to be expected as acetone has better solvent properties than supercritical CO_2. There are, however, several exceptions to this rule, including instances for 3-penten-2-one 4 methyl; dodecanoic acid; and methyl isobutyl ketone. The standard extraction method recovered a higher proportion of the aforementioned compounds.

sCO_2 liquefaction generally produces a higher proportion of products that can be recovered in the sCO_2 extraction process. This holds for 2-Cyclohexen-1-one 3 methyl-; 2-Cyclopenten-1-one 3-methyl-; 3-Penten-2-one 4-methyl-; Isophorone; Phenol 2,3-dimethyl-; Phenol 2,5-dimethyl-; and Phenol 3-methyl-. Certain components are produced from sCO_2 Liquefaction that are not produced in Nitrogen Liquefaction. These components include Methyl isobutyl ketone and phenol 2,5-dimethyl-. To an extent, the same can be said in reverse with N_2 Liquefaction sCO_2 extraction being the only case containing acetic acid, 2-Cyclohexen-1-one 3,5-dimethyl-, isopropylidene, and phenol 4-ethyl-2 methoxy.

3.6 Discussion

Chapter Objective One was achieved. The goal was to have liquid yields in excess of 40% and this was achieved in the 100 mL and 1200 mL reactors which produced 42% and 46% respectively. This allowed for sCO_2 extraction to be investigated without severe reduction in recovery to proportional losses.

Chapter Objective Two was also achieved. The goal was to recover greater than 20% liquid yields from supercritical carbon dioxide extraction. This was demonstrated for both of the cases involving either N_2 liquefaction or sCO_2 liquefaction which produced 22.4% and 40.2% respectively. The sCO_2 liquefaction sCO_2 extraction combination surpassed expectations. This is believed to be the result of sCO_2 liquefaction tending to produce products that are readily soluble during sCO_2 extraction. On the contrary, nitrogen is inert and non-soluble meaning that it has no ability to impact the production of products that would be conducive to any particular extraction method.

An important note is that there are ten non-standard products produced by the investigation cases. The nature of bio-oil production means that the products are largely dependent on the conditions. There is, however, reasonable evidence to suggest that acetone is not acting as a solvent but rather as a reagent, namely the large proportion of ketones relative to the base cases. The exceptionally high relative production of ketones specifically, 3-penten-2-one 4-methyl, as well as the high liquid yield rates, means that it is highly likely that acetone is reacting and contributing to the products.

Chapter 4: Conclusions and Future Work

4.1 Conclusions

4.1.1 Heating Investigation Conclusion

Resident time and total time do not affect the liquid or solid yields in the range of 10 to 80 minutes. The heating rate will affect the liquid yields:

$$L = 13.01 \cdot H^{0.1687}$$

where L is the liquid yield and H is the heating rate for heating rates between 5 and 300 °C per minute. The heating rate will also affect sold yields:

$$S = 58.57 \cdot H^{-0.08348}$$

where S is the solid yield. The investigation has also proven that liquid yields in excess of 30% can be achieved in less than 45 minutes while maintaining a solid yield of less than 40%.

4.1.2 Supercritical Carbon Dioxide Extraction Conclusion

Between carbon dioxide and nitrogen, the liquefaction gas has a limited impact on the proportion of solid residue to liquid products for cases using acetone as a solvent or co-solvent. The presence and choice of a solvent does affect the composition of the products.

While the liquid yields improved, it is highly probable that this is the result of acetone reacting as discovered via GC-MS. A better indication of performance would be based on the solid residue yield which was significantly higher than typical. This means that it can be reasonably determined that using acetone as a solvent actually inhibits biomass conversion to the liquid products more so than it aids in it.

Analysis of the extraction process revealed several key points. The first confirms the assumption that standard extraction, enabled by acetone, would obtain a larger range of products. The second is that supercritical carbon dioxide extraction is a viable option for liquid yield recovery in bio-oil production as determined by its ability to recover liquid yields over 20% by weight. The third point is that sCO_2 Liquefaction produces compounds moderately more conducive for sCO_2 extraction than N_2 Liquefaction. sCO_2 extraction can obtain similar results as standard extraction for sCO_2 Liquefaction.

4.2 Further investigation:

The field of hydrothermal liquefaction of biomass for the production of bio-oils is still a relatively new and unexplored area. Work has been done to improve the liquefaction process, but there is still a large amount of unexplored territory, especially in the derivative realm of supercritical fluid-aided liquefaction. It would be impossible to produce an exhaustive list; however, some areas that could benefit from investigation are outlined below.

Further investigation into the relationship of heating rate and resident / total reaction times would be beneficial. A key discovery of this work was that resident times and total reaction times within a certain window do not greatly affect yields. There is, however, a minimal necessary resident / total reaction time that needs to be reached. It is theorized that this may be dependent on the heating rate.

Further investigation could also be conducted into the heating rate itself. As noted in Chapter 1 Section 1.2, flash pyrolysis is conducted with heating rates greater than 1000 °C per minute. This leaves a significant range that has not yet been tested in the context of liquefaction, and it is reasonable to assume that the relationship proposed in this work would not hold for significantly higher heating rates.

Further investigation into solvents and cosolvents could not be exhausted. The yields from acetone-assisted liquefaction leave more in the way of questions than answers. The overarching question is, did acetone have any positive effect on liquid production or was it solely acting as a reactant? While evidence suggests this may be the case, it has not yet been confirmed and additional research is needed. This lends itself to even further inquiries. If acetone is indeed reacting then are there other potential solvents that could achieve the same theoretical benefit without reacting? Or is it inevitable given the reactor conditions that any organic solvent will react? This raises the question of the feasibility of inorganic solvents, such as acids or bases.

Another interesting direction for further investigation would be to take the next step in the NILE system and attempt to integrate the reaction and extraction. This, theoretically, would improve yields by reducing transfer losses. This integrated process adds even more variables to an already inundated experiment which would require significant experimentation to optimize.

Appendices

Appendix (A): Temperature versus Time plots and other post processing data for all tests related to heating investigation.

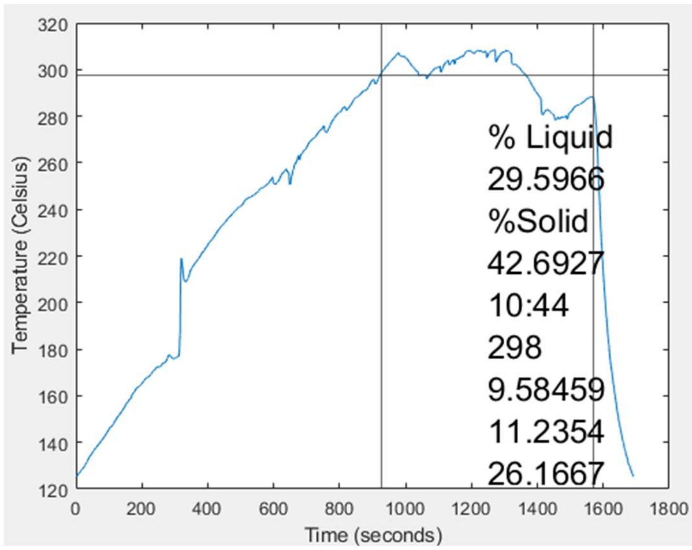


Figure A.1: Test 1 Temperature versus time plot.

Test 1 Conditions:

Mass of weigh boat: 6.60g; Mass of weigh boat + biomass: 16.59g; Mass of weigh boat + biomass + K_2CO_3 : 17.59g; Mass of liquid yields: 2.9567g; Mass of Solid Yields: 5.265g

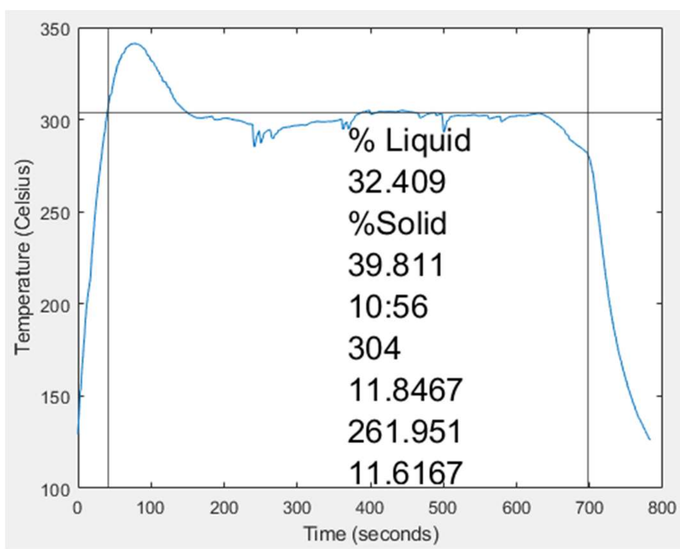


Figure A.2: Test 2 Temperature versus time plot.

Test 2 Conditions:

Mass of weigh boat: 5.77g; Mass of weigh boat + biomass: 15.77g; Mass of weigh boat + biomass + K_2CO_3 : 16.79g; Mass of liquid yields: 3.2409g; Mass of Solid Yields: 5.0011g

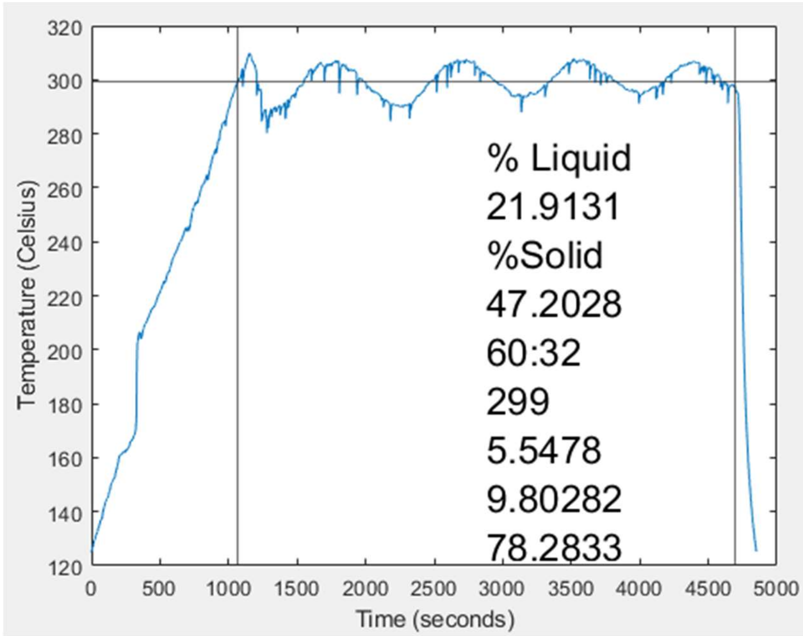


Figure A.3: Test 3 Temperature versus time plot.

Test 3 Conditions:

Mass of weigh boat: 6.36g; Mass of weigh boat + biomass: 16.37g; Mass of weigh boat + biomass + K_2CO_3 : 17.37g; Mass of liquid yields: 2.1935g; Mass of Solid Yields: 5.7250g

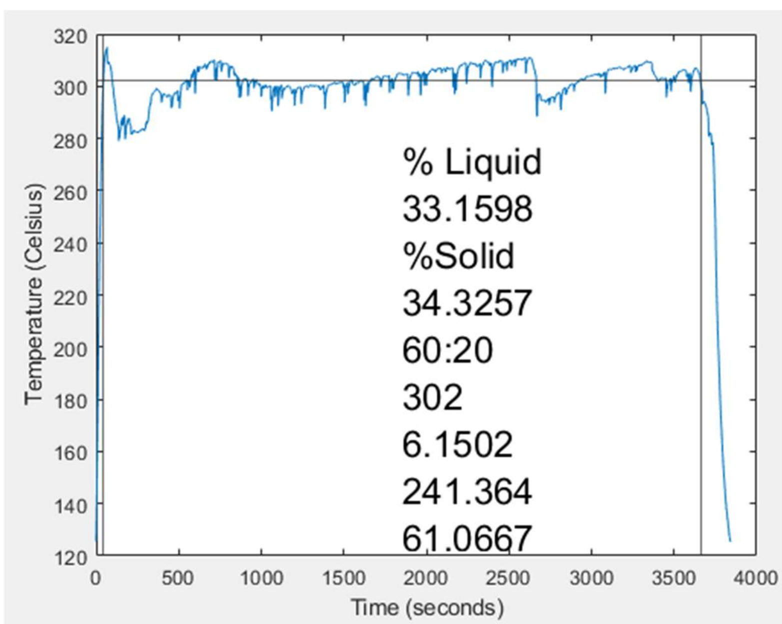


Figure A.4: Test 4 Temperature versus time plot.

Test 4 Conditions:

Mass of weigh boat: 6.52g; Mass of weigh boat + biomass: 16.53g; Mass of weigh boat + biomass + K_2CO_3 : 17.53g; Mass of liquid yields: 3.3193g; Mass of Solid Yields: 4.436g

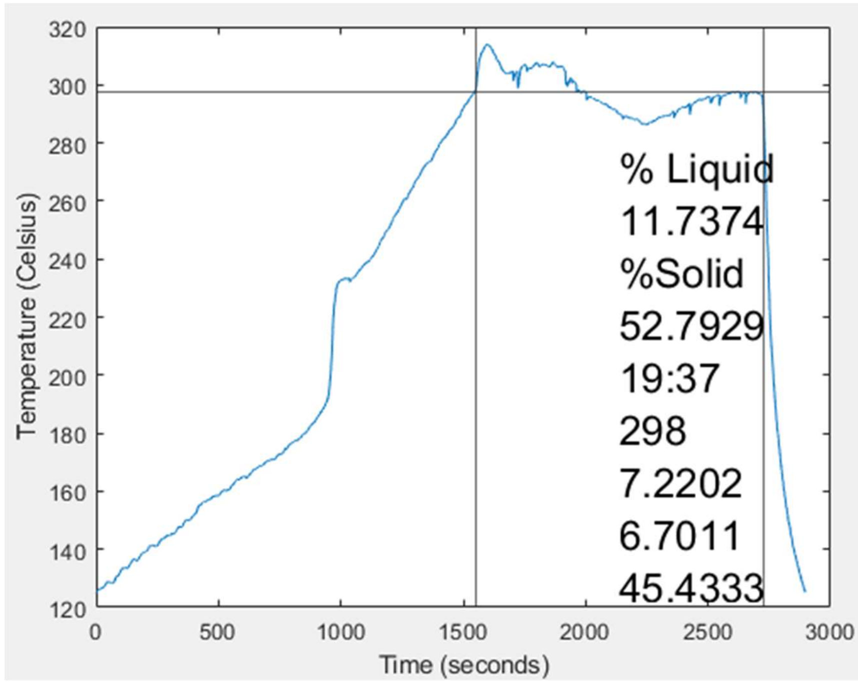


Figure A.5: Test 5 Temperature versus time plot.

Test 5 Conditions:

Mass of weigh boat: 6.2930g; Mass of weigh boat + biomass: 16.3148g; Mass of weigh boat + biomass + K_2CO_3 : 17.3460g; Mass of liquid yields: 1.1763g; Mass of Solid Yields: 6.322g

Appendix (B) Acetone preliminary investigation data.

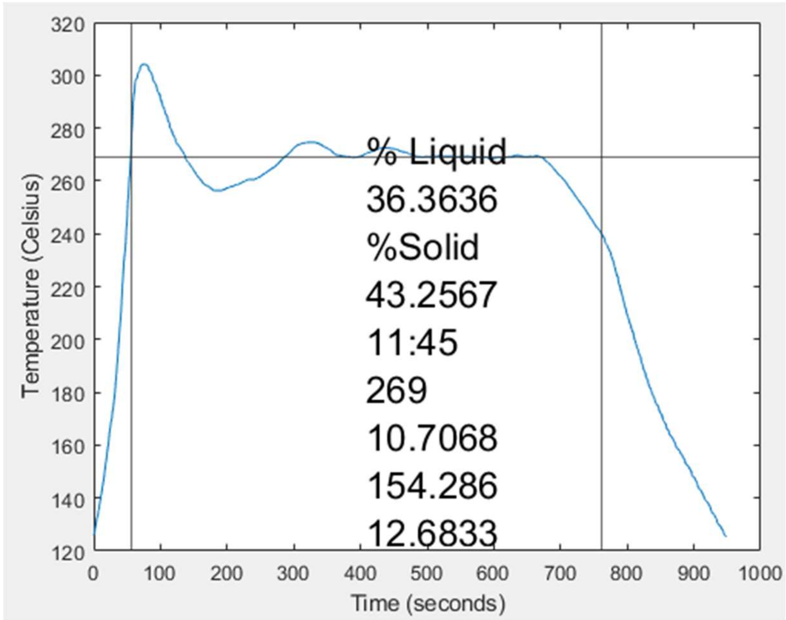


Figure B.1: Test 1B Temperature versus time plot.

Test 1A Conditions: 20g Acetone with 650 PSI CO_2 100 mL pressure vessel.

Mass of weigh boat: 5.94g; Mass of weigh boat + biomass: 15.95g; Mass of weigh boat + biomass + K_2CO_3 : 16.95g; Mass of liquid yields: 3.64g; Mass of Solid Yields: 5.33g

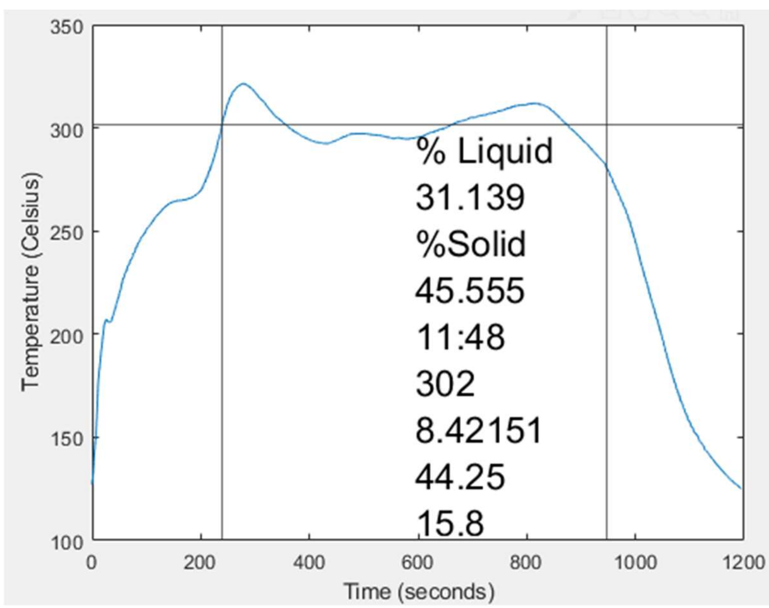


Figure B.2: Test 2B Temperature versus time plot.

Test 2A Conditions: 4g Acetone with 600 PSI CO_2 100 mL pressure vessel.

Mass of weigh boat: 6.32g; Mass of weigh boat + biomass: 16.32g; Mass of weigh boat + biomass + K_2CO_3 : 17.34g; Mass of liquid yields: 3.1139g; Mass of Solid Yields: 5.5755g

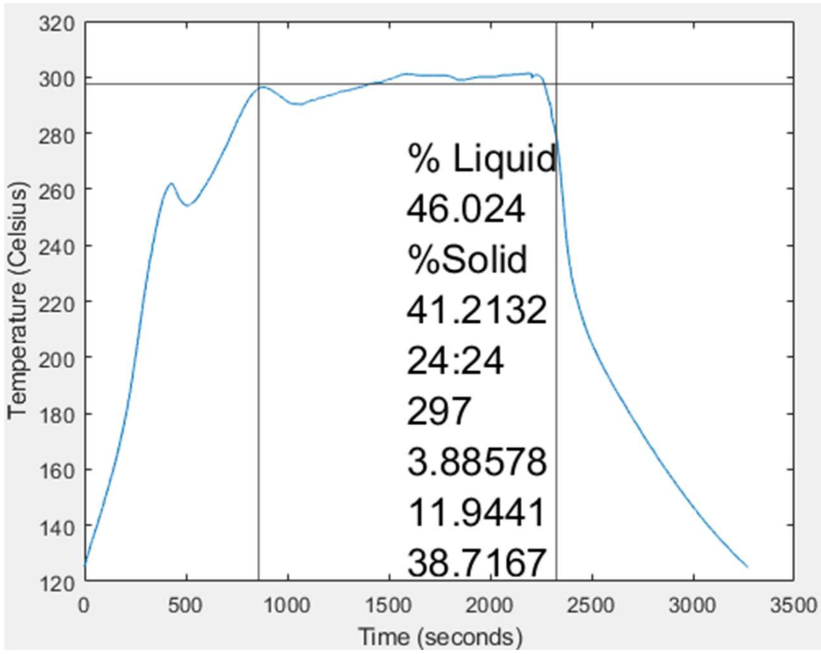


Figure B.3: Test 3B Temperature versus time plot.

Test 3A Conditions: 100g Acetone with 500 PSI N_2 1200 mL pressure vessel.

Mass of weigh boat: 5.91g; Mass of weigh boat + biomass: 55.91g; Mass of weigh boat + biomass + K_2CO_3 : 60.91g; Mass of liquid yields: 23.012g; Mass of Solid Yields: 25.6066g

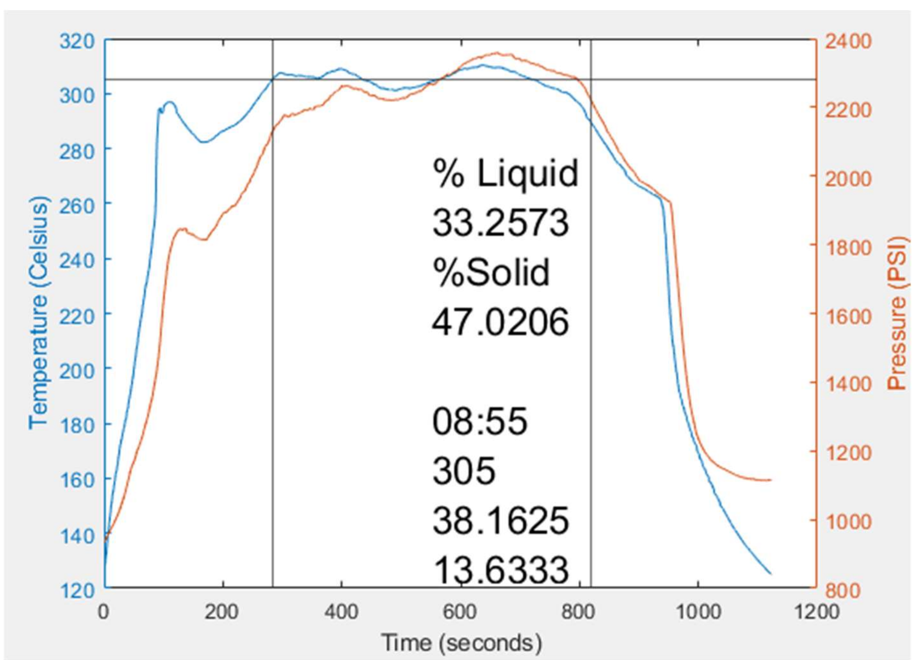


Figure B.4: Test 4B Temperature and pressure versus time plot.

Test 4A Conditions: 20g Acetone with 500 PSI CO_2 100 mL pressure vessel.

Mass of weigh boat: 1.118g; Mass of weigh boat + biomass: 11.190g; Mass of weigh boat + biomass + K_2CO_3 : 12.209g; Mass of liquid yields: 3.3264g; Mass of Solid Yields: 5.722g

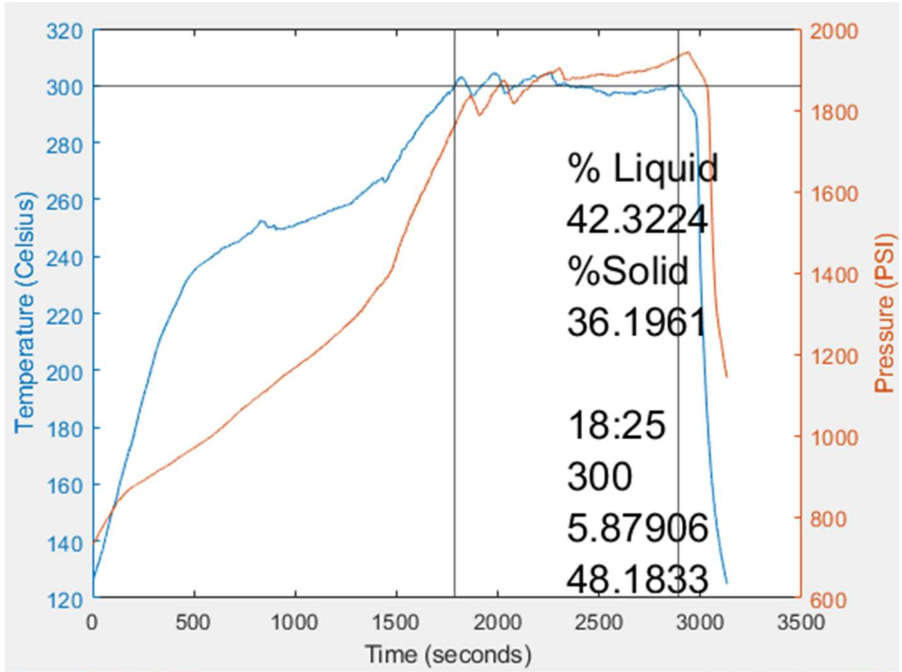


Figure B.5: Test 5B Temperature and pressure versus time plot.

Test 5A Conditions: 20g Acetone with 500 PSI CO_2 100 mL pressure vessel.

Mass of weigh boat: 5.9166g; Mass of weigh boat + biomass: 15.9210g; Mass of weigh boat + biomass + K_2CO_3 : 16.9482g; Mass of liquid yields: 4.2341g; Mass of Solid Yields: 4.6484g

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