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Hydrothermal Liquefaction of Lignin to Produce Bio-crude

Comparative Analysis of the Effects of Feedstock type and Operating Conditions on Bio-crude

JAMES AKOR GODWIN

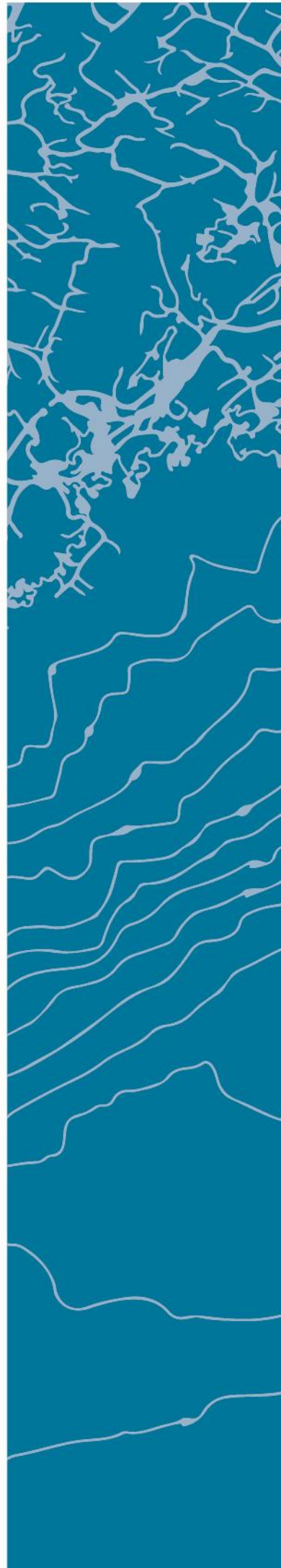
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Abstract

Lignin is one of the most abundant non-food biomass resources in the world today and several attempts are ongoing to harness its huge potential. Due to its rigid structure however, different processes are being experimented on how best to depolymerize it and maximize its product streams. Some companies like Borregarrd have recorded successes in recent time, on producing vanillin from lignin using a catalytic oxidation process, but still acknowledge that more products can be obtained from it. Hence, their quest to investigate the energy potential of one of the lignin types in their product line; Lignosulfonate. The challenge is therefore how best to depolymerize this lignin for energy production in a cost effective and environmentally friendly manner. The objective of this work was to explore the use of hydrothermal liquefaction process to depolymerize the lignosulfonate from Borregarrd as well as alkali lignin from Sigma-Aldrich, for production of bio-crude and compare the effect of the feedstock on the yield and quality of bio-crude produced and other potential energy recovery product that may arise from the process. Hydrothermal Liquefaction (HTL) is one of the thermochemical processes for conversion of biomass that has gained considerable attention in recent times due to its lower energy consumption when compared to other thermochemical processes. This liquefaction was performed in a batch system at sub-critical conditions without a catalyst, and results showed that alkali lignin produced yield of 21% bio-crude at 300°C in comparison with lignosulfonate with 9% bio-crude. The bio-crude yield tend to decrease with increasing temperature and vice-versa. The bio-char on the other hand, tend to increase in yield with increasing temperature. The bio-char from alkali lignin showed higher carbon and energy recovery of 38.5 % and 19.54%, compared to 6.3% than the 6.28% from lignosulfonate. The results from this work has demonstrated that lignosulfonate has some energy potential but the use of catalyst will be necessary to fully tap its energy potential, though at an extra cost. Future work on the HTL process, should be geared towards a comprehensive LCA study to properly quantify its environmental impacts in comparison with other thermochemical processes.

Preface

Coming from a background of Agricultural and Bio-resources engineering, I focused on biofuels production from agricultural waste materials and this informed my enrolment for a master program in Environmental engineering and sustainable energy. The transition from my bachelor to master was a very interesting and welcome development and has equipped me technically and given me the opportunity to explore deeper into the bioenergy research field, by interacting with professionals in this area.

My motivation for this thesis came from my earlier work on biodiesel production from agricultural waste resources, precisely, used vegetable oil (UVO), mostly referred to as the first generation biofuel. The recent drive towards the second and third generation biofuel from non-food resources with limited environmental impacts, as an alternative to the first generation biofuels, has also been of great interest to me. The idea is to produce bioenergy and biofuels from resources that do not compete with food, and processes with limited environmental impacts capable of bringing down potential carbon footprint to its barest minimum. To this end, I sort to delve into further study on the conversion of potential high fuel density biomass, also capable of producing other valuable resources other than fuel. This conversion will be a process considered to be of less energy utilization, and overall adjudged as a sustainable process, when the net energy balance is considered. Lignin as a non-food biomass has great potential for bioenergy and valuable chemicals, and even though a lot of work has started for its conversion and utilization in recent times, lignin still holds great potentials yet to be fully tapped. Hence, the recent interest in conversion processes that would aid complete depolymerization of lignin to produce valuable aromatic compounds. Hydrothermal liquefaction has shown great promise in recent times and this work aims to lend credence to previous studies, while also giving a further understanding of the relationship between the type of lignin used for a process like this and its potential yield. This is important in order to maximize yield at an overall lower operating cost when compared to the similar thermochemical processes for conversion of biomass.

Acknowledgments

I want to express my profound gratitude to God almighty for making this dream a reality. I will like to extend my deepest gratitude to Associate Professor Souman Rudra, who mentored, guided and supervised this thesis. His willingness to accept me as one of his student for this work, the insightful discussions we had in the course of this work and he created the warm reception I enjoyed within the group. I will also like to thank the following people who through their support have made this work a success.

- Many thanks to Professor Nielsen and the entire members of the Bioenergy and thermal energy group of the University of Agder for their warm reception into the group and immense support during this work.
- I want to thank Madhawa Jayathilake, Lorenzo Riva and Antoine, all PhD research fellows for their support during this work and not forgetting the support received from Dr. Tore Vehus and Nils Kristiansen for their guidance and help when I needed it.
- Special thanks to Mr. Gudbrand Rødsrud, a Technical Director in Borregarrd's biorefinery business division, for his technical support towards this work and making available the lignosulfonate used for this work.
- Not forgetting also the immense contributions of Mrs. Monier Chidinma Okoro and Mr. Moses Okoro for their generosity and benevolent support towards my study, it would not have been possible without God's blessings flowing through them. God bless them richly.
- Finally, my warm gratitude also goes to my entire family for their financial, moral, emotional and spiritual support throughout my study period.

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Nomenclatures

UiA – Universitetet i Agder

HTL – Hydrothermal Liquefaction

SCC – Sub Critical Condition

MC – Moisture Content

VM – Volatile Matter

AC – Ash Content

FC – Fixed Carbon

D.B – Dry Basis

W.B – Wet Basis

HHV – Higher Heating Value

LHV – Lower Heating Value

GCV – Gross Calorific Value

NCV – Net Calorific Value

ER – Energy Recovery

TGA – Thermogravimetric Analyzer

DTG / Derivative Thermogravimetric Analysis

GC-MS – Gas Chromatography-Mass Spectrometry

GHG – Green House Gas

PFD – Process Flow Diagram

RCF – Centrifugal Force

RPM – Revolution per Minute

LCA – Life Cycle Analysis

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Chapter 1

Introduction

In this section, an attempt is made to give a brief historical background on the emergence of this technology, the importance of biomass in the emerging clean energy economy and the problem this work is intended to proffer a solution for

1.1 Historical background

With the global population currently estimated at 7.8 billion and projected to hit 9.7 billion by 2050, according to the United Nation's Department of Economic and Social Affairs, the need to address the growing demand for energy has become paramount. While the energy industry has made efforts to meet the growing energy demand of the growing population, the environmental challenges associated with the current fossil energy mix has been a source of concern for some time now. Global leaders have all agreed that there is an urgent need to get environmentally friendly energy sources as a way of meeting the current demand for energy and safeguard our environment while doing so. In this light, Bioenergy, as is a type of sustainable energy, will no doubt play a critical role in helping us meet the increasing demand for energy while also addressing the environmental concerns raised in the past from fossil energy sources. This will also provide long-term solutions to the current challenges of climate change confronting the world. Biomass is a major carrier of bioenergy, mostly produced by plants converting sunlight into a plant material directly or indirectly through photosynthesis [1]. Besides being an abundantly available and CO₂-neutral energy source, biomass is a practical source of renewable liquid fuel [1]. Biomass is considered as one of the most promising alternatives to fossil fuels for the production of bio-fuel, chemicals and energy. In this light, there is growing attention for the development of technologies to convert biomass into more valuable environmentally friendly fuels like bio-oil, syngas, and other valuable chemicals. The growing interest in biofuels from lignocellulosic biomass feedstock can provide a path towards replacing petroleum-based fuels with sustainable biofuel, which have potential to lower the GHG emissions [2].

Different biomass feedstock have shown great promise for its bioenergy content in the past, Some of which include Agricultural residues like used vegetable oil, corn grains, Jatropha seeds, woody crops, municipal solid wastes and wastes from the paper and pulp industry like lignin. Lignin has proven to be a very promising feedstock for this purpose, owing to its relative availability in large quantity, high energy density and non-competition with edible agricultural products, which was the case with the first generation biofuels from agricultural products. Different conversion processes have been applied for the decomposition of biomass to bio-crude in the past. Some of these processes include; transesterification, pyrolysis, gasification and oxidation which have all shown good results in time past but have their own challenges that

accompany those techniques. Hence, the need for researchers to find other ways to decompose biomass that will make it competitive with the current traditional technologies employed for fossil-based energy sources. Developing a new technique that will compete economically and environmentally has become imperative, as that will ensure its competitiveness with the currently available technologies. Hydrothermal liquefaction (HTL) of biomass has shown great promise in this light, and researchers are developing it as a more competitive alternative to pyrolysis and gasification for example. HTL is a technology that dates back to the 1970s and 1980s but, was often referred to then as direct liquefaction and was mostly done in a continuous process until recently where efforts are being made by researchers to critically examine the technology in a batch process to understand the reaction kinetics [3]. Several works have been done in the past and more work is still ongoing to improve the HTL process for biomass conversion. To the best of our knowledge, only a few studies have shown the effects of feedstock, as an operating parameter without a catalyst, on HTL of biomass in literatures and more so on lignin. The current work provides some more detailed investigation on the effects of feedstock on the yield of bio-crude in the absence of a catalyst in order to ascertain the type of lignin best suited for HTL to maximize bio-crude yield at specific operating conditions without a catalyst.

1.2 Problem statement

Biomass is environmentally friendly and, in some cases, CO₂ neutral source of aromatic compounds for platform chemicals and environmentally friendly energy, especially wood-based biomass, which contains mostly hemicellulose, cellulose and lignin. Lignin is one of the most common organic compounds in the world [4] and seeking the best possible route in harnessing it, with the least possible environmental impact for the production of energy and platform chemicals, has been on the front burner of many research activities in recent time. Researchers in recent times have studied extensively on different depolymerization routes for lignin due to its vast potentials. Borregarrd, a Norwegian company that is one of the top global producers of vanillin, have been producing it from lignosulfonate with good successes recorded so far. However, due to the numerous potentials of lignin, the company is interested in exploring other products that could be harnessed from lignin, as a way of diversifying their product portfolio. One of such is the conversion of lignin to produce bioenergy, which has shown great promise in recent times. This is one of the challenges; this work also seeks to investigate in order to help the company make informed decisions about their products. Although some successes have been recorded from the thermochemical, catalytic and enzymatic processes and in some cases, oxidation process, and have all been reported by different researchers [5-6]. One of the thermochemical routes is the hydrothermal liquefaction process, which is still an emerging technology and presents a competitive way to depolymerize lignin when compared to other depolymerization processes. Hence, the need to embark on this study to further explore more possibilities to optimize this technology. Several studies in recent times have focused on liquefaction with the use of a catalyst to inhibit char formation and improve oil quality. However, the use of catalysts also presents its challenges, which could be an obstacle for a broader implementation of this technology. Some of these challenges include; the cost of

catalysts and cost of the Alkali lignin feedstock mostly used by researchers presents an additional cost, which could negatively affect the cost competitiveness of the technology. This research will seek to explore the feasibility of using two types of lignin comparatively, without a catalyst to ascertain its competitiveness with the current trend in terms of bio-crude and bio-char yields.

1.2.1 Key Assumptions and Limitations

The following assumptions are considered for the purpose of this thesis:

- The liquefaction experiment is based on relevant literatures on HTL and Lignin.
- The liquefaction experiment is performed in triplicates for each process conditions.
- The liquefaction experiment is performed under sub-critical conditions.
- The feedstock characterization is performed in triplicates for all analyses.

1.2.2 Limitations and Challenges Encountered

The following limitations were considered in this project, and some challenges were encountered which affected the intended scope of this work. These challenges coupled with the time constraint affected the number of experiments performed for the product phases. These limitations and challenges include:

- Literatures on lignin liquefaction in the absence of catalysts are limited.
- Product analysis is limited to the bio-crude and bio-char contents of the product due to some technical challenges.
- Elemental composition of product was limited to the bio-char only, due to technical challenges encountered with the elemental analyzer during the experiment, which hindered further analysis. A technical fault developed by the elemental analyzer, took a longer time to get fixed, hence the need skip the elemental composition of the bio-crude due to time constraints for this work due to my limited stay.

1.3 Research Questions

From the above-stated problem, some research questions that this work will attempt to provide answers to include;

- Is lignosulfonate from Borregarrd a suitable biomass to use for energy purposes?
- If lignosulfonate from Borregarrd is used for energy purpose, to what extent does it differ from alkali lignin in terms of their combustion and decomposition properties?
- When alkali lignin and lignosulfonate are liquefied for production of bio-crude in the absence of a catalyst, how does the operating parameters affect the product yield and quality?

1.4 Objectives of study

The aim of this work is to amongst other things; study the impact of different lignin types on the yield when subjected to a liquefaction process to obtain bio-crude under subcritical conditions. It will also analyze the output in each case to see their impact on yield quality. To this end, the study was conducted at the University of Agder using the pilot HTL rig set-up and analytical tools available in the combustion and hydrogen laboratories, respectively. A breakdown of this study objectives are as follows;

- Characterization of the two lignin samples obtained from Borregarrd and Sigma-Aldrich
- Hydrothermal liquefaction of lignin samples at subcritical conditions with ultrapure water (UPW) acting as solvent and catalyst at a temperature range of 300°C to 350°C, residence times of 10 through 20 minutes and the constant pressure of 250 bar respectively.
- Analyze the impact of solvents used on the yield and quality of bio-crude using different analytical tools.
- Deduce a conclusion from the obtained results to ascertain the viability of liquefaction in the absence of conventional catalysts.

Recommendations for future research work on HTL of lignin and different biomass resources.

1.5 Proposed plan to achieve objectives

The above-stated goals will be realized by first characterizing the feedstock samples gotten from Borregarrd, as well as the Alkali lignin from Sigma-Aldrich. The analysis will involve both proximate and ultimate analysis and comparisons will be made for both samples. The samples will be liquefied under subcritical conditions and the yield and quality of bio-crude and bio-char will be compared in both cases. The output from both samples will help to draw a tentative conclusion of the better lignin sample to utilize for better yield using the HTL process in the absence of a conventional catalyst.

Chapter 2

Background of study

2.1 Biomass

Biomass is referred to as organic matter and includes crops, forestry, marine products as well as organic wastes and pulp derived black liquor. Biomass, as an energy source, has some notable characteristics, one of such is that biomass is a renewable organic and the most abundant resource. Furthermore, biomass is a desirable and more sustainable energy resource because the CO₂ emitted during the combustion of biomass is mostly absorbed from the atmosphere through photosynthesis during plant growth, making it CO₂ neutral when used as a renewable energy source. Due to its high moisture content and low calorific value, biomass is not suitable for direct use as energy, hence the need to subject it to conversion processes to produce energy and liquid fuels with a high energy density that can be easily transported for use in different areas and different purposes [6-7].

2.2 Lignin

Lignin is the main component of wood, which also contains cellulose and hemicellulose and is the second-largest source of organic raw materials and a valuable resource for platform chemicals and energy [8]. It is a highly reactive amorphous polymer consisting of cross-linked, branched aromatic monomers with phenyl propyl units and characterized by the presence of different functional groups (hydroxyl, methoxyl, and carbonyl) [9]. Lignin is the second most common earthbound biopolymer available and the most significant naturally occurring source of aromatic compounds [10], it is the only renewable source of aromatics, which consists of 3 basic structural units, p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [11].

Lignin is usually produced by plants to give strength and rigidity, and also help in water conduction. Lignin constitutes up to 30% by weight and 40% of the fuel value of biomass and hence used to produce fuel. It is usually a by-product of paper and pulp as well as lignocellulosic bioethanol industries but the predominant pulping process seems to be the most significant source of lignin [11]. As a by-product of the paper and pulp industry, lignin is used by paper mills as fuel for energy recovery [8]. The amount of lignin extracted in the pulping process in the western hemisphere alone is estimated to be in the order of 50 million tons per year [10]. However, due to the large quantity generated, it is increasingly considered as a potential source of valuable chemicals and studies of its thermal degradation have received much interest [8]. Figure 1 shows the different degradation processes for lignin and its potential products. As a renewable source of aromatic hydrocarbons, lignin is a potential source for the valuable synthons that are used in the production of various platform chemicals and by-products [12].



Fig 1: Scheme of conventional and potential products from lignin [13].

2.3 Thermal decomposition of biomass

The most popularly used thermochemical processes include pyrolysis and gasification, and until recently, the oxidation process. These are all used for conversion of biomass for different purposes, but presents some weak sides like the need to dry the feedstock to achieve a positive net energy balance and the need for further processing of raw product in order to obtain commercially valuable liquid and gaseous fuels [14]. Hydrothermal liquefaction of biomass has generated increasing attention because of its advantages over other processes, concerning its high energy density, short residence time, its applicability to different raw materials, and easy of commercialization. HTL is one of the techniques of thermo-chemical conversion of biomass, and unlike pyrolysis and gasification, which are often done at elevated temperatures and longer residence time, HTL, on the other hand, is usually done at moderate temperatures and shorter residence times. As shown in figure 2 below, a conventional decomposition pathway for biomass conversion shows its huge potential when used as an alternative to the conventional fossil-based sources for energy and chemicals.

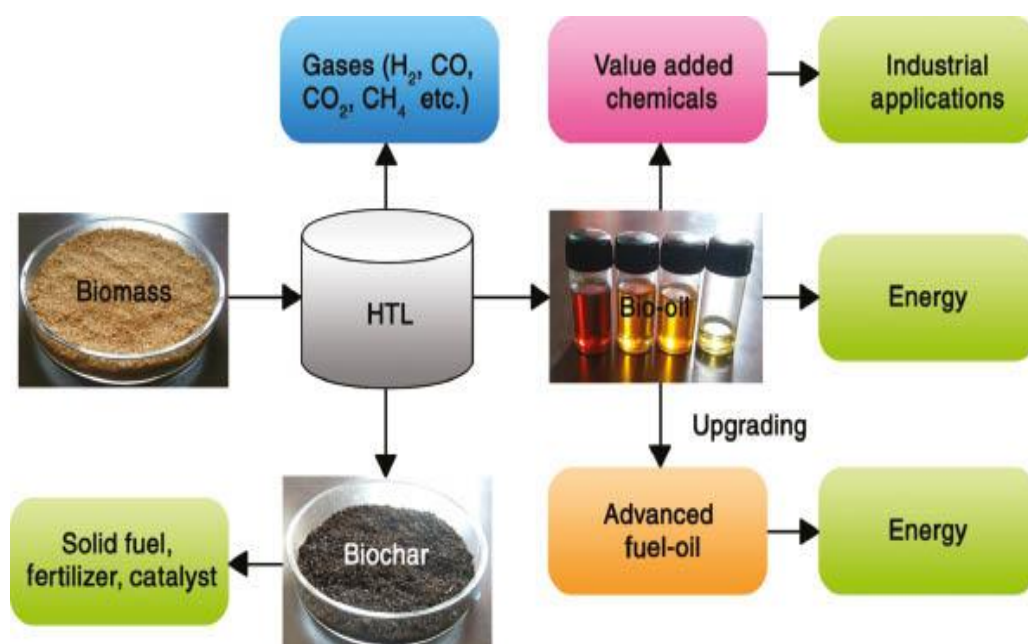


Fig 2: Biomass decomposition pathway [15]

2.4 Depolymerization of Lignin

Depolymerization of the complex lignin structure is a key element for the upgrading of lignin and involves the breaking down of the complex lignin structure into simpler monomers using processes like the thermochemical process (liquefaction, pyrolysis, gasification, hydrogenolysis, hydrolysis and alkaline oxidation) as well as enzymatic and catalytic cracking. The process temperatures for some thermal processes range from 100°C to 600°C, and depolymerization is partly supported with base, metal and acid catalysts, and sometimes carried out at sub or supercritical conditions [16-17]. Oxidation process takes place at between 100 and 320°C with pressures ranging from 5 to 200 bar, Pyrolysis is usually performed at temperatures between 450 and 800°C with rapid heating rate, and gasification at over 700°C [18]. Hydrothermal liquefaction is another lignin depolymerization technique and is usually performed under sub and supercritical water with no feedstock pretreatment required. Depolymerization of lignin has been studied and found to be a very complex reaction due and the C=C bond present and oligomers are more likely to cleave together at high temperatures. It has also been reported that the concentration of base catalysts like K_2CO_3 tends to promote the depolymerization of lignin which is why in most liquefaction studies, base catalysts have been used to enhance the decomposition of lignin and enhance product quality [19]. The products obtained from hydrothermal depolymerization are diverse and depend on the method used and the type of lignin [20]. Fache *et al.*, 2016 [16] reported on the commercialization of lignin-derived vanillin by Borregarrd, a Norwegian company, who uses the oxidation process in the presence of a NaOH concentrated solution.

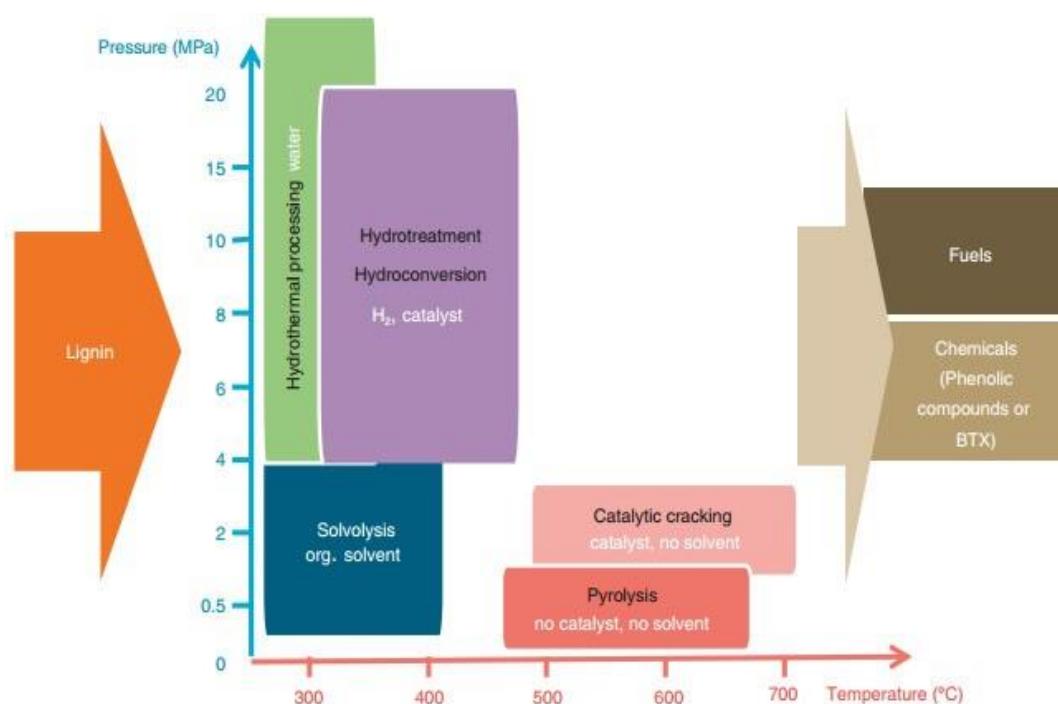


Fig 3: Thermochemical pathways for lignin conversion to chemicals and fuel [21].

2.5 Hydrothermal Liquefaction

Hydrothermal liquefaction (HTL) refers to a thermochemical process in which biomass and organic waste are decomposed into small fragments with hot compressed water behaving as a reactant, solvent, and catalyst. HTL, unlike other thermochemical processes, is usually done at moderate temperatures and shorter residence times ($T = 250 - 374^{\circ}\text{C}$ and $P = 10 - 30$ MPa at SCC) [3]. Four product streams can be obtained from a typical HTL conversion, including liquid oil phase, aqueous phase, solid residue and gaseous phase [14]. The bio-crude is considered as the most popular product among them as it can be further upgraded into a variety of platform chemicals and liquid biofuels. Most recent research on HTL, therefore, has been centered on the improvement of the yield and quality of bio-crude and bio-oil, including the effect of catalysts, selection of solvents, co-liquefaction, etc. [22]. HTL is considered superior to other biomass conversion processes in terms of the relatively low oxygen content of the resulting liquid, hence bio-oils produced from HTL process are of significantly higher energy density than pyrolysis oils. This process is particularly attractive for conversion of wet biomass since, unlike gasification or pyrolysis treatments, pre-drying of the feedstock is unnecessary and other gaseous by-products (like CO_2 and small amounts of CH_4 and H_2) are also formed [23]. The HTL process, as with any chemical unit operations, can be performed in a batch or continuous operation. A comparison of different thermal process show their different operating conditions as reported by some authors in books. Both types of operations will be further elaborated in the next sub-sections.

Table 1: Comparison of Thermochemical Processes for Biomass Conversion

Process	Temperature (°C)	Pressure (MPa)	Drying
Liquefaction	250 - 374	10 - 30	Unnecessary
Pyrolysis	400 - 800	0.1 - 0.5	Necessary
Gasification	> 800°C	22 - 40	Necessary



Fig 4: Pilot Hydrothermal Liquefaction Rig Designed and Fabricated by the HTL team

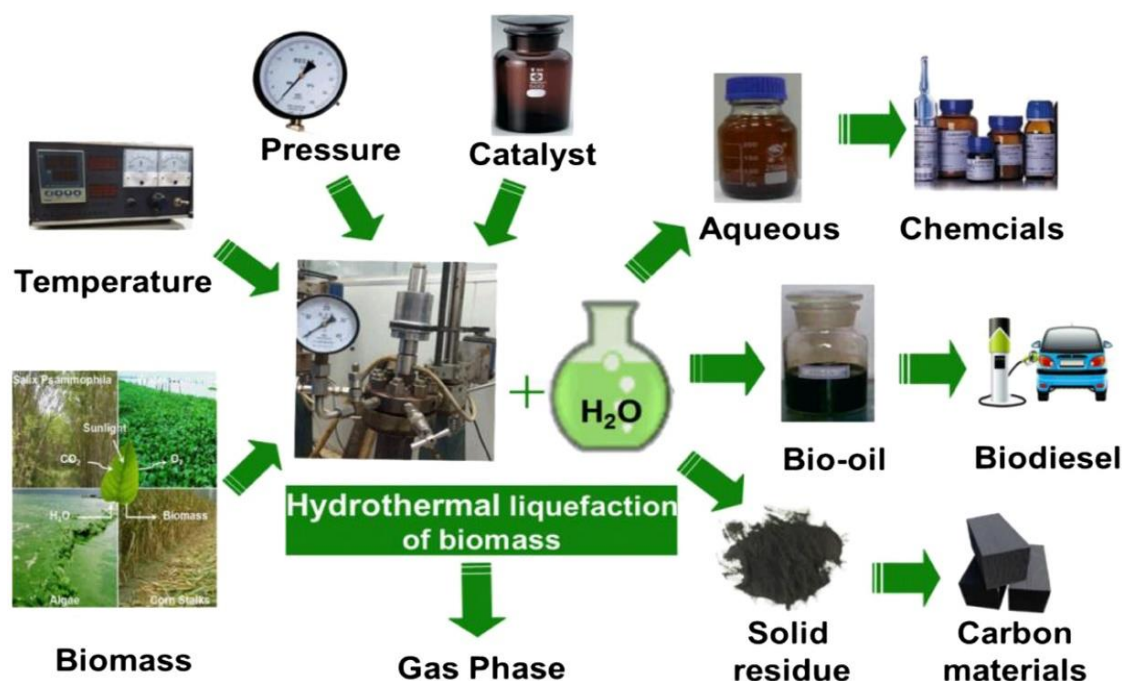


Fig 5: Hydrothermal Liquefaction of Biomass and Potential End products [24]

2.5.1 Batch Process

A batch process mainly entails performing an experiment under a controlled condition within a given time frame, that is; fixing all the operating parameters and allowing for a single run process within a predefined time-frame. Most HTL studies have centered on batch operations and different researchers have varied operating parameters as well as product separation and reported yields in each case [25]. Many researchers perform the batch operations with the use of catalysts which they have reported, inhibits char formation and improves the quality of the oil produced [26-29]. The experiment conducted for this report is based on a batch system without a catalyst and the procedure, products and analysis, will be discussed in details in subsequent chapters of this report.

2.5.2 Continuous process

A continuous HTL process will be in the form of connected series of processes flowing simultaneously to achieve a desired product in a continuous manner. The process is usually performed at supercritical water conditions with temperatures and pressures of over 400°C and 600 bar respectively [30]. Unlike the batch process, the continuous operation is mostly intended towards an upscaling and commercialization of the technology. The commercialization of the HTL process is strongly tied to its upgrading to a continuous unit operation, which will ensure bio-crude production is done at a higher volume and eliminates some time and energy consuming operations that are prevalent in a batch operation [30]. To this end, some critical parameters necessary for the success of a continuous unit operation will include but not limited to; Feedstock type, Operating Solvent, Operating temperature, Fluid flow pattern and flow rate, Product separation and extraction as well as system energy recovery. A couple of these parameters will be elaborated below;

2.5.2.1 Feedstock

Unlike a batch process where a 10% feedstock has been used in most reported cases, in relation to water, for a continuous process however, a higher percentage of feedstock is desirable. This can translate to a higher bio-crude yield and would have little or no impact on the process flow considering the supercritical temperatures mostly used as reported by some early researchers for their pilot continuous HTL systems [31]. Wet biomass feedstock with high water content is usually ideal for a continuous HTL process due to their less water required for processing. Some feedstock examples include microalgae and sewage sludge, as **Konstantinos *et al.*, 2018 [31]** reported yields for different feedstock in their pilot plant with the microalgae species producing the highest yield with a little over 16wt% dry matter content in the feedstock.

2.5.2.2 Solvent

In a continuous operation, the need for adopting a solvent that can be recirculated is also a critical success factor to the operation. Possibility to recycle solvent will also cut the cost of utilizing fresh water for each run, as is the case with the batch system and has also shown to improve the quality of bio-crude produced when incorporated in a continuous system as reported by **Pedersen *et al.*, 2016 [32]**.

2.5.2.3 Fluid flow pattern and flow rate

The flow pattern of the slurry developed inside the reacting system, whether a laminar or turbulent flow, is also taken into account. This will translate to the expected flow rate of slurry needed to maintain continuous operation, and this flow will depend on the size and type of the reactor used. **Castello *et al.*, 2018 [30]** in their critical review of a continuous HTL process reveal that some pilot-scale operators of the system has mostly used a PFR while a few others use a CSTR. The CSTR has its strength but also has some weak side to it. It helps in the fast heating and mixing of the reaction mixtures within the tank, as well a temperature control within the reactor but may have lower theoretical conversions compared to PFR due to their structural set-up, and they are more challenging to scale up when compared to the PFR.

2.5.2.4 Energy recovery

Energy consumption of the HTL process is one of the challenges associated with the process and attempts to recover energy from the operation of a continuous system a massive boost for the upscaling of the technology, in terms of cost and energy efficiency. **Konstantinos *et al.*, 2018 [31]** also reported that with the introduction of a heat exchanger and hydraulic oscillation system, liquefaction of microalgae attained a thermal efficiency of 47%. This is a sound output for emerging technology and they also pointed out that more work still needs to be done in their aspect.

2.5.3 Subcritical Condition

HTL is usually performed at the sub and supercritical conditions, depending on the solvent type and the desired product yield. At conditions close to the critical point, water, as a solvent, has several interesting properties, some of which include; low viscosity, low dielectric constant and high solubility of organic substances, which make subcritical water a desirable medium for fast, homogeneous and efficient reactions [33]. Water, for example, at subcritical

state is liquid water under pressure at temperatures above the boiling point of 100 °C. **Kang et al.**, 2013 [20] reported that at subcritical conditions, the tendency to produce oil with low oxygen content is very high since a portion of the oxygen present in lignin is hydrolyzed into small organic compounds that are further dissolved in the liquid phase containing water fraction. This will ultimately increase the energy density of the produced bio-crude or bio-oil. It has been suggested from different literatures that processes performed under subcritical conditions supports the degradation of lignin and formation of phenolic compounds in a batch operation.

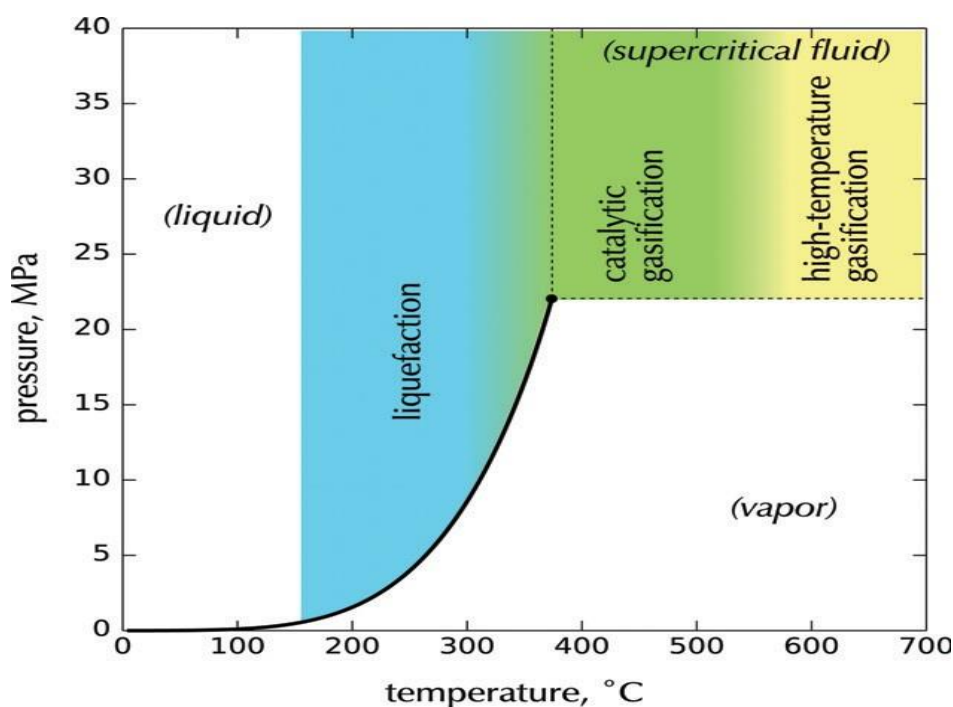


Fig 6: Hydrothermal processing regions with pressure–temperature phase diagram [34].

2.5.4 Reaction Mechanism

In the hydrothermal liquefaction of lignin for the production of phenolic compounds, hydrolysis and cleavage of the ether bond and C-C bond, demethoxylation, alkylation and condensation reactions usually occur, and these reactions seem to compete. On the other hand, the aromatic rings are not affected by hydrothermal reactions [11]. The lignin-derived phenolic compounds from the demethoxylation and alkylation will be intensified as the temperature increases, so different alkyl phenols could be obtained at high temperatures. **Lin et al.**, 1997 [35] found that in lignin liquefaction, the reaction intermediates with aliphatic side chains showed large reactivity, causing them to further condensed with phenol or with each other to convert into the multi-condensed product.

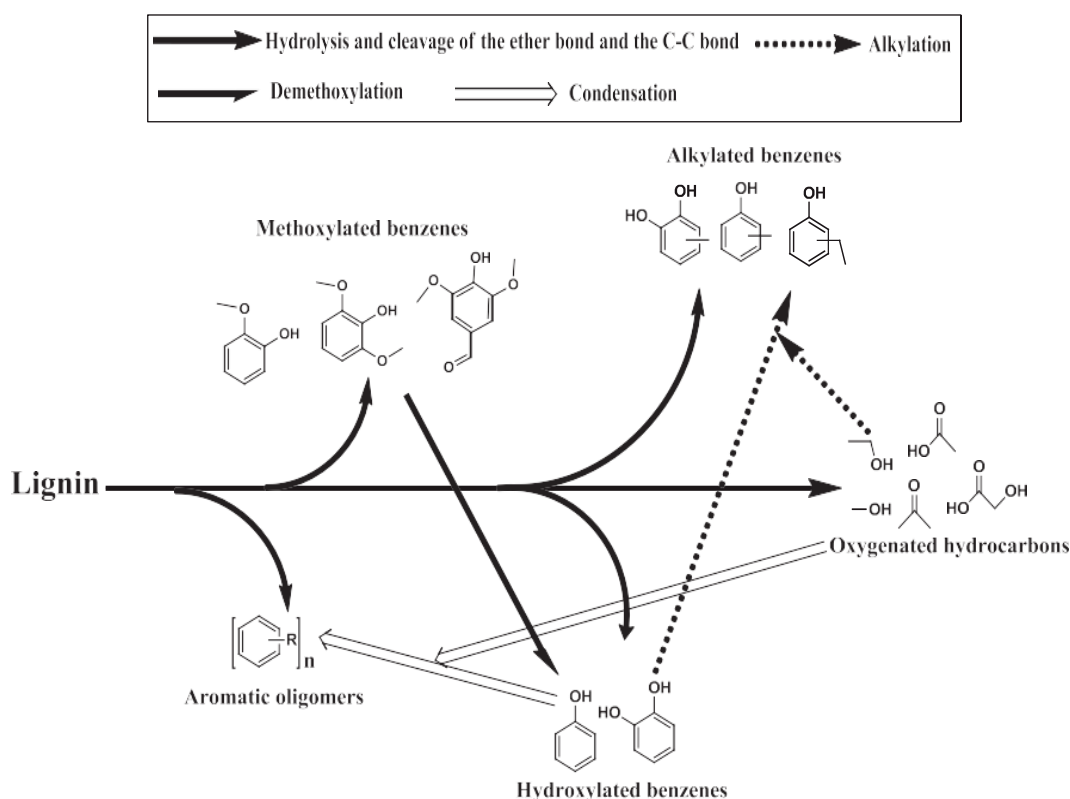


Fig 7: Proposed mechanism of hydrothermal liquefaction of lignin [11].

2.6 Analytical Methods

In the analysis of lignin as a feedstock for HTL process, different researchers have explored the use of different analytical tools. These methods are used to determine the chemical and physical properties of the feedstock and liquefaction products, respectively. The most commonly used methods include; proximate analysis, ultimate analysis, thermogravimetric analysis, the calorific test, as well as the GC-MS analyzer. Each of these methods will be discussed in detail below.

2.6.1 Gas chromatography-Mass spectrometry (GC-MS)

GC-MS is an analytical tool used for the analysis of unknown organic chemical compound mixtures present in a given sample of interest. The instrument separates chemical mixtures (the GC component), and identifies the components at a molecular level (the MS component) and is one of the most accurate tools for analyzing samples with potential environmental impacts [36]. This method is a chromatographic method that separates the compound by means of volatility and retention by the stationary phase in the column. It identifies compounds in a practically straightforward way, as it provides a characteristic spectrum of each molecule.

2.6.2 Proximate Analysis

In performing a proximate analysis, four major variable constituents present in any substance is of interest. Moisture content (MC), volatile matter (VM), Ash content (AC) as well as the fixed carbon (FC). These constituent fractions of the substance, provide

valuable information on the elemental and combustion properties of such substance.

2.6.2.1 Moisture content (MC)

The MC of material, often referred to as the water content also is mostly used to ascertain the damp state of material to know its suitability for a particular purpose. To determine the moisture content of biomass, a certain amount of the material is introduced into a crucible and weighed. Depending on the type of material and the intended use of the material, it is kept in an oven over a period of time at predefined temperatures according to established standards. The retention time varies from one material to another. Wood biomass usually at 103°C according to the ASTM E871-82 standard, while coal and coke are usually kept at 104°C and 110°C respectively, according to ASTM D 3173-03 standard. The sample is then retrieved from the oven and weighed to check the resultant weight loss. The difference in the weight before and after oven drying is what is usually referred to as MC [37].

$$\% MC(\text{wet basis}) = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Wet weight}} \times 100\% \quad (1)$$

2.6.2.2 Volatile Matter (VM)

The VM of a material is determined by introducing a small quantity of a given sample of that material into a crucible with lid and weighed on a scale. The VM for most biomass materials like wood is determined using the ASTM E872-82 standard for wood. The weighed sample is then placed inside a muffle furnace and for 7 minutes at 950°C ± 20°C. The resulting sample after the heating process is then kept to cool to ambient temperature inside a desiccator and weighed according to afterward. All this is performed after the MC of the material has been determined as described above. The VM percentage is determined by using the equation stated below as adapted from [37];

$$\% VM = \frac{v_i - v_f}{v_i} \times 100\% \quad (2)$$

Where; v_i is the initial sample weight before heating the sample

v_f is the final weight after removing and cooling the sample.

2.6.2.3 Ash content (AC)

The AC of a material is usually determined after performing the VM test of the same material as earlier described above. The main difference this time is the removal of the lid over the crucibles and a change in the heating temperature of the muffle furnace according to established standards in literature. ASTM D 1102-84 is the standardized test for woody biomass at a temperature of 600°C for 1 hour. Other biomass as coke and coal are determined according to the ASTM D 3174-04 standard at temperatures of 950°C and between 700°C and 750°C respectively, for 4 hours heating time [37]. This standard method will be further elaborated in detail, later in this report. In Europe,

however, The European Standard used to determine the ash content in solid biofuels is EN 14775 [38].

$$\%Ash = 100 - \%VM - \%FC \quad (3)$$

2.6.2.4 Fixed Carbon (FC)

The fixed carbon component of the proximate analysis is mostly computed as the fraction of what is left when the other components (MC, VM & AC) are summed up together and subtracted from 100%. [38]

$$\%FC = \frac{f_i - f_f}{v_i} \times 100\% \quad (4)$$

Where; f_i is the sample plus crucible weight before placing it in the muffle furnace

f_f is the sample plus crucible weight after removing from the muffle furnace.

2.6.3 Ultimate Analysis

The ultimate analysis is used to measure the elemental composition of the biomass. The main elements usually investigated are Carbon, hydrogen, nitrogen, sulfur and oxygen. The value Ash content of the biomass which has been measured using the proximate analysis earlier described, is used to compute the oxygen content by summing up the C, H, N, S and Ash contents and deducting the sum from 100% [37]. From the chemical composition determined by the ultimate analysis, the ratio of C/H and O/C could be determined. The results of the ultimate analysis could be useful in determining the heating value of that particular biomass.

The ASTM E 777 standard is for carbon and hydrogen content, ASTM E 775 standard is for sulfur content while ASTM E 778 is for nitrogen content [37]. The EN 15104 standard [39] is used to determine the C, H, and N of solid bio-fuels. ASTM and EN are widely accepted American and European standards for analysis and measurements respectively. The ultimate analysis is usually performed on a dry basis for accuracy of results, especially with respect to hydrogen and oxygen content in moisture which could alter their values during ultimate analysis.

2.6.4 Calorific Test

The calorific test is simply a test performed to determine the heat of combustion or energy content of a material or substance. The value is expressed as HHV, LHV, GCV or NCV and can be either calculated using the elemental composition or performed experimentally with the aid of a bomb calorimeter. The use of a bomb calorimeter is rapidly gaining acceptance, due to its relatively stable precision results and helps to determine the heat of combustion of the material. A commonly used equation for determining the HHV is Dulong's formula where elements used in the equations are expressed with the assumption that only C, H, O, and N are contained in the biomass [40].

$$\text{HHV (MJ/kg)} = 0.3383 C + 1.442(H - O/8) \quad (5)$$

Where; C, H, and O are the weight percentages of carbon, hydrogen and oxygen, respectively.

Dulong's equation uses the C, H, O and S elements, and is valid if the oxygen content is below 10 % [37]. There is a little difference in the values reported in Europe and USA for calorific value, the LHV that is the function of the NCV is used in Europe and the HHV which is a function of the GCV, is mostly used in the USA. The predominantly used equation for determination of GCV for biomass [41] is expressed as;

$$\text{GCV} = 0.3491 \cdot X_C + 1.1783 \cdot X_H + 0.1005 \cdot X_S - 0.0151 \cdot X_N - 0.1034 \cdot X_O - 0.0211 \cdot X_{\text{ash}} [\text{MJ/kg, d.b.}] \quad (6)$$

2.6.5 Thermogravimetric Analysis

The Thermogravimetric Analyzer (TGA) measures the change in weight of a sample as tested through a temperature profile over a period of time. The TGA can provide information about the physical and chemical properties of a substance. Physical properties like a phase transition, absorption and adsorption, as well as the chemical phenomena including chemisorption, thermal decomposition and dehydration and solid-gas reactions such as oxidation or reduction. It is performed by gradually raising the temperature of a sample in a furnace as its weight is measured on an analytical balance that remains outside of the furnace in an atmosphere of nitrogen, helium, air, argon and sometimes other gases in different combination/mixture as maybe needed for the substance to be analyzed. Inorganic materials, metals, polymers and plastics, ceramics, glasses, and composite materials can be analyzed using the TGA methodology. Measuring temperatures usually range from ambient temperature to as high as 1500°C, at a controlled heating rate from 1°C/min to as high as 20°C/min depending on the sample specimen to be analyzed under controlled atmosphere. Sample weight can range from 1mg to 150mg. There is usually a Weight change sensitivity of 0.01mg accounted for, depending on the equipment and sample specimen. Samples can be analyzed in the form of powder or small pieces so the interior sample temperature remains close to the measured gas temperature. Determines temperature and weight change of decomposition reactions, which often allows quantitative composition analysis [42-43].

Chapter 3

Materials and Method

This experiment was performed at the University of Agder, mostly in the combustion/liquefaction and microscopic laboratories, respectively. The HTL pilot rig in the combustion and liquefaction laboratory was used for the actual HTL process, the TGA and Elemental analyzers in the microscopic laboratory was used. The bomb calorimeter was used for the determination of the HHV of the feedstock. The mode of operations of these and more equipment used will be discussed in detail below.

3.1 Materials

The Lignin biomass samples used were gotten from two different sources. One was purchased from Sigma-Aldrich, and the other was obtained from Borregarrd. The collected lignin samples are both soluble in water. Some chemicals used include methanol of 99% purity and an analysis grade of acetone of 95% purity, both from the laboratory in UiA, ultrapure water in the building laboratory of University of Agder. All the chemicals were used as received without further purification. Other materials also used during this experiment are the PerkinElmer 2400 Series II System CHNS/O Elemental analyzer, Mettler Toledo TGA/DSC1 Thermogravimetric analyzer, as well as a Nabertherm LT 40/11/330 muffle furnace. An Eppendorf 5430 centrifuge with a maximum rpm of 7830 was also used, as well as a 24ml High Pressure 20-21LF16HF4 (316SS) HT #266397model batch reactor from HiP, USA. The use of software tools like excel and MATLAB was also deployed for the accurate interpretation of results obtained. Details of their use and operations during the experiments will be elaborated in subsequent sections of this chapter.

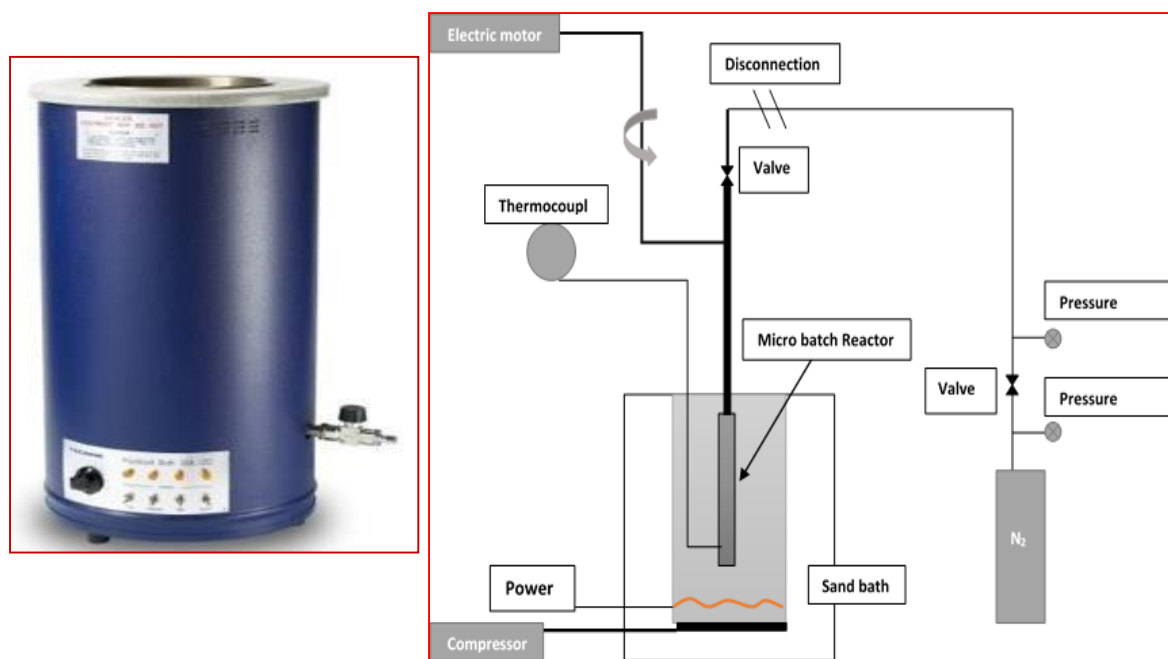


Fig. 8: Schematic experimental set-up of the HTL Rig in combustion lab.



Fig 9: Alkali Lignin from Sigma-Aldrich.



Fig 10: Lignosulfonate from Borregarrd

3.2 Experimental Method

The TGA was used to determine some thermal properties of the lignin samples and the results were exported and plotted with a MATLAB program accordingly. The hydrothermal liquefaction of lignin was performed using a batch reactor. As in a typical liquefaction experiment, the total volume of the reactor used was 25ml and a total feed slurry of 16ml in volume was used, allowing for 2ml dead-volume in the reactor to allow for the smooth reaction. A feedstock to a solvent ratio of 1 to 9 (10% to 90%) is maintained for all the reaction temperatures and solvents used. The fluidized sand-bath is heated from ambient temperature up to the desired reaction temperatures of 300°C, 330°C and 350°C, and maintained at each of

these temperature levels for reaction residence times of 10, 15 and 20mins respectively. The frequency controller motor has a maximum frequency of 35Hz, but is kept at 32Hz and maintained an oscillation of approximately 6.5rpm during the test. A compressor was also connected to the fluidized sand-bath which helps in the heating and cooling process of the sand-bath. There is also a temperature controller connected to the sand bed with a thermocouple which helps to monitor the temperature inside the sand-bath before, during and after each experimental run. The feedstock slurry is then fed into the reactor with the aid of a syringe and the reactor is tightly covered and a leak test is performed to ensure that the reactor is leak-free before starting the experiment. The reactor is fastened to the frequency controller motor, which controlled the oscillatory movement of the reactor within the fluidized sand-bath during each test run. At the end of each test run, the reactor is uncoupled from the frequency controller and placed inside cooling water to allow for cooling of the reactor to room temperature for about 30 to 40 minutes. The cooled reactor is then opened and the product is extracted using methanol as an extraction solvent. The methanol is used to wash the reactor three times to ensure complete extraction and the product is collected into a small beaker with the aid of a funnel. The collected product is allowed to settle inside the beaker for some time to facilitate phase separation of the product stream as shown in figure 11 below.

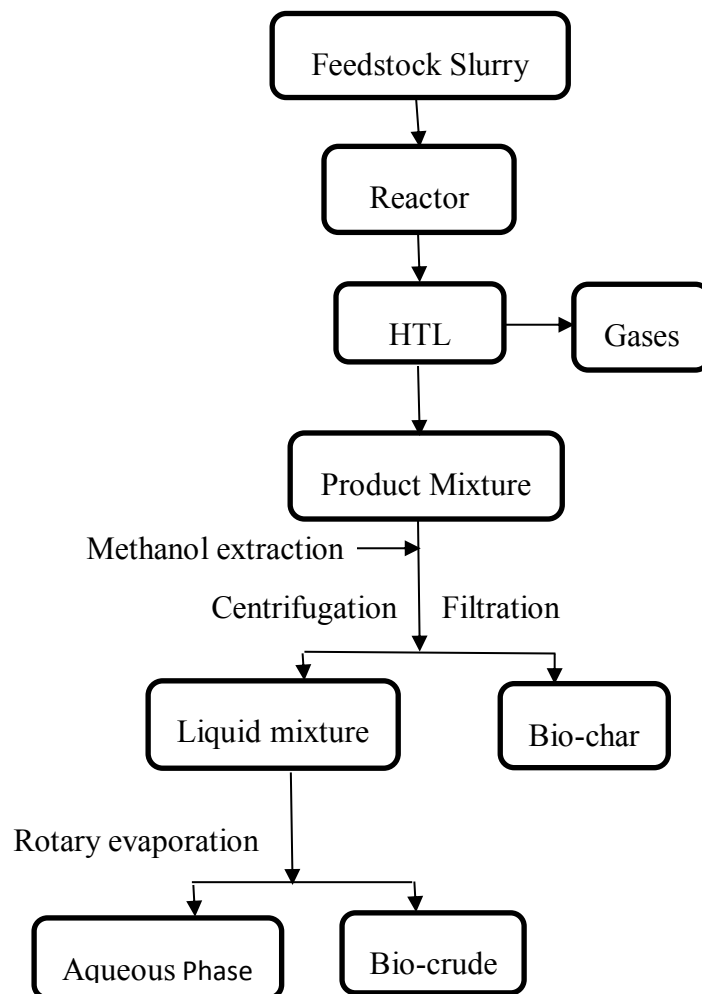


Fig 11: Process Flow Diagram for the HTL Experiment in Combustion Laboratory

3.2.1 Post Reaction Phase Separation

In the separation process adopted for this experiment, as with most liquefaction studies, extraction solvent plays a crucial role in product extraction and separation. The use of methanol as an extraction solvent was chosen to help for total product removal from the reactor. Methanol was used due to its favorable polarity, which tends to be suitable for lignocellulosic biomass, in terms of relative ease of evaporation and termination of bond between the methanol and extracted product. Methanol and acetone have similar polarity, but methanol was used for this work due to its availability as at the time of this work. **Jerome *et al.*, 2015 [44]** reported yields from the use of different solvents for extraction of bio-oil from HTL based on the polarity of the solvents and the type of feedstock. Their report provided some evidence to see that acetone and methanol have a more promising yield when used especially for extraction of oil from thermochemical processes and most liquefaction studies have reported decent yields using acetone and methanol [45] due to their polarity and relative volatility. The liquefaction product consist of four main components; the gas phase, the bio-crude, the aqueous phase and the bio-char. Each of these product phases contains substances that can be further fractionated or refined into other valuable products. In order to ensure the complete collection of these product phases, different techniques are deployed to ensure adequate phase separation. The produced gases are released after the liquefaction experiment as described in fig 11 above. A centrifuge was then used to separate the liquid and solid products after settling for a few hours in a beaker. The centrifugation was performed in the chemical laboratory of Havforskninginstituttet research institute located in Arendal, in the southern part of Norway. The centrifuge used has a maximum RPM of 7,830 and an RCF of 4,500. The centrifugation was performed in two rounds consecutively for each sample, to ensure a complete phase separation. Figure 12 below shows the process flow diagram of the separation process performed at Havforskninginstituttet research institute.

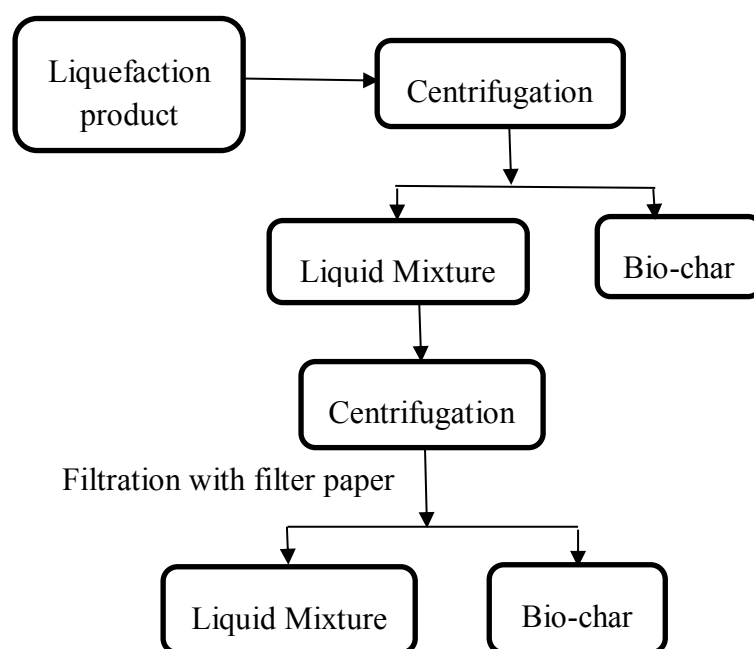


Fig 12: Process Flow Diagram of the Solid-Liquid Separation Process

The separated liquid product still contains a little bio-char, which was further subjected to a filtration process with a filter paper, to further remove the left over char. The resulting liquid phase is a mixture of bio-crude, aqueous phase and some water and methanol. The collected bio-char is added to the earlier quantity obtained via filtration. The liquid products were subjected to an evaporation process, using a rotary evaporator show in fig 12 below. In the rotary evaporator, the temperature is initially set between 60 to 70°C to evaporate the methanol into a hollow container, after which the temperature is further increased to a little below 100°C to separate the aqueous phase from the bio-crude. Both phases are collected into separate plastic tubes for further analysis. The collected bio-char is heated at a low temperature to evaporate the methanol and then washed trice with the use of acetone to ensure the collection of a pure bio-char sample, which is weighed and recorded for each sample.



Fig 13: Rotary evaporator for liquid phase separation.

3.3 Analytical Methods

The analytical methods deployed for this experiment is broadly categorized into two main components. The feedstock characterization and the product analysis. These two broad components will be elaborated in details in the following sections.

3.3.1 Feedstock Characterization

The characterization of the feedstock was necessary to determine specific properties of the feedstock and ascertain its suitability for the intended experiment. This process will also give us a basis for a comparison of the properties of the products after the experiment in relation to the properties of the feedstock used. Some of these properties include the moisture content of the feedstock, the volatile matter content, the ash content, the fixed carbon content, the thermal decomposition properties as well as the calorific value of the feedstock.

3.3.1.1 Proximate Analysis

The proximate analysis was conducted in a sequence of two orchestrated tests, with the second test largely independent on the first but with sample from the same source. Both tests were performed on the two lignin samples. Test 1 was used to measure the MC and AC, while the second test was used to determine the VM. Separate crucibles were used for the two tests, big crucibles in test 1 and small crucibles with lid in test 2.

Test 1

First, the crucibles were weighed, and the weights recorded accordingly. 1g of each lignin sample was introduced in each crucible. The crucibles with the samples were weighed again and were placed inside the oven for 24 hours at 105°C to ensure the stability of the weight before removing it. The oven-dried samples were taken out of the oven and placed inside a tightly closed glass desiccator to avoid interactions with ambient air within the laboratory and is allowed to cool down to ambient temperature. Afterward, the crucibles with the samples left in them were weighed again, and then placed inside the muffle furnace following the procedure highlighted below;

- The muffle furnace was heated from ambient temperature to 250°C for 30 minutes and kept at that temperature for 1 hour.
- The temperature was then programmed to increase to 550°C, and kept at that temperature for another 2 hours.

The crucibles containing the ash left after combustion were placed in a tightly closed glass desiccator and kept there for cooling to ambient temperature. After the cooling process, the samples were weighed again.

Test 2

Small crucibles with lid were weighted and 1g of each lignin sample was weighed and introduced into the crucible. The samples were prepared in triplicates for repeatability of results. The crucibles with samples were weighed again before placing them inside the muffle furnace for 7 minutes at 900°C. Afterward, the samples were removed and placed inside a tightly closed glass desiccator and was allowed to cool as in test 1 above. After cooling, the sample with crucible plus lid was weighed, and the loss in weight in this instance is due to the loss of MC and VM.

In both tests, the results obtained were tabulated accordingly. From test 1, the initial weight of the sample and the sample weight after drying was used to compute the MC using equation 1 earlier stated in chapter 2. The average value for each of the triplicate lignin samples were recorded. The

AC was computed using equation 3 in chapter 2, and the average MC of the lignin samples. From test two the VM was computed using the initial weight of the crucible and lid, the weight of sample and the crucible with lid, the weight after heating and the MC.

3.3.1.2 Ultimate Analysis

The ultimate analysis, often referred to as the elemental composition, was performed with the use of a CHNS/O elemental analyzer stationed in the microscopic laboratory of UiA. The process involved the use of a tin cup, which is weighed on a digital scale connected to the elemental analyzer. A sample weight of between 0,9mg and 1,5mg was used in all test cases performed. The tin cup was then neatly folded and weighed again and the corresponding weight and sample name were entered into the digital display screen of the analyzer and the sample was placed in the corresponding chamber after running three blank samples before each actual sample test. The running of the blanks is to ensure proper purging of the chamber of any left-over gases that might interfere with the results of the next sample. The system is configured to run automatically and the corresponding results are displayed on the PC connected to the analyzer. The results for all samples were extracted from the PC to an excel sheet for record purpose and the mean values were computed in each case. Oxygen content is calculated by subtracting the sum of C, H, N, and Ash from 100 % since no sulfur test was performed. The equation below was used to compute the oxygen content.

$$O(\%) = 100(\%) - C(\%) - H(\%) - N(\%) - ASH(\%) \quad (7)$$



Fig 14: PerkinElmer 2400 CHNS/O Series II System

3.3.1.3 Thermogravimetric Analysis

This analysis was performed using the TGA instrument pictured below. The essence of this analysis is to understand the thermal decomposition behavior of the lignin samples, and as such, an appropriate method was created. The method created, took into account the intended process temperature and pressure for the liquefaction experiment, to give a better understanding of how the lignin samples will behave during the liquefaction. To create the method, the purging gas to be used was selected, the purging rate of the gas, the heating rate, the starting and ending temperatures, as well as the temperature steps (Isothermal and Dynamic). After creating a method, each sample was assigned same method to ensure uniformity of operating conditions. The purging gas used is Nitrogen due to its inert nature, as this will give a more realistic result, given that the operating conditions inside the reactor of the liquefaction is void of air or oxygen. Afterwards, the Nitrogen was substituted with Air as purging gas to have a comparative analysis of the behavior of the lignin with and without oxygen.



Fig 15: Mettler-Toledo Thermal Analyzer

The following method was used for the TGA test in all cases:

- Purging gases selected were Nitrogen and Air, used one after the other for two separate runs, with a purging rate set at 50ml/min
- Starting temperature of 25°C

- Heating rate of 10°C/min was defined in all cases
- The entire heating process is set at dynamic condition to better understand the properties as it decomposes from the start to stop temperatures.
- Stop temperature was set at 400°C, considering the maximum liquefaction to be used is 350°C.
- Temperature was kept in Isothermal condition for 60 minutes with Nitrogen as purging gas, and afterwards for 120 minutes with Air as purging gas. Both isothermal conditions were at 400°C to understand the behavior of the biomass at this temperature.

After creating the method, sample names were created and same method was applied in all cases for uniformity of conditions. The crucible used was a 150µl Alumina crucible for all the samples to ensure uniformity of weight and measurements. Empty crucibles were placed on the turn table and the TGA was configured to read its weight and record it accordingly. After which, all the crucibles, except the first one, were filled with sample of between 10 to 50mg and placed on the turn table of the TGA after the blank. The TGA was configured to operate in auto mode to allow for continuity of the experiments and the experiment lasted for 6 and 20 hours respectively, for the first and second tests. After the run time, the result data was exported to an excel sheet for computation of the mean values and interpretation respectively. More details on the results and its interpretation will be discussed in the next chapter.

3.3.1.4 Calorific Test

The calorimeter used is an IKA C6000 Global standard type, shown in figure 15 below. A sample of the feedstock obtained was weighed (around 1g with an error of 0.01g) and placed directly inside the crucible. The crucible was tared before the weighed feedstock was introduced into it, and then placed inside the bomb of the calorimeter. A 4ml of ultrapure water was introduced into the flat open plate inside the bomb, using a pipette. The sample weight was manually inputted using the digital screen on the calorimeter and the necessary settings were put in place. The combustion gas used was oxygen. The bomb with the sample inside, was closed and scanned with a detector on the calorimeter and then placed inside the calorimeter. The calorimeter was closed and observed for a few minutes to ascertain the rate of change of temperature, this was allowed to continue until the sample is fully combusted. The corresponding calorific value displayed on the digital screen at the end of the process was recorded accordingly.

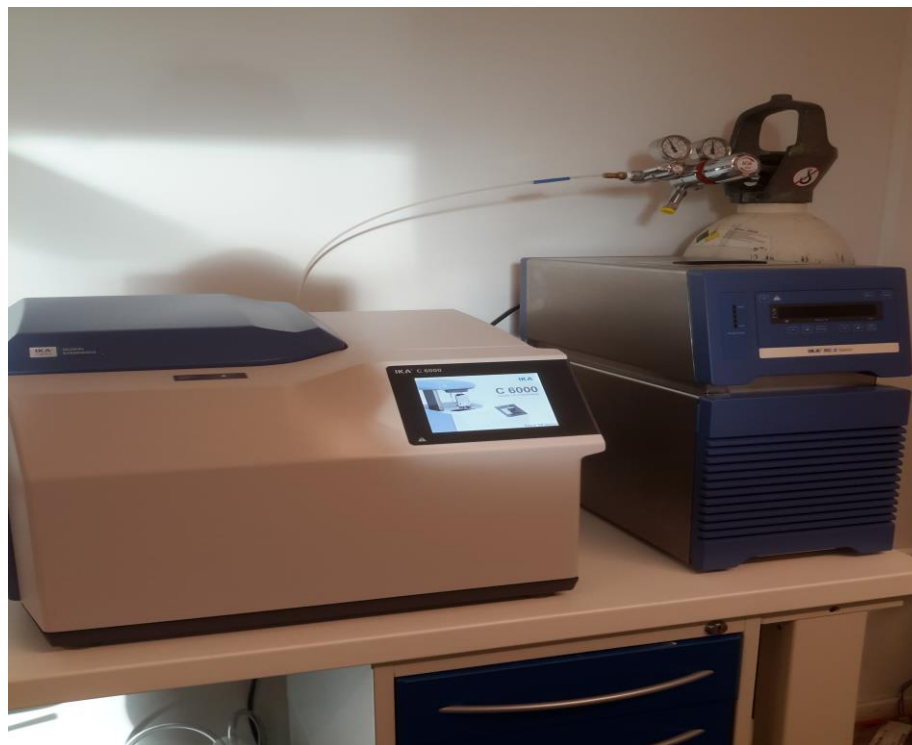


Fig 16: IKA C6000 Global standard Bomb Calorimeter

3.3.2 Product Analysis

The product phases collected as earlier described is analyzed accordingly. For the purpose of this project, the product phases of interest are the bio-crude and bio-char, which were analyzed separately. Due to technical breakdown of the equipment after analyzing the bio-char phase, I was unable to analyze the bio-crude phase, as the machine was not fixed in time to carry out the test and my stay with the group was limited for this work.

3.3.2.1 Bio-char Analysis

The analysis of the bio-char was performed using the elemental analyzer earlier described, as used for the feedstock. The main difference in the elemental analysis of the bio-char and bio-crude is the crucible used for the analysis. The crucibles used is the same with the one used for the feedstock analysis. The results were extracted and computed using an excel program. The elemental composition was also used to compute the HHV and the results recorded accordingly, as will be seen in the next chapter.

3.4 Computation of Total Product Yield

The product phase contains four main components (Released Gases, Heavy Bio-crude, Liquid phase and the Char) and these components will be computed individually to ascertain the overall product yield.

3.4.1 Char Content

The Char content of the product phase was separated by filtration using a filter paper with a pore size of 150 microns. The char content taken out initially contains the extraction solvent and was washed thoroughly with acetone and water three times before being oven dried to determine the actual char content.

$$\text{Total sieve residue} = \text{Weight of filter paper} + \text{Char} + \text{Extraction solvent content}$$

$$\text{Char content (dry basis)} = \text{Total sieve residue} - (\text{weight of filter paper} + \text{Solvent} + \text{Ash content}).$$

3.4.2 Gas Content

The gases obtained at the end of the reaction were released as the focus of this research is the bio-crude yield. The total gases in the product phase were computed using a mass balance of the entire process stream as shown below;

$$\text{Total product yield} = \text{Gas phase} + \text{Char content} + \text{Liquid Phase} + \text{Aqueous phase}$$

$$\text{Gas content (\%)} = 100\% - (\text{Bio-Char} + \text{Bio-crude} + \text{Aqueous content}) \% \quad (8)$$

3.4.3 Bio-crude Yield

The total bio-crude yield was determined using the formula below by **Gan *et al.*, 2013 [46]**

$$Y = \frac{\text{Weight of bio-crude}}{\text{Weight of lignin feedstock}} \times 100\% \quad (9)$$

$$Y = \frac{W(\text{product})}{W(\text{feedstock}) - W(\text{Ash}) - W(\text{Moisture})} \times 100 \quad (10)$$

3.5 Elemental Composition of Products

The elemental composition of the product is performed for the two main products of interest, i.e; the bio-crude and the bio-char. This is considered to be an integral component of the analysis to help extract more information about the energy content of the product phase.

3.5.1 Elemental Composition of Bio-crude

The elements of interest present in the bio-crude produced are C, H, N and O. These elements provide relevant information like the hydrogen/carbon ratio as well as the oxygen/carbon ratio. The oxygen content of the bio-crude is also an indication of the energy density of the crude produced, which is related to its combustion properties. Due to technical breakdown of the elemental analyzer and time constraints, as earlier stated, this test was not performed.

3.5.2 Elemental Composition of Bio-char

The elemental composition of the bio-char also help to quantify the carbon as well as nitrogen content of the char. The carbon content is an indication of the energy potential of the char and can also help in the computation of the HHV to get an estimate of the combustion properties of the char when used as fuel. To this end, the elemental analysis was performed and the results extracted and computed with an excel program.

3.5.3 Carbon recovery

From the results of the elemental composition, we are able to calculate the carbon recovery of the bio-crude produced, in relation to the initial carbon content of the feedstock earlier obtained.

$$C = \text{Bio - crude yield} \times \frac{\text{Bio-crude carbon content}}{\text{Lignin feedstock carbon content}} \times 100\% \quad (11) \quad [46]$$

3.6 Determination of HHV of Feedstock and Products

3.6.1 HHV for Lignin Feedstock

The HHV, similarly referred to as the calorific value, was determine with the aid of a bomb calorimeter available in the combustion laboratory of the University of Agder. A sample of the bio-crude obtained was placed in a glass/plastic enclosure and weighed using a weighing scale. A crucible was also weighed and the weighed bio-crude sample was placed inside the crucible and then placed on the bomb of the calorimeter. A 4ml of distilled water was introduced into the flat open plate inside the bomb, using a pipette. The measured sample weight was manually inputted using the digital screen on the calorimeter and the necessary settings was put in place. The bomb with the sample inside it, was closed and scanned with a detector on the calorimeter and then placed inside the calorimeter. The calorimeter was closed and then observed for some minutes for the rate of temperature change until the sample is burnt in the presence of oxygen introduced from an external cylinder. The corresponding calorific value was displayed on the digital screen at the end of the process and recorded accordingly.

3.6.2 HHV for Bio-crude

The HHV for the bio-crude is determined by computation from the results of the elemental composition of the bio-crude obtained. This computation is based on the Dulong's formula [40] referenced in chapter 2 of this report. And is again stated below;

$$\text{HHV (MJ/kg)} = 0.3383 C + 1.442(H - O/8)$$

3.6.3 HHV for Bio-char

Similarly, the HHV for the bio-char was also computed using same Dulong's formula [40]. The essence of using the equation for this purpose again is to get an approximate value for the HHV

for the total product phase, so we can quantify the energy recovery of the bio-crude since the quantity of char obtained is not much. This will be further elaborated in the next point.

$$\text{HHV (MJ/kg)} = 0.3383 C + 1.442(H - O/8)$$

3.7 Energy Recovery (ER)

The chemical energy recovery for the key products of particular interest (bio-crude and bio-char) were computed using the formula below, adopted from [47]

$$\text{ER} = \frac{\text{HHV}(\text{product}) \times W(\text{product})}{\text{HHV}(\text{feedstock}) \times W(\text{feedstock})} \times 100 \quad (12)$$

Chapter 4

Results and Discussion of Results

An outline for the presentation of the results in this chapter of the report, is schematically presented in figure 17 below. The results presented will be briefly discussed in each case in subsequent sections following.

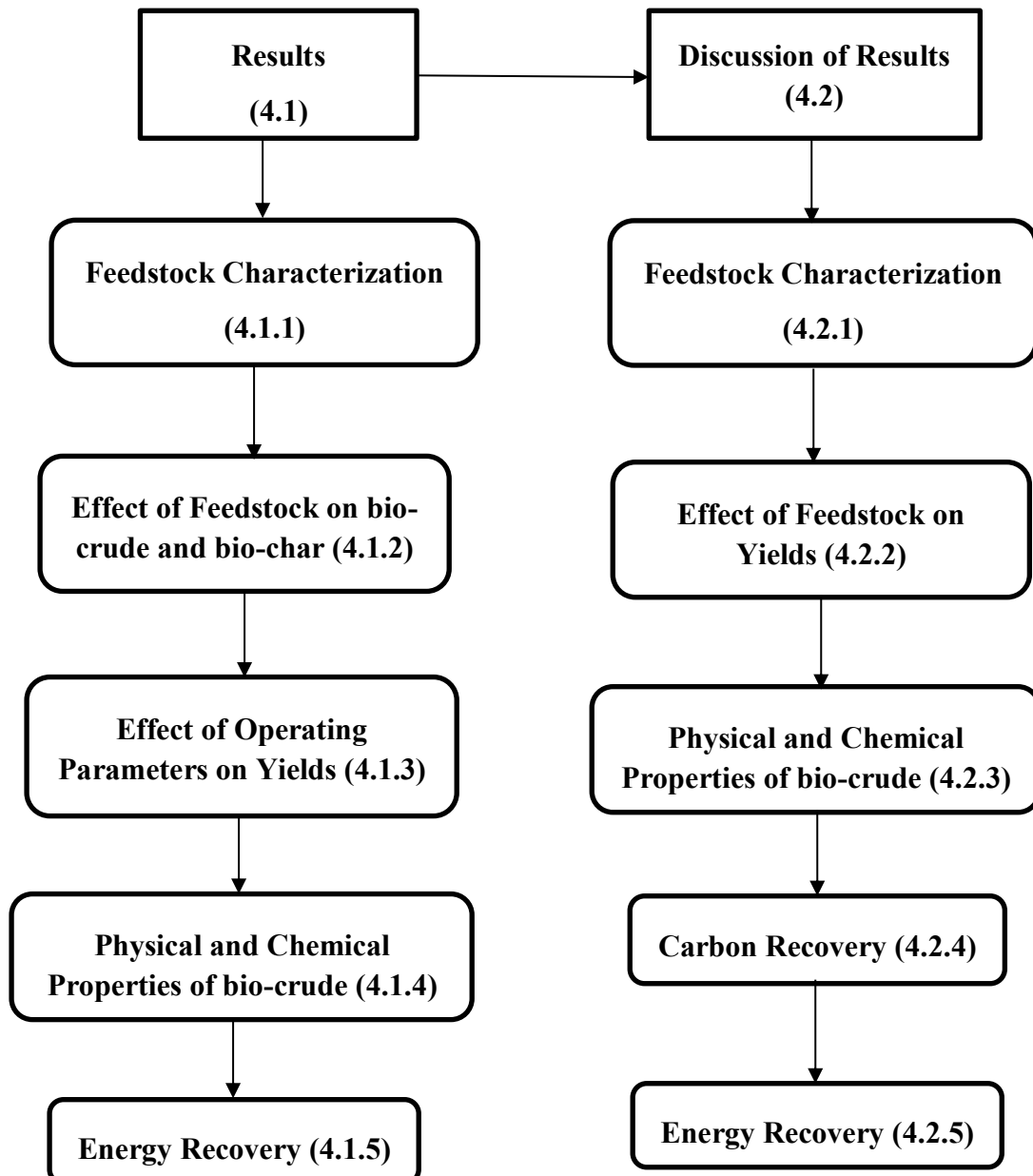


Fig 17: Process flow of Results and discussion presentation

4.1 Results

4.1.1 Feedstock Characterization

The feedstock characterization, which was earlier discussed above using different analytical tools, produced some results, which is tabulated below for clarity.

4.1.1.1 Proximate Analysis Results

The proximate analysis of a material provides some important information about the carbon, ash and volatile matter contained in that material and is therefore of fundamental importance to ascertain the suitability of any biomass for energy use. The results presented in table 2 below, are for average values from the triplicate tests performed for each lignin type. Figures 18 and 19 shows the ash contents of the alkali lignin and lignosulfonate respectively, while figure 20 also show the volatile matter remaining for each lignin sample after combustion in the muffle furnace.

Table 2: Proximate Analysis Results

	MC (%)	VM (%)	ASH (%)	FC (%)
Alkali Lignin	7.5	67.50	9.62	17.38
Lignosulfonate	5.90	59.23	14.40	20.47



Fig 18: Ash for Alkali lignin



Fig 19: Ash for Lignosulfonate



Fig 20: Crucibles with Lid for the VM test for the Alkali lignin and Lignosulfonate

4.1.1.2 Ultimate Analysis Results and HHV of Feedstock

Ultimate analysis, on the other hand, is more comprehensive and is the quantitative analysis of the various elements present in the lignin samples as seen in table 3 below. The HHV was determined with the use of a bomb calorimeter as described in chapter 3 earlier and the oxygen values were computed with equations 7 earlier stated.

Table 3: Ultimate Analysis Results and HHV of feedstock

	C (%)	H (%)	N (%)	O (%)	HHV (MJ/kg)
Alkali Lignin	51.50	4.12	0.35	44.03	19.42
Lignosulfonate	65.1	8.6	1.9	19.2	18.33

4.1.1.3 Thermogravimetric Analysis: Lignosulfonate vs Alkali Lignin

The results obtained from the TGA analysis of the lignin samples showed a very similar decomposition pattern for the two types of lignin as seen in fig 19, 20, 21 and 22 below.

4.1.1.3.1 Nitrogen as Purging Gas

Lignosulfonate

The sample weight used here was 4.66mg. The early part of the decomposition witnessed just a small weight loss of about 8.07% between 36 and 183°C of heating temperature, but when observed over a wider temperature range of 36 and 400°C, the weight loss experienced a spike

of up to almost 44%, close to half of the test sample initial weight. This gives an indication that decomposition tends to occur faster at temperatures of over 183 and less than 400°C. This is because, at 400°C, where the system was kept at isothermal condition, the weight loss was very negligible. Interestingly, the weight loss experienced during the liquefaction temperature range of 226 ad 360% was 25.5%, with a residual 63.7% of the sample weight still unreacted. Moreover, the reaction is generally an exothermic one with an integral energy release of approximately 5.6Joules and the peak energy release occurred at 380.8°C. This brief is based on the TG/DTG profile graph.

Alkali Lignin

This brief is based on the TGA/DTG profile graph. Alkali lignin on the other hand, about 5.98mg of the sample was used. When observed over a temperature range of 33 and 400°C, the weight loss was 36.7% of the initial weight, which is less than the weight loss experienced for the lignosulfonate over similar temperature range. Implying that the Alkali lignin decompose slower than the lignosulfonate when treated in an inert environment. However, the moisture content might have played a role in the combustion process because earlier results of the proximate analysis suggests that the Alkali lignin contains more moisture than the lignosulfonate and the TGA experiment was performed with fresh samples prior to removing their moisture content. The weight loss experienced around the liquefaction temperature range of 226 and 360°C was around 19.6% with a residual weight of 70% still yet to combust. The reaction was equally exothermic with an integral energy release of 8.8Joules, with the peak energy release occurring at around 346.5°C.

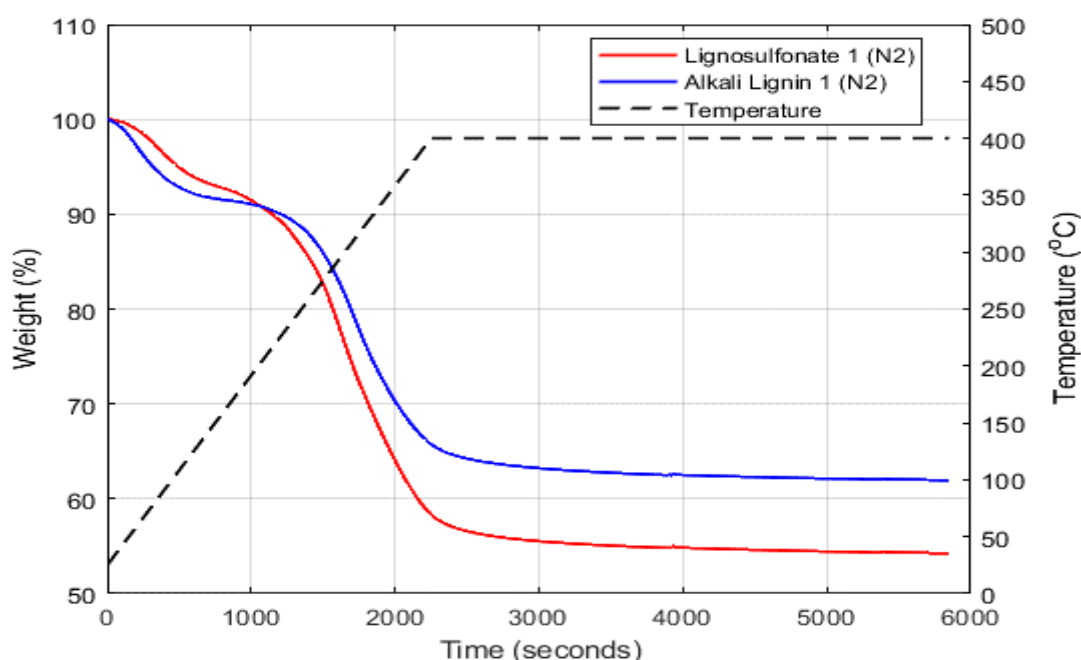


Fig 21: TGA results obtained with N₂ used as purging gas.

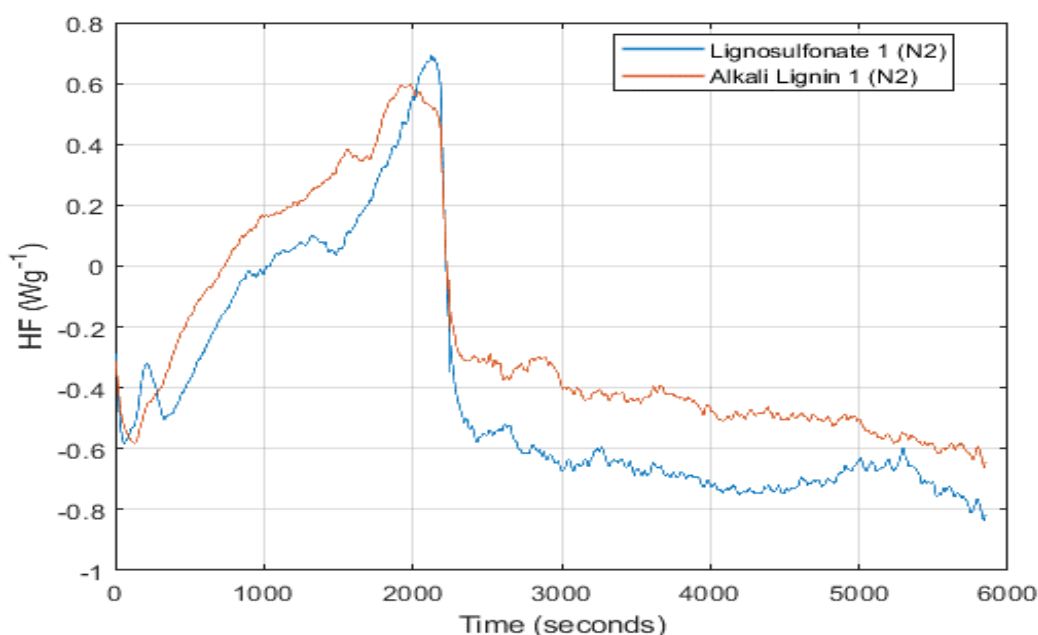


Fig 22: DTG results obtained with N₂ as purging gas.

4.1.1.3.2 Air as Purging Gas

Lignosulfonate

With air as the purging gas, over a similar temperature range earlier state for lignosulfonate, the weight loss observed was around 43.9%, almost same as with Nitrogen as purging gas. Between temperature ranges of 43 and 189°C, the weight loss observed was 7.92%, very close to the results from Nitrogen. The weight loss experienced between the temperature range of 222 and 363°C was 27.8% with a residual weight of almost 62%, this is considered the liquefaction temperature range. The reaction being an exothermic one as before, had an integral energy release of 11.69Joules and the peak release was at 348°C. The increase in energy released from the system is likely as a result of the oxygen component present in air, which must have aided the combustion. This can be seen on the TGA/DTG profile graph

Alkali Lignin

With Air as purging gas, the decomposition rate was similar to that of Nitrogen as a purging gas. The weight loss between temperature ranges of 40 and 400°C was around 34.7%, and the loss between 39 and 198°C was around 8.79%. Beyond the 200°C temperature values, almost 90% of the sample weight was still intact. Interestingly, the weight loss between 222 and 363°C, which is the subcritical liquefaction temperature range used for this work, showed a loss in weight of 20.80% with a residual weight of 69.46%. This could suggest that the liquefaction temperatures will only convert a fraction of the lignin samples and there is a possibility of having unreacted lignin samples form part of the solid residue. The integral energy released is even much higher for Alkali lignin, at 21.4Joules, nearly twice the energy released from the lignosulfonate as earlier stated.

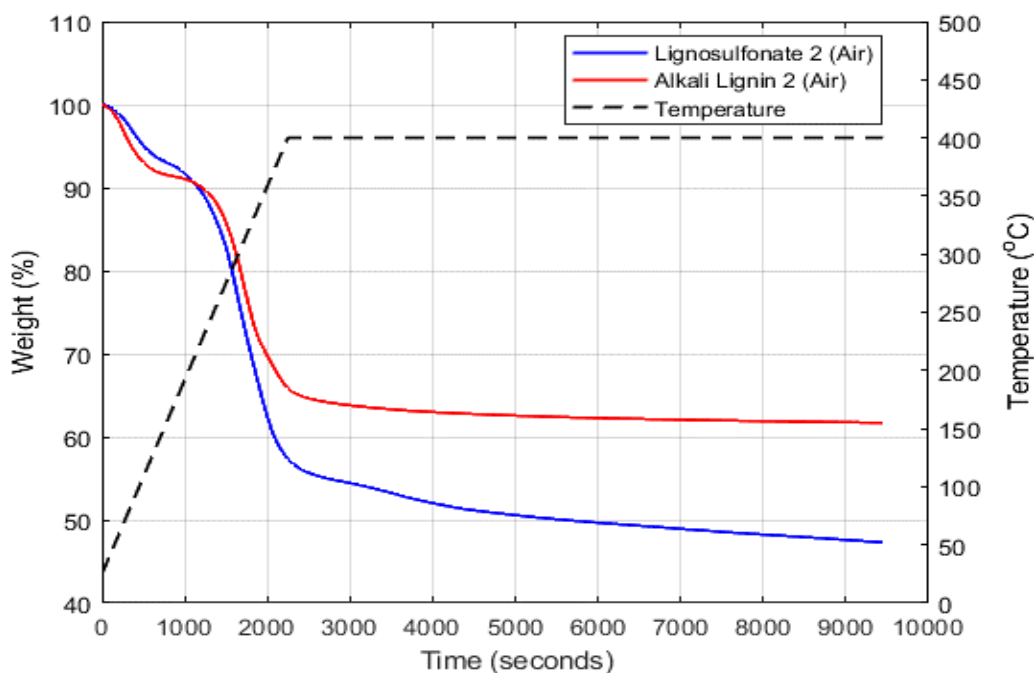


Fig 23: TGA results obtained with Air used as purging gas.

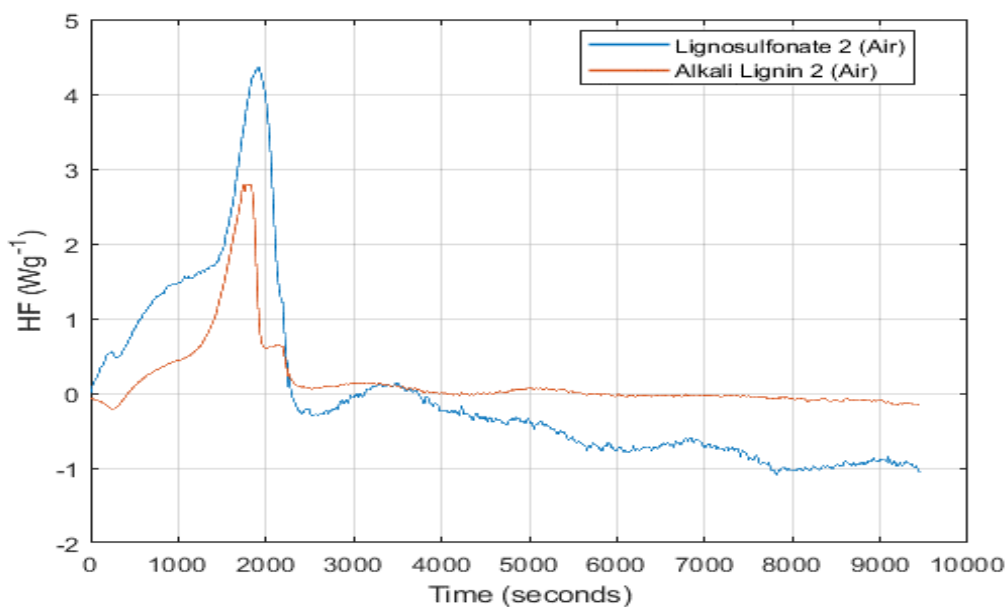


Fig 24: DTG results obtained with Air used as purging gas.

4.1.2 Effect of feedstock on bio-crude yield and Quality

A comparison is made here, between the bio-crude and bio-char yields at different operating conditions of temperature and residence time. This will show a better presentation of how the feedstock and operating parameters affect the yield of products of interest (bio-crude and bio-char).

4.1.2.1 Total Bio-crude and Bio-Char Yield

The bio-crude and char yields were computed from the results obtained and presented in table 4 below. The result presented is an average value of the triplicate test performed for each residence time and temperature. The test was performed in triplicates to ensure repeatability of the results obtained. The results showed some wide difference in terms of the bio-crude and char yields from Alkali lignin and lignosulfonate. The lignosulfonate tends to produce more aqueous phase than the bio-crude phase, but this work is focused on the bio-crude and char phases, hence the results presented in table 4 below depicts only these two phases. The test for the lignosulfonate conducted was limited to only at 300°C for residence times of 10 and 15 minutes due to time constraints.

Table 4: Bio-crude and bio-char percentage yields at different operating conditions

Samples	Temperatures		
	300°C	330°C	350°C
Bio-crude (A-Lignin):			
10mins	21	18	18
15mins	21	19	16
20mins	20	18	14
Bio-char (A-Lignin)			
10mins	12	31	33
15mins	14	33	34
20mins	17	34	35
Bio-crude (Lignosulfonate):			
10mins	9.0	xxx	xxx
15mins	10.0		
Bio-char (Lignosulfonate)			
10mins	8.0	xxx	xxx
15mins	7.0		

As seen in table 4 above, the results for temperatures of 330 and 350°C for the lignosulfonate, was not recorded and is depicted with the symbol “xxx”, signifying that the experiment was not conducted for both temperatures due to time constraints. Sequel to the table above depicting the yields at various temperatures and residence times, a graphical presentation is displayed in

figures 23, showing the bio-crude and bio-char yields with respect to temperature. Subsequently, figures 24 and 25 further shows a vivid picture of these results and will be discussed in detail in below. The results for the bio-crude yield from liginosulfonate was not plotted due to limited experimental data for reasons earlier cited.

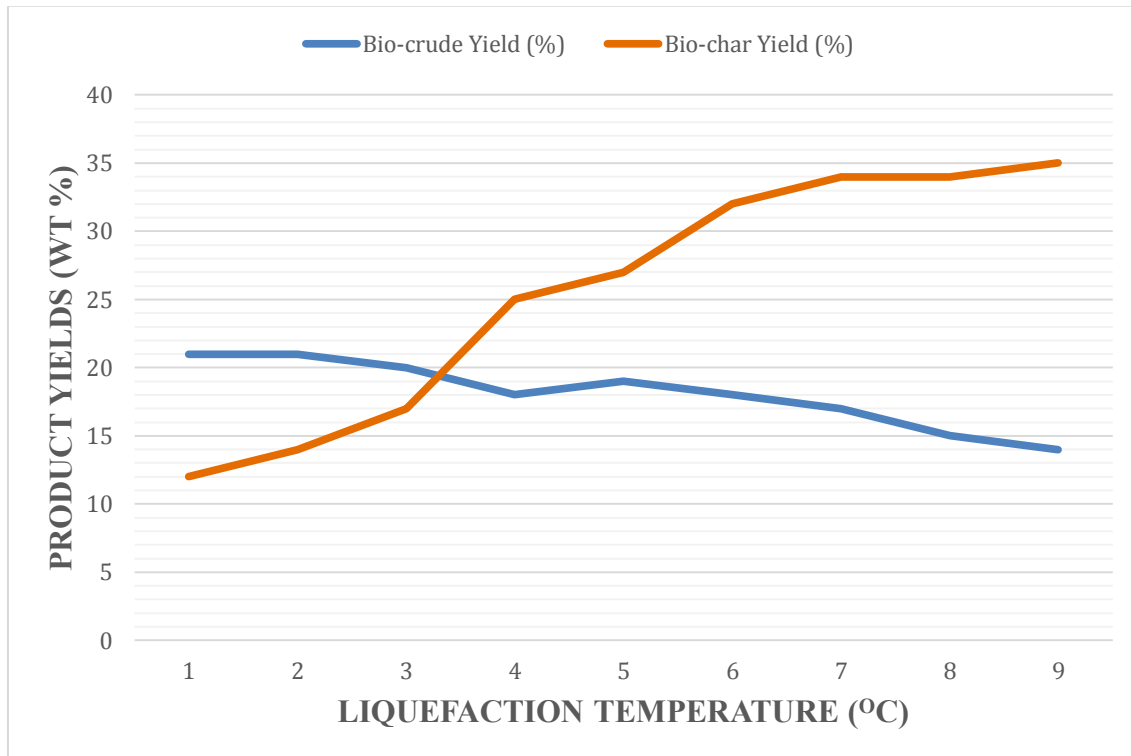


Fig 25: Combined product yield graph

From this figure 23 above, the liquefaction temperatures depicted by 1,2,3,4,5,6,7,8 and 9 represents 300,300,300,330,330,330,350,350 and 350 respectively with residence times of 10,15 and 20 in that ascending order. Figures 24 and 25 below further clarifies the yields in each case.

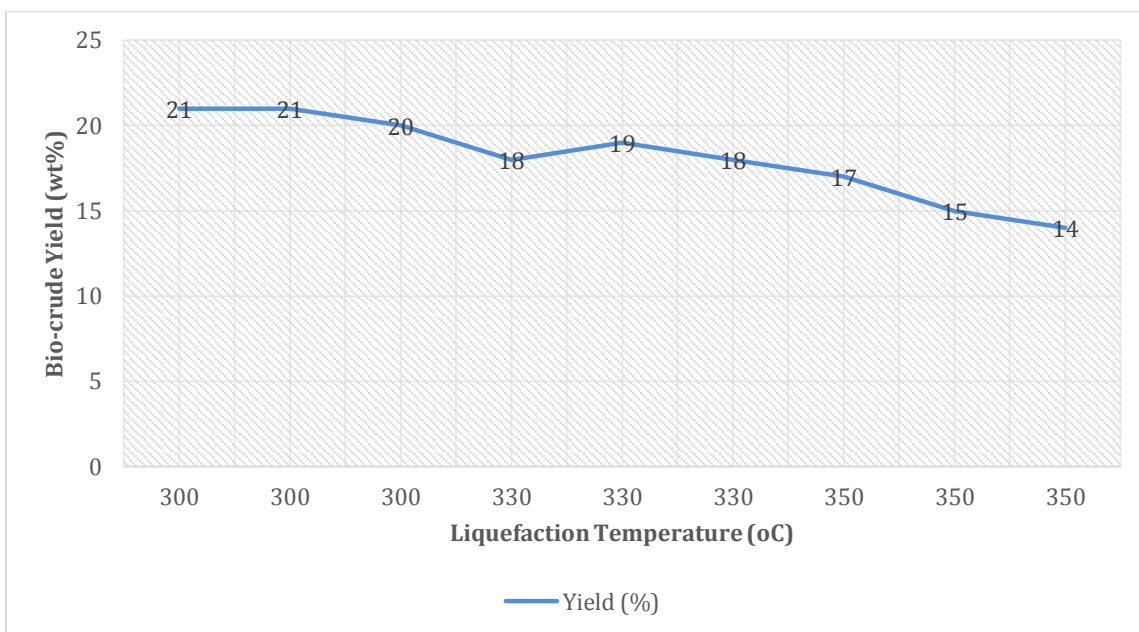


Fig 26: Bio-crude Yield with Respect to temperature (Alkali lignin)

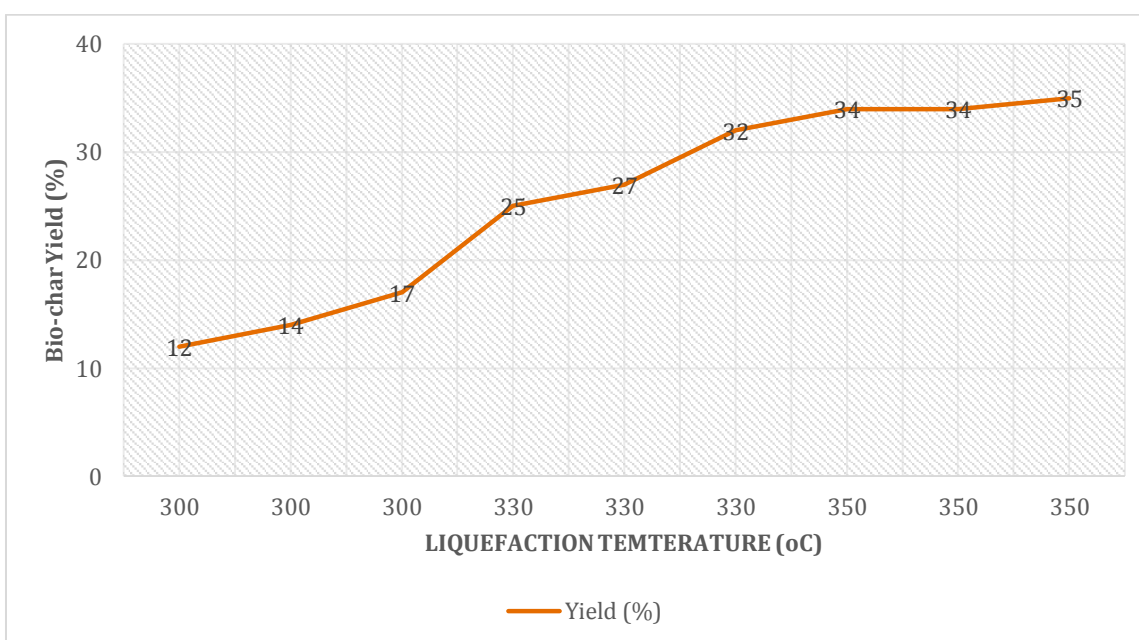


Fig 27: Bio-char Yield with Respect to temperature (Alkali lignin)

4.1.2.2 Properties of Bio-char from different lignin samples

The quality of the bio-char obtained is a function of the type of lignin sample used and a function of the operating temperature as well. The properties in table 5 below is for peak residence times where the yield and properties are considerably at its highest point.

Table 5: Properties of Bio-char from Alkali lignin sample

Temperature	Elemental Composition	Alkali Lignin
T = 330°C	C (%wt)	63.93
	H (%wt)	4.13
	N (%wt)	2.07
	O (%wt)	29.87
	HHV (MJ/kg)	22.20
T = 350°C	C (%wt)	63.80
	H (%wt)	4.10
	N (%wt)	1.25
	O (%wt)	30.85
	HHV (MJ/kg)	21.93

Similar to the properties of the bio-char produced for alkali lignin as earlier stated, the char also differ in terms of quality, depending on the type of feedstock used. Below is table 6 showing the char produced from each lignin sample used at 300°C and a residence time of 10 minutes each. The HHV was determined with the Dulong's formula earlier stated in this report as equation 5.

Table 6: Comparative Properties of Bio-Char from different lignin samples

		Alkali Lignin	Lignosulfonate
T = 300°C	C (%wt)	63.11	51.1
	H (%wt)	4.46	4.10
	N (%wt)	2.11	3.87
	O (%wt)	30.32	40.93
	HHV (MJ/kg)	22.32	14.38

4.1.3 Effect of Operating Parameters on Yield

The operating parameters have a direct impact on the products phases obtained at the end of each test and this is no different. It should be mentioned also, that the products obtained from this test, was based on a catalyst-free experiments. The results presents the yields of the different phases based on the operating conditions as seen below.

4.1.3.1 Total Product Yield in Phases

The total product yield after liquefaction was computed for the gases, bio-crude, bio-char and aqueous phases respectively. The gas phase was determine through a mass balance according to equation 8 above and is based on the total feedstock slurry fed into the reactor before liquefaction. All yields are expressed in percentages as seen in table 7 below.

Table 7: Yield of Product Phases from Alkali lignin liquefaction

Sample		Bio-crude (%)	Bio-char (%)	Aqueous (%)	Gas (%)
Alkali Lignin	300 : 10mins	21.0	12.0	61.0	6.0
	15mins	21.0	14.0	58.0	7.0
	20mins	20.0	17.0	55.0	8.0
	330 : 10mins	18.0	31.0	41.0	10.0
	15mins	19.0	33.0	38.0	10.0
	20mins	18.0	34.0	37.0	11
	350 : 10mins	18.0	33.0	36.0	13.0
	15mins	16.0	34.0	35.0	15.0
	20mins	14.0	35.0	39.0	12.0
Lignosulfonate	300 : 10mins	9.0	8.0	72.0	11.0
	15mins	10.0	7.0	70.0	13.0

4.1.3.2 Elemental Composition of Bio-char

The bio-crude and bio-char produced at different conditions, possess different qualities and the elemental composition of these yields at peak levels are brought together for ease of comparison. To this end, the product of interest (bio-crude and bio-char) from each of the lignin samples, are highlighted in table 8 below.

Table 8: Elemental composition of lignin and products at peak yield

Sample	Bio-char (A-Lignin)	Bio-char (Lignosulfonate)
C (%)	63.93	51.10
H (%)	4.13	4.10
N (%)	2.07	3.87
O (%)	29.87	40.97
HHV (MJ/kg)	22.20	14.38

4.1.4 Some Physical Properties of the Bio-crude produced

The bio-crude produced from both lignin samples tend to possess different properties, both physically and chemically from first look. Due to time constraint however, the chemical properties was not further investigated in details, but some physical properties observed from both samples is depicted by figure 28 below. These samples are the liquid phase of the product, after expanding the gases and removing the bio-char. These liquid phases contains both the bio-crude and the aqueous phases.



Fig 28: Liquid phases of product after liquefaction

From the figure above, a close physical look gives us an idea of the physical properties of these liquid phases. In terms of color, one tends to be darker than the other is. The darker one here is the liquid phase from the lignosulfonate while the brighter/lighter one is the liquid phase from the lignosulfonate.

4.1.5 Carbon Recovery

Carbon is an important element to look out for, when considering bio-char for energy purposes. The higher the carbon content, the higher its energy potential. Equation 11 was used to determine the carbon content of the bio-char from both lignin samples. Results show that bio-char from alkali lignin has 38.5% carbon recovery from the feedstock, while bio-char from lignosulfonate has 6.3% of carbon, using same equation.

4.1.6 Energy Recovery

Energy recovery has become an essential component to consider in evaluating the potential of biomass and its related conversion products. Application of the equation 12 earlier stated to determine the energy recovery of the bio-char shows a recovery of 19.54% for the alkali lignin, which is a decent result for the bio-char content. In contrast, the energy recovery of the bio-char from lignosulfonate shows a 6.28%, when computed with the same equation.

4.2 Discussion of Results

Here, a detailed discussion on the results obtained will be presented and compared with previous work done by researchers, as presented in literatures. This will help determine the conformity of the results obtained from this work.

4.2.1 Feedstock Characterization

Lignin as a potential biomass source for renewable energy and valuable chemical, is generated mostly through the pulping process as earlier described in the review of this work. However, having different types of lignin entails that care must be taken to ascertain the one best suited for a process of this nature. While in most cases, the energy content of lignin evident, the amount of energy obtained in each case varies according to the properties of the lignin sample used. The results obtained from the feedstock characterization presents some differences and similarities with results from literature as seen in tables 9 (proximate analysis) and 10 and 11 (ultimate analysis) below.

The proximate analysis for this work showed a lower VM when compared to result from literature as seen in table eight below. This is largely because the literature results reported were on dry basis for the alkali lignin. The VM is an indication of the combustible tendency of the lignin samples and has a direct correlation to its energy content. The results showed that the Alkali lignin has a higher tendency to combust under the influence of heat than the lignosulfonate. The lower VM in the lignosulfonate contributed to the higher Ash content

observed in it. Thus, a higher biomass VM lead to greater gas production instead of the solid and liquid phases. Higher ash content also tends to imply that there are more incombustible materials in the lignosulfonate than those found in alkali lignin.

Table 9: Proximate Analysis Results

Composition	Alkali Lignin	Literature (d.b)	Lignosulfonate	Literature
MC (%)	7.5	-	5.90	7.80 [50]
VM (%)	67.5	72.60 [48]	59.23	58.90 [50]
ASH (%)	9.62	9.50 [48]	14.40	14.30 [50]
FC (%)	17.38	17.90 [48]	20.47	19.00 [50]

The ultimate analysis on the other hand, showed some stark difference in the properties of both lignin types in terms of the elemental composition and heating value. The carbon content of the alkali lignin used for this work showed a slightly higher percentage when compared to what is reported in literature but quite lower than the carbon content of lignosulfonate. Interestingly, this should translate into higher energy content for the lignosulfonate than the alkali lignin. While the nitrogen content of the alkali lignin remains very low, lower than the lignosulfonate, this presents a case for the potential environmental impact of the two samples when used for energy purposes. A higher nitrogen content in lignosulfonate is an indication of its potential NO_x gas released into the atmosphere during combustion, making alkali lignin more environmental friendly lignin to use for energy production. Several literatures have used alkali lignin for bio-crude production, mostly due to its environmentally friendly nature. The oxygen content was obtained by subtracting the sum of the C, H, N and Ash from 100% as reported in table 10 below.

Table 10: Ultimate Analysis Results and HHV of Alkali Lignin

Feedstock	Alkali Lignin (Present Work)	Literature	Literature
C (%)	51.50	49.0 [48]	59.6 [49]
H (%)	4.12	4.4 [48]	5.63 [49]
N (%)	0.35	0 [48]	0.69 [49]
O (%)	34.41	(S & O) 46.6 [48]	34.08 [49]
HHV (MJ/kg)	19.42		22.14 [49]

As stated above, the nitrogen content is always a course for pollution concern. Even though the lignosulfonate showed a higher carbon content than the Alkali lignin from the analysis conducted, the high nitrogen and sulfur content is a major drawback when considered for biofuel purposes. The table below show the results for the lignosulfonate in comparison with previous studies from literature.

It is also worthy of mention, that the ultimate analysis conducted was with fresh samples with moisture content still present in them. This is likely responsible for the high oxygen content observed in the results. The higher carbon and hydrogen content in lignosulfonate also makes it a valuable raw material for production of other valuable organic compounds which some companies like Borregarrd have ventured into and have recorded great success so far.

Table 11: Ultimate Analysis Results and HHV of Lignosulfonate

Feedstock	Lignosulfonate (Present Work)	Literature
C (%)	50.1	71.8 [50]
H (%)	10.6	9.8 [50]
N (%)	1.9	1.2 [50]
O (%)	19.2	13.8 [50]
HHV (MJ/kg)	18.33	

The heating values for both samples were obtained with the use of a bomb calorimeter following the procedure described in previous chapters. The result clearly showed a higher calorific value for the alkali lignin when compared to the lignosulfonate, making the alkali lignin a more desirable type for energy purposes. The significantly lower heating value of the lignosulfonate is a result of the calcium and sulfur content observed at the end of the combustion process. The residue left after the combustion evidenced the calcium and sulfur content and was further analyzed under the microscope. It was observed that the calcium and sulfur content had an impact on the heating value and the incomplete combustion observed. In contrast to the current work, the literature value reported for the HHV of lignosulfonate tends to be higher because it was a fresh unprocessed sample. The lignosulfonate from Borregarrd on the other hand, is the product of an industrial process by the company, which could have added some additives or chemical to support their industrial production process with lignosulfonate. This can equally be said about the carbon content of lignosulfonate, which showed wide variation between the results from this work and the literature. The lignosulfonate from Borregarrd could be better suited for production of other chemical compounds, other than used for energy purposes. As **Demirbas, 2005 [51]** noted in his report, that moisture content, Ash content and the carbon content of biomass has a direct impact of the heating value. A similar pattern was noticed in the results obtained from this work when compared to the HHV from literature.

The TGA results obtained for both samples showed some similarities in terms of decomposition rate. The purging gas played a role as well in the results observed, which could be responsible for the variable seen in the TGA and DTG graphs respectively. With the HTL experiment to be performed under a condition void of oxygen, the TGA was experimented with and without oxygen just to see the effect of oxygen on the decomposition rate. Results showed that decomposition under nitrogen (an inert gas) was slightly slower than when air was used as a purging gas. This is possibly due to the roughly 21% oxygen present in air, which catalyzed the decomposition process as against a pure nitrogen gas without oxygen interference. The reaction for both samples exhibited similar characteristics, though a bit different in some aspects. Under both conditions (Nitrogen and Air), the alkali lignin showed a higher integral energy released. The results obtained from the tests suggest that the Alkali lignin has a higher energy potential than the lignosulfonate, hence would be a better choice for a liquefaction process like this.

Extensive characterization of feedstock has become necessary, as it affects not just the product yield, but also the potential environmental impact of the end use of the products. Lignocellulosic biomass for example, have been found to substantially reduce GHG emissions when used for energy purposes, compared to the first generation bioenergy from agricultural crops. [52-54]

4.2.2 Bio-crude and Bio-char Yields

The results from the bio-crude and char yields clearly shows a pattern, which tends to be in line with literatures on similar liquefaction experiments.

The bio-crude yield was higher at 300°C and the peak yield was at 10mins residence time. Conversely, lower yields were observed at 330 and 350°C with the least yield coming at a residence time of 20mins. This clearly suggests that higher temperatures favors formation of bio-char, which results in less bio-crude yield partly due to temperatures gearing towards super-critical conditions which tend to favor formation of gases. A proof of this is seen from the mass balance results obtained to quantify the yields by phases. Figure 29 below shows a somewhat negative slope for the bio-crude yield curve, which is a further demonstration of the earlier assertion about higher temperatures.

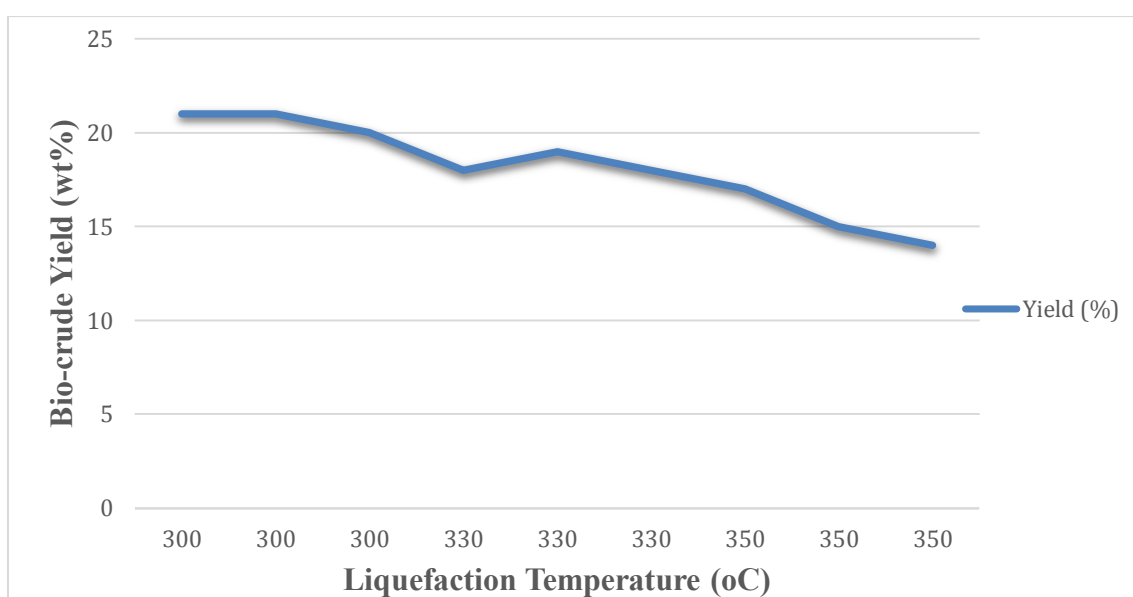


Fig 29: Bio-crude yields curve at different temperatures

In an almost direct inverse relationship to the bio-crude, the bio-char yields tend to be higher at higher operating temperatures. The results showed higher bio-char yields at 350°C and lower yields at 300°C. The TGA analysis however, also suggests that only a fraction of the lignin sample is likely to be liquefied within the operating temperatures considered at sub-critical conditions. This implies that there will be some unreacted lignin as part of the char obtained and a further analysis of the char could reveal the constituent component of the char phase. Figure 30 below shows an increasing bio-char yield with increase in temperature, giving a positive slope and further illustrates the earlier point made.

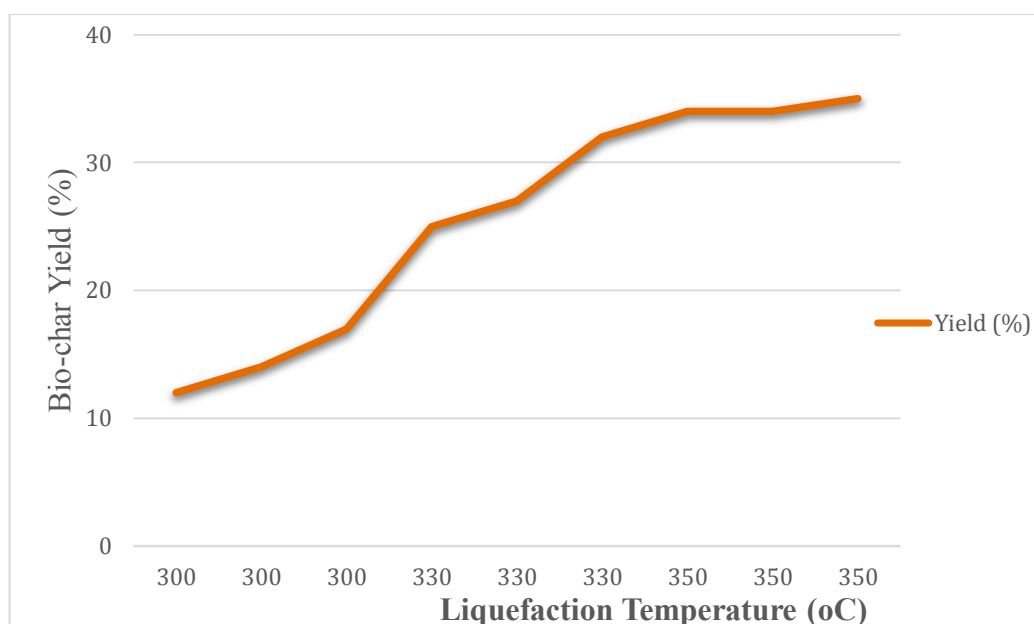


Fig 30: Bio-char yields curve at different temperatures

The curve further showed a sharp increase in bio-char yield from a temperature of 300 to 330°C but this yield increase tend to slow down between 330 and 350°C and remains relatively stable at 350°C. The curve showed a positive slope for the bio-char yields, which is a sharp contrast to the negative slope displayed from the bio-crude yield. Yields have been seen to be affected by temperature and residence time, but also some literatures have emphasized the importance of catalysts on yields [55]. This experiment however, was performed in the absence of a catalyst, hence, the level of yield reported. The presence of catalyst could result in higher yields at lesser residence time but that comes at an additional cost to the process, hence the need to experiment without a catalyst.

4.2.3 Some Physical Properties of Bio-crude and Bio-char

Just as the yields differ for both lignin samples, the quality of the products also differ both in terms of its physical and chemical properties. Due to time constraints however, the chemical properties for the bio-crude could not be determined for this work. However, from the physical noticeable properties, it clear that bio-crude from alkali lignin tend to be more viscous than bio-crude from liginosulfonate. The color of the bio-crude from alkali lignin is also darker, which tends to give close comparison with the conventional crude from fossil sources. Figure 31 below shows a close similarity in appearance between the bio-crude from alkali lignin and the conventional crude from fossil and also shows how their appearance differ from the crude obtained from alkali lignin.



Fig 31: Bio-crude samples from Alkali lignin.

The bio-char produced also show some noticeable differences in terms of appearance and structure. The bio-char obtained at higher operating conditions of 350°C tend to be darker and of higher volume, this is also reflected in the elemental compositions observed in the bio-char using the elemental analyzer. It is also reflected in the heating value of the bio-char from both lignin samples. The HHV tend to be much higher for alkali lignin than for the lignosulfonate, making the alkali lignin a more energy friendly source when compared to lignosulfonate. Figure 32 below show the physical appearance and structure of the bio-char from both lignin samples.



Fig 32: Bio-char samples from Alkali lignin

4.2.4 Carbon Recovery

The carbon recovery from the bio-char obtained from both feedstock show a wide disparity and energy potential in each case. A carbon recovery of 38.5% for the bio-char from alkali lignin is an evidence of its energy potential when compared to the 6.3% recovery for the bio-char from lignosulfonate. Beyond energy uses, bio-char with higher carbon content makes it suitable material for soil remediation and can be added to soils with low carbon content, thereby improving its nitrogen retention capacity. Its application in improving soil quality makes it a valuable resource to enable the effectiveness of fertilizers like NPK and improve feed security in the long. The lignosulfonate on the other hand may not be suitable for these stated reasons, hence making the alkali lignin a better fit for energy and agricultural purposes.

4.2.5 Energy Recovery

The energy recovery computed from the yields obtained also showed a 19.54% for the bio-char from alkali lignin, which is a decent result considering the operating conditions used for the test and the properties of the feedstock used. Conversely, the energy recovery of the bio-char from lignosulfonate shows a much lower percentage of 6.28%, showing that alkali lignin holds greater energy potential than the lignosulfonate based on these experiments. The bio-char tends to hold great energy potential and can provide a dual positive net energy for an alkali lignin of this type.

Chapter 5

Conclusion and Recommendation

5.1 Conclusion

From the results obtained, the following conclusions were deduced in response to the research question this work aims to answer.

- Alkali lignin tend to contain more carbon than lignosulfonate from Borregarrd, as the lignosulfonate happens be to an already processed one, which has reduced its carbon and energy content.
- The lignosulfonate from Borregarrd, however, tend to hold great potential for other chemical compounds. This was evident in the higher aqueous phase content after liquefaction.
- The lower temperature in this case (300°C) shows to enhance higher quality of bio-crude and higher yields as well, when compared to the peak temperature of 350°C used for this work. But the higher temperature tend to support higher bio-char yields and gas phases.
- Alkali lignin is a better lignin to use for the purpose of energy production, as against the lignosulfonate from Borregarrd, owing to the energy recovery from the Alkali lignin, which tend to be higher. This was also seen in the heating value of the samples obtained from the bomb calorimeter tests.
- The results clearly shows that both lignin types hold great potentials for both energy and valuable chemical compound when depolymerized through a liquefaction process in the absence of a catalyst. Though the yields obtained appears to be low, the absence of a catalyst makes this route an interesting route to consider in terms of cost and efficiency, as the absence of catalyst tend to reduce the operating cost..

Energy recovery of the system is an important parameter to consider for a process like this, owing to the energy consumption of the process. From a sustainability point of view, where the environmental, social and economic aspects of a process or project is considered, the technical aspect is often left out by most scholars and it is closely related to the economic aspect. This is the techno-economic evaluation of a project, which gives some information about the feasibility and viability of a proposed project. The energy recovery is part of the techno-economic evaluation that will help determine how sustainable the energy generated from this process will be. In this light, considerations should be given to the net energy balance, because if the energy needed to produce certain quantity of biofuel from a specific biomass type, is more than the energy required to generate that particular biomass, than that energy cannot be termed as a sustainable one and vise-versa.

5.2 Recommendation

It is noteworthy to mention that some tests which would have been interesting to analyze, were not performed for this work due to breakdown of some equipment in the course of the experiment. My limited stay period and the longer time needed to address the technical challenges that led to the breakdown of equipment, meant I was unable to perform the following tests;

- Elemental analysis of the bio-crude
- GC-MS analysis of the bio-crude and the aqueous phases.

These tests, if performed would have given more details as to the actual heating value of the bio-crude produced, as well as the organic compounds present in the bio-crude and aqueous phases. This information would help quantify these phases based on potential compounds that can be obtained from them.

In line with the results obtained from this work so far, certain limitations experienced will be interesting to address in future work. Though the batch HTL process used here tends to be a desirable process owing to its low operating temperature and absence of catalysts, it will be interesting to consider the following in future research work:

- A complete LCA for this process to actually quantify the footprint and compare it with related thermochemical processes. A detailed LCA will help present a strong case for the use of this process, from the environmental point of view.
- Another interesting future consideration for work in related areas will be the use of ICP to help analyze in detail the metal content of each phase. The metal content in the bio-crude for example, will be of great interest, as this will give a vivid picture of its potential environmental impact during combustion, when upgraded to fuel for use.
- Future work should focus on the use of GPC and NMR, to properly analyze the molecules present in the organic solvent produced, as well as its physical properties and quantify the concentration of these constituent molecules.

It will be also interesting for future work to analyze the bio-char with a fiber analyzer, as this will give us a better understanding of the fiber content of the unreacted lignin present in the char. The fiber analyzer could also help in the determination of the fiber content of the lignin samples before the liquefaction test to know its solubility and rate of digestion and ensure the suitability of the sample. This will help understand what the potential outcome could be when subjected to a liquefaction test.

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Appendices

Appendix A.

A.1 Depolymerization of Lignin

The depolymerization of lignin is further elaborated here with structures of its monomers as well as the the degradation mechanism adopted from referenced literature.



Fig 33: Lignin structural units (monomers) [13]

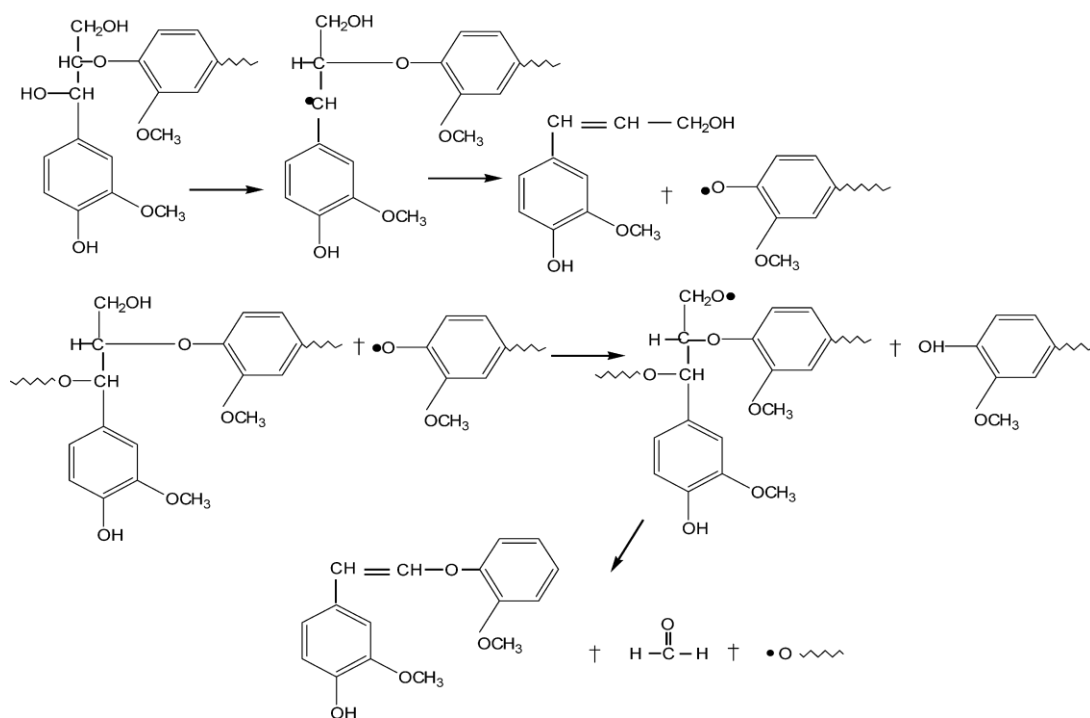


Fig 34: Lignin degradation mechanism (adopted from Ref. [19]).

Appendix B.

B.1 Feedstock Characterization

The tests for the characterization of feedstock used was performed in triplicate in each case and the table below shows the results obtained and computed to ensure that reported results were within error limit. In all cases, the sample size used were similar in weight, about 1g for the MC and VM and 3g for the ASH test. The crucible weight is however, of different sizes, hence the wide variation in results recorded.

Table 12: Complete Proximate Analysis of Lignin samples

	MC (%)	VM (%)	ASH (%)	FC (%)	HHV (MJ/kg)
Alkali Lignin	7.2400	95.7718	7.9002	Average	19.2640
	7.7700	36.0125	18.5152	17.38	19.3970
	7.5100	87.2025	2.4222		19.4400
Lignosulfonate	0.0591	51.21179	17.1035	Average	18.3210
	0.0597	57.67213	15.6900	20.47	18.3390
	0.0582	68.81298	10.4066		18.3310

B.2 Thermogravimetric Analysis

The TGA analysis results are further presented below in graphical representation, depicting the bio-crude and bio-char yields and graphical presentation of both yields on same plane.

The graph in figure 35 below shows the bio-crude and bio-char yields within the same temperature range, and how at a certain temperature, the bio-crude and bio-char tend to produce similar yields.

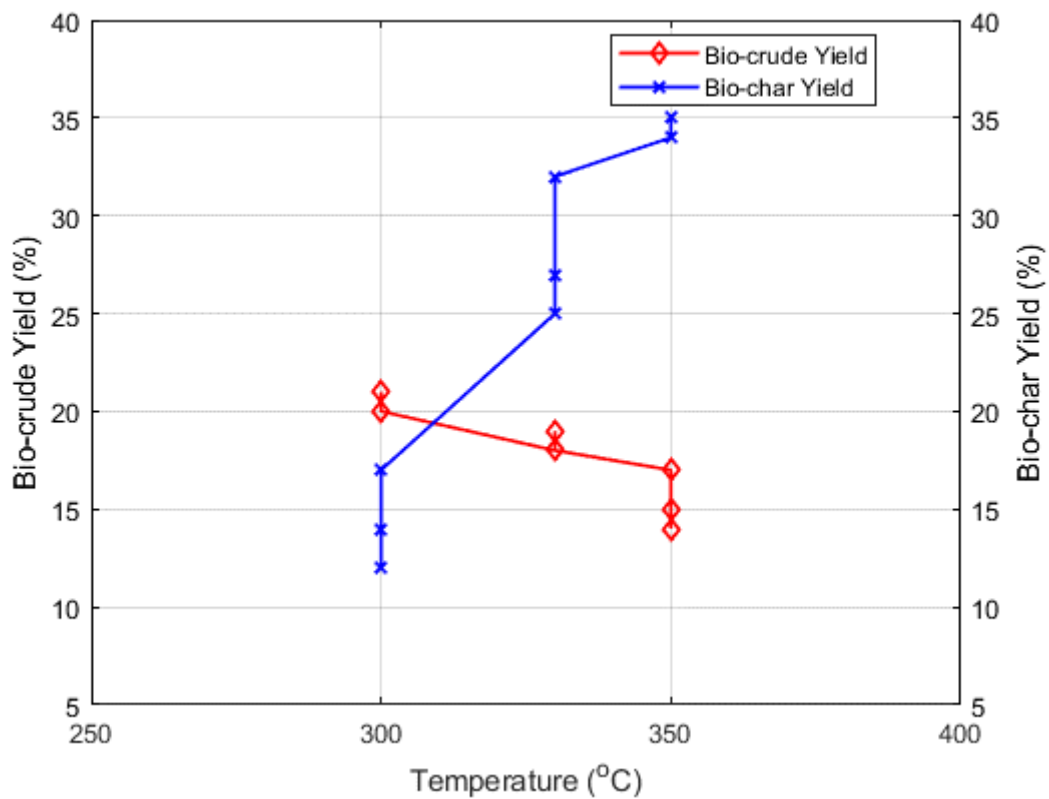


Fig 35: Bio-crude and Bio-char Combined Yield Curve

Appendix C.

Post Reaction Phase Separation

The separation of the product phase was a key aspect of this work. It involves selection of appropriate solvent to ensure complete collection of the different phases in the product. Solvent polarity is a key factor in selecting the solvent to be used, considering the volatility of the solvent and its suitability with the feedstock type used for this experiment. Methanol and Acetone showed good compatibility with the lignin feedstock as they exhibit high and similar polarity as seen in the table below.

Table 13: Solvent Polarity Index adopted from [56]

Solvent name	Polarity Index (P)
Pentane	0.0
1,1,2-Trichlorotrifluoroethane	0.0
Cyclopentane	0.1
Heptane	0.1
Hexane	0.1
Iso-Octane	0.1
Petroleum Ether	0.1
Cyclohexane	0.2
<i>n</i> -Butyl Chloride	1.0
Toluene	2.4
Methyl <i>t</i> -Butyl Ether	2.5
<i>o</i> -Xylene	2.5
Chlorobenzene	2.7
<i>o</i> -Dichlorobenzene	2.7
Ethyl Ether	2.8
Dichloromethane	3.1
Ethylene Dichloride	3.5
<i>n</i> -Butyl Alcohol	3.9
Isopropyl Alcohol	3.9
<i>n</i> -Butyl Acetate	4.0
Isobutyl Alcohol	4.0
Methyl Isoamyl Ketone	4.0
<i>n</i> -Propyl Alcohol	4.0

Tetrahydrofuran	4.0
Chloroform	4.1
Methyl Isobutyl Ketone	4.2
Ethyl Acetate	4.4
Methyl <i>n</i> -Propyl Ketone	4.5
Methyl Ethyl Ketone	4.7
1,4-Dioxane	4.8
Acetone	5.1
Methanol	5.1
Pyridine	5.3
2-Methoxyethanol	5.5
Acetonitrile	5.8
Propylene Carbonate	6.1
<i>N,N</i> -Dimethylformamide	6.4
Dimethyl Acetamide	6.5
<i>N</i> -Methylpyrrolidone	6.7
Dimethyl Sulfoxide	7.2
Water	10.2
