

Lappeenranta-Lahti University of Technology LUT  
School of Energy Systems  
Master's Degree Programme in Bioenergy Technology

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**HYDROTHERMAL CARBONIZATION OF KRAFT LIGNIN:  
PROCESS PARAMETERS EFFECT**

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D.Sc. (Tech.) Clara Mendoza Martínez

# **ABSTRACT**

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Hydrothermal carbonization (HTC) is a thermochemical process that by subjecting wet biomass to moderate temperatures (180 to 260 °C) under certain conditions, converts it into a solid carbon-like compound called biochar. HTC is a clean technology that allows waste to be disposed of in a sustainable way, without drawing on to landfills and contributing to green management within the energy industry, without the need for intensive use of energy for drying biomass, before or during the process.

This process can be used to create a wide variety of structured carbonaceous materials e.g. production of lignite substitutes, synthesis gas, liquid petroleum precursors and humus from the initial biomass, with a net generation of energy. This work focuses on the hydrothermal carbonization of lignin, in addition on the effects of its operational parameters such as temperature, residence time and concentration of recirculated process water on the final solid product.

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## List of symbols and abbreviations

°C	Celsius degree
CHP	Combined heat and power
EC	Energy yield
EDF	Energy densification
FC	Fix carbon
FTIR	Fourier-transform infrared spectroscopy
HHV	Higher heating value
HPC	Hierarchical porous carbons
HTC	Hydrothermal Carbonization
kg	kilogram
LHV	Lower heating value
MC	Moisture content
MJ	Megajoule
PID	Proportional-integral-derivative controller
RL	Raw lignin
TFEC	Total Final Energy Consumption
TFED	Total Final Energy Demand
TGA	Thermogravimetric Analysis
TPES	Total primary energy supply
VM	Volatile matter
Wh	Watt-hora

## 1 INTRODUCTION

Climate change is an absolute reality. The global mean temperature of the Earth's surface has risen by almost one degree since the middle of the last century because of the excess of greenhouse gases, which is damaging both our ecosystems and way of life. The loss of ice masses at the poles, the rise in sea level and, in general, the warming of the atmosphere and the oceans are irrefutable signals for humanity to take action.

The legislative advances achieved at the local and international level on occasions do not measure up to the real magnitude of the problem, since it is not only necessary to discourage the burning of fossil fuels in this century, but it is essential to put in place adequate mechanisms and policies for adaptation and counteracting the worst impacts of climate change by communities and ecosystems. In this way, and looking to achieve these purposes, it is essential to generate a change towards a new energy and consumption model based on efficiency, decentralization, renewable energies, and proper waste disposal. It is in this global context where bioenergy come to play a fundamental role since it enable to achieve these objectives.

With a large share of total global energy demand, bioenergy is by far the most relevant form of renewable energy in the world. However, despite its important contribution to the world's energy supply, it receives limited attention, both in terms of public recognition and in energy policy planning, compared to other renewable energy sources such as solar or wind. One possible reason for the lack of consideration for bioenergy is the fact that on a global scale a great part of its use is still based on primitive and, in some cases, deliberately unsustainable technologies and practices.

However, despite the aforementioned drawbacks, in recent years technologies that increase the efficiency of energy processes focused on the use of biomass as an energy source have been developed. These technologies follow the global trend of not only improving the general performance of the processes, but also allowing and/or expanding the range of materials that could be used as raw materials in energy production, as well as in the generation of high added value bioproducts.

Such is the case of lignin, a natural and renewable polymer that can be derived from the residual black liquor of the pulp and paper industry, it is considered one of the biological materials that could totally or partially replace petroleum-derived polyols, with an immense field of applications such as in the manufacture of polyurethanes. Moreover, it is also used in the generation of solid fuels, due to the high carbon content of this biopolymer.

Regarding the development of new biomass transformation technologies, the hydrothermal carbonization (HTC) is one of those technologies which is presented as a solution for the treatment of biological material and industrial, agricultural, and urban waste. This treatment reduces the hydrogen and oxygen content of the biomass, mainly through dehydration and decarboxylation reactions, with the aim of increasing its homogeneity, raising its carbon content, and increasing its calorific value, thus achieving a material with improved fuel properties.

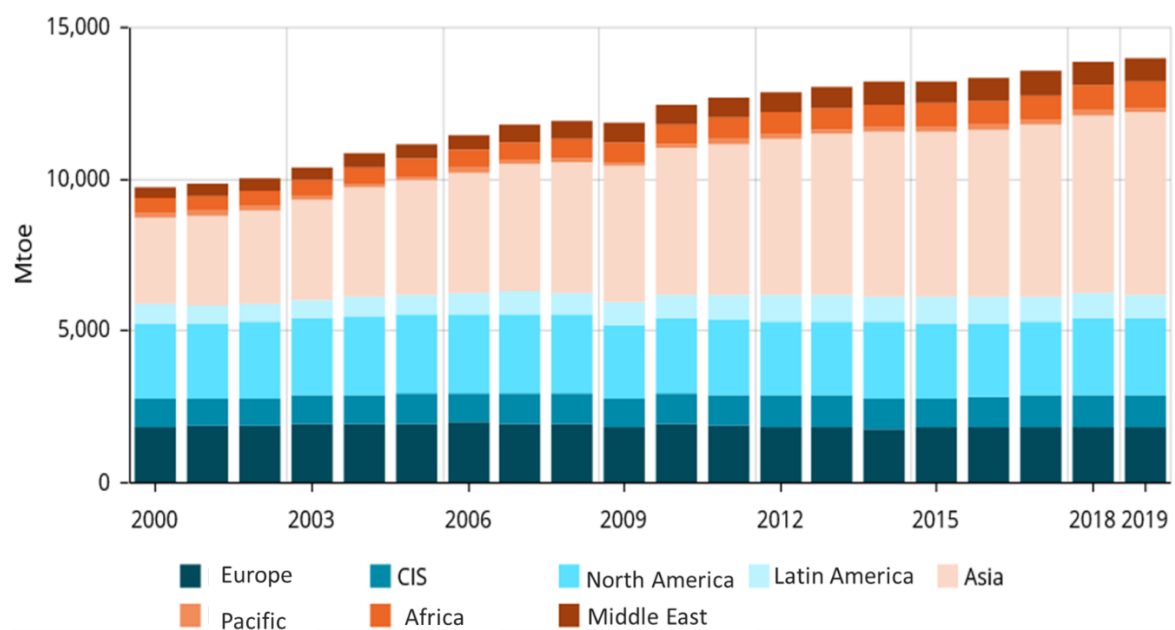
The present investigation focuses on the hydrothermal carbonization of lignin under different operating conditions. The hydrocarbon samples produced are characterized in order to know how the variation of parameters such as temperature, reaction time and concentration of the recirculating process water would affect its properties for potential use as fuel.



## 2 BACKGROUND

### 2.1 Renewable energy

Energy consumption is continuously growing throughout the world, and it is vitally important to develop techniques and technologies that allow an efficient addressing to the required demand. According to Enerdata (2020) and as can be seen in Figure 1, in 2019 global energy consumption was approximately 14,000 Mtoe, representing a slowdown in energy consumption growth of + 0.6%, well below its historical trend of + 2% since 2000.

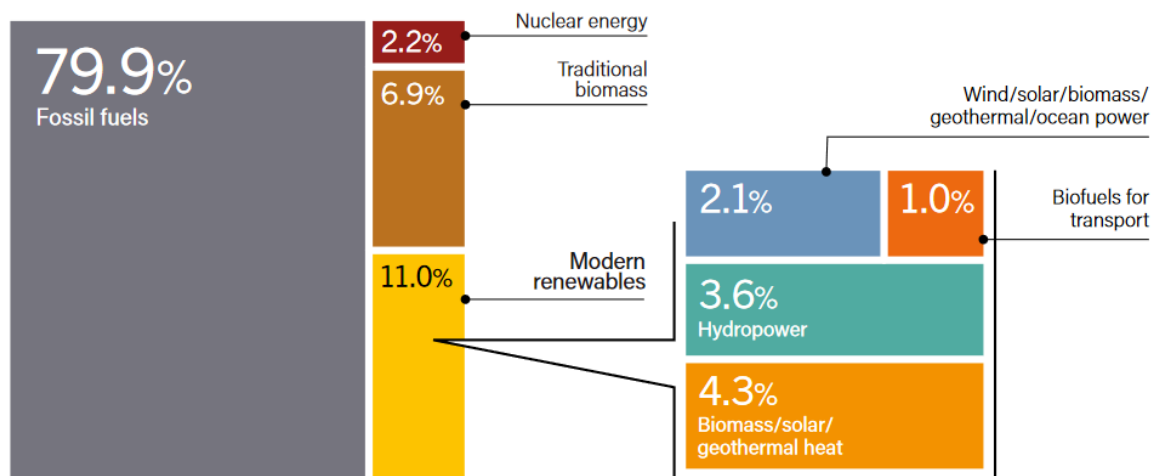


**Figure 1.** Energy consumption by regions 2000-2019 (Enerdata, 2020)

Renewable energy is defined as energy obtained from natural or seemingly inexhaustible sources (either due to the large amount of energy it contains or because it is capable of being regenerated naturally). This kind of energy source produces few secondary waste and has a small or no impact on the environment, while being sustainable based on current and future socio-economic needs. The main renewable sources are hydropower, solar energy, ocean-wave energy, geothermal and bioenergy. The countries with a higher share of renewables in their electricity production are Norway-97.6%, Brasil-82.3%, New Zealand-81.9%, Colombia-72.6%, and Canada-64.9% (BP, 2020)

Compared with fossil or nuclear energy sources, the share of renewables in total final energy consumption (TFEC) has grown three times faster in recent years. According to REN 21, in 2019 renewable energies had strong growth by increasing installed energy capacity by

approximately 200 gigawatts, mainly composed of photovoltaic energy. Despite this increase in the use of renewables, these represent less than a third of the increase in total final energy demand (TFED), having a share for 2018 of 11% in TFEC (excluding the traditional use of biomass, Figure 2) however, this represents an +0.6% increase in the share of renewables compare to 2016 data (REN21, 2018). Fossil fuels continue to play an important role in power generation, accounting for almost 80% of TFEC's share.



**Figure 2.** Estimated renewable share of total final energy consumption (REN21, 2020)

## 2.2 Biomass and Bioenergy

### 2.2.1 Biomass

The term biomass covers a quite heterogeneous and varied set of organic matter and is used to refer to an energy source based on the transformation of organic matter. European Commission (2004) indicates that biomass can be divided into subtypes such as: by-products of forestry and agriculture, energy crops, animal manure and urban/municipal waste. These materials, unlike product synthesized from fossil fuels, are renewable, inexpensive, and environmentally friendly. According with the International Energy Agency data browser (IEA, 2018), biomass as a source of energy generation is the main renewable source of energy in the world, without considering nuclear energy.

The traditional use of biomass today represents 6.9% of the world's final energy consumption, while the rest of renewable energy sources (including modern uses of bioenergy and biofuels) together represent 11% (REN21, 2020). Biomass remains today, and as it has been throughout human history, the traditional source of renewable energy with the largest share in the world energy basket, being the protagonist especially in underdeveloped

and developing countries due to the use of firewood as an energy source (commonly used for tasks such as cooking food and lighting) by rural or resource-limited communities.

Lignocellulosic biomass is made up of cellulose (25% -55%), hemicellulose (24% -40%) and lignin (15% -35%), as well as other minor compounds such as proteins, oils, and ash (Wei et al, 2017; Chio et al, 2019). The wide range covered by these values is because of, depending on the nature of the biomass, these polymers will be found to a greater or lesser extent. (See section 4.2.5)

Cellulose is the main component of plant cell walls; its content varies between species in the range of 38 to 55% (Kumar 2010) and it is what gives plants strength and chemical stability. This biopolymer can be found in both crystalline and non-crystalline forms and the coexistence of several polymeric chains allows the formation of microfibrils that join to form fibers until obtaining a crystalline structure. Cellulose is relatively hygroscopic, capable of absorbing between 8–14% of water in atmospheric conditions of 20°C and relative humidity of 60%. The solubility of the polymer is highly related to the degree of hydrolysis achieved. In basic solutions, cellulose swells as the polymer breaks up into low molecular weight pieces.

With regard to hemicelluloses, these are heteropolysaccharides (polysaccharide composed of more than one type of monomer). Broadly speaking, it is formed by a heterogeneous set of polysaccharides, in turn formed by two types of monosaccharides (mainly xylose, arabinose, galactose, mannose, glucose and glucuronic acid), which form a branched linear chain. Hemicelluloses are part of the walls of plant cells, covering the surface of cellulose fibers and allowing pectin to bind. They constitute 20 to 35% of the dry weight of the wood (Asif, 2009). There are many varieties of hemicelluloses, and they differ markedly in composition in soft and hardwoods.

And the last main component of the lignocellulosic material is the lignin. After polysaccharides, lignin is the most abundant vegetal organic polymer in the world. In general, it is a hydrophobic substance that removes water from cell walls, limits lateral diffusion, facilitating longitudinal transport and reinforces the mechanical resistance of tissues, in addition to making cells resistance to bacterial attacks. **This topic is covered in section 3.**

### 2.2.2 Bioenergy

Bioenergy can be defined as that potential energy stored inside the biomass, which can be harnessed through various processes such as direct combustion for heat production, thermochemical conversion to produce solid, gaseous and liquid fuels, conversion chemistry to produce liquid fuels and biological conversion to produce liquid and gaseous fuels (EIA, 2019).

The most widespread conversion method of biomass in useful energy is combustion, since practically all biomass can be burned directly, thus generating heat that could be further used for energy purposes (production of heat and electricity). For such purpose, the energy density of biomass can be significantly increased by drying it and compacting it into pellets or briquettes for subsequent co-combustion with coal. Compacting and granulating the biomass reduces the probability that bed corrosion and agglomeration happens when using fluidized bed combustion technologies. However, there may be slag problems in the furnace and scale on the heat transfer surfaces (Roni et. Al, 2017), due to the alkali content in the biomass.

Technologies, also called modern bioenergy, such as pyrolysis, gasification, torrefaction, and hydrothermal carbonization (HTC) have been developed that seek to overcome these drawbacks and improve the use of energy within biomass. **HTC process is covered in deep in section 4.**

The total primary energy supply (TPES) of renewable sources was 82.7 EJ in 2018 (WBA,2020), where 55.6 EJ came of biomass-based sources representing 67.2 % of all renewables. Modern bioenergy represents 5.1% of the world's total final energy demand in 2018 (REN21,2020).

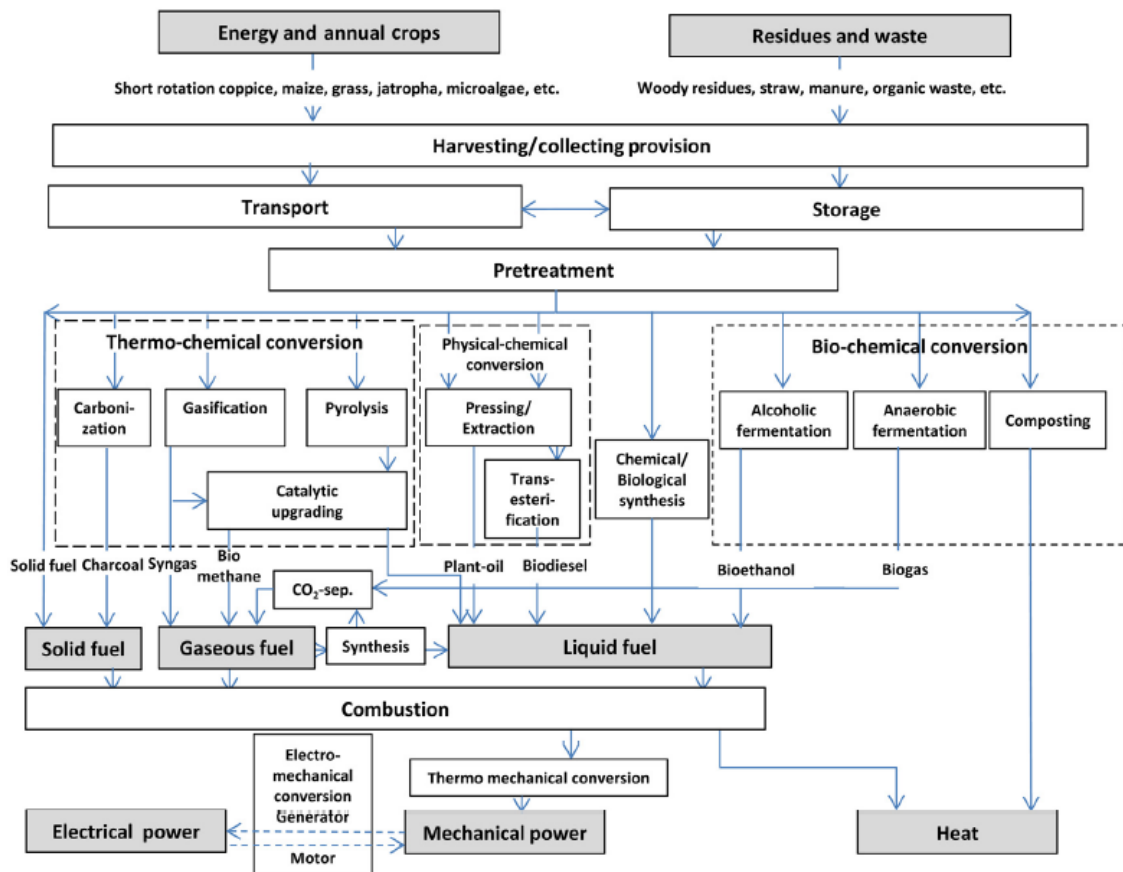
Likewise, modern bioenergy directly provides around 4.6% of total heat demand in buildings in 2018, representing the largest source of renewable energy use in this sector. Overall, in the industry sector renewables meet around 14.5% of total industrial energy demand where bioenergy supply nearly 90% of the demand for renewables and 7.2% of it comes from modern bio-heat. Pulp and paper (46%), wood products (37%) and food industries (27%) are the sectors with the highest penetration of renewables and bioenergy supply more than 75% of it.

Concerning transport sector, this one remains the sector with lowest penetration of renewables. In 2018, the 96.3% of the energy needed for this sector account from oil and

petroleum products, with small shares met by biofuels (3.4%) (IEA, transport 2019) divided in 114, 47 and 421 billion liters of ethanol, FAME biodiesel and HVO biodiesel respectively (REN21. 2020).

### 2.3 Conversion technologies

The use of biomass for energy purposes requires its suitability for use in conventional systems. The possible paths for the conversion of biomass into energy are presented in Figure 3. Conversion processes can be thermochemical, physical-chemical, or biochemical with a prior physical treatment, such as processes that physically act on biomass and are associated with the primary transformation phases, including crushing, chipping, compacted and even dried.



**Figure 3.** Methods of biomass conversion to energy. (IPCC, 2011)

The thermochemical processes are based on the chemical biomass transformation at high temperatures ( $300^{\circ}\text{C} - >900^{\circ}\text{C}$ ) (Zhang & Zhang, 2019). When biomass is heated, a process of drying and evaporation of its volatile components occurs, followed by decomposition reactions of its molecules and reactions in which the products resulting from the first phase

react with each other, together with the components of the atmosphere. in which the reaction takes place, in this way the final products are obtained. Depending on the control of the process conditions, different end products are achieved, which gives rise to the three main thermochemical conversion processes of biomass.

The basic application of biomass for energy purposes is direct combustion. Currently, the direct combustion of biomass is used by the vast majority of the world's rural population for heating and cooking food and in some industrial facilities to generate heat and steam. Direct combustion systems whose principles of operation are well known include open fires, simple ranges, boilers, and fluidized bed units (BFB and CFB).

In direct combustion units for cogeneration (CHP) in an optimal design it is possible to achieve an efficiency of up to 60-80%, while in open-air combustion it is reduced to 5 or 10% (EPA, 2015). Most of the industrial systems of direct biomass combustion uses cellulosic biomass. Although materials with up to 65% humidity can be used, but the lower the humidity, the higher the efficiency of the systems.

Another possible application is pyrolysis. In this thermochemical decomposition process the organic material is converted into a carbon-rich solid and a volatile matter in the absence of oxygen or water at temperatures between 400°C to 700 °C. (Zhang &Zhang, 2019). The main products of this process are solid product known as biochar which is high in carbon content, bio-oil and non-condensable gases. This technique can be divided in slow pyrolysis and fast pyrolysis mainly depending on the residence time. For slow technique, the resident time varies between hour to days with a moderate heat rate of 30-50° C/min. Besides, for the fast case resident time is several reduces (e.g., several minutes) with a heating rate of hundreds of degrees per minute.

Gasification is other widely used technique. This is similar to pyrolysis due to involves heating and devolatilization. Here the biomass is directly converted into a mix of fuel gases like CO, H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, etc. Two types of gasification techniques are used, common gasification by air or pure O<sub>2</sub> environment, or in a supercritical aqueous environment (HTG). Temperatures between 700 and 900°C are used in non-aqueous technique, allowing yields of up to 85% of gaseous products. In HTG, temperatures between 370 and 500°C are used.

Regarding bio-chemical conversions, have been considered as a viable technologies for the treatment of organic waste materials and for bioenergy production (Sant'Anada Silva et al, 2017). The aim of biochemical conversions is to help achieve ideal conversion effects, but not to produce end products, which is an essential difference compared to other conversion methods.

Fermentative processes are part of these technologies, which are a metabolic process that produces chemical changes in organic substrates through the action of biological enzymes in the absence of oxygen caused by the activity of some microorganisms that process carbohydrates (generally sugars). The main products are hydrogen, ethanol, butanol, organic acids, acetone, gaseous CO<sub>2</sub> among other products. Petroleum-based can be replaced by those produced by biochemical technologies.

## **2.4 Potential of biomass**

Ninety percent of biomass energy consumption takes place in developing countries. For two billion people, biomass is the principal source of energy for domestic use, also covering the energy needs of many traditional and agricultural industries such as bread making, the textile sector, the drying of tobacco and tea, the fish smoking and brick making.

Biomass has a greater availability and can be collected virtually anywhere in the world. However, the relative importance of biomass energy varies considerably between rich and poor nations, as does its potential use in energy generation, this is directly related to the lack of available technologies to take advantage of it.

Interest in the modernization of biomass energy is evident in the efforts of developing countries to increase the conversion to liquid and gaseous fuels (modern biomass). This so-called modern biomass works with better levels of efficiency, it does not have to give rise to health problems and is used to generate energy (electricity, heating/cooling or biofuels).

Biomass energy applications reduce CO<sub>2</sub> emissions by up to 55% compared to fossil fuels, even if the raw material must be transported long distances, as long as the biomass production for energy purposes does not cause changes in the use of land. Likewise, it must be produced, processed, and used in an efficient way maintaining the balance of ecosystems and without compromising food security. A significant proportion of the biomass potential is based on the use of wastes and residues that offer low GHG emissions and mitigate land use change concerns.

Some of the drawback's biomass must face when compared to fossil fuels is that it has lower calorific values, which vary by source, and it is usually almost half the value compared to fossil fuels. Moreover, the high relative humidity of biomass and the different volumes necessary for its storage are other problems to be faced. This can be partially solved by increasing the manufacture and use of pellets.

There is great support in terms of new policies generation, such as RED II in the EU and its respective local representation depending on the country, and economic incentives such as tax reduction or government grants in R&D, which drive the growth of new biomass-based technologies such as ethanol and wood-based diesel and algae fuel. Some of the pioneer countries in the use of this technology are China, USA, Brazil and Finland.

It is expected that by 2050 the world can reach the net-zero emissions goal, and that by 2100 the share of biomass in world energy production will be between 25% and 46%.

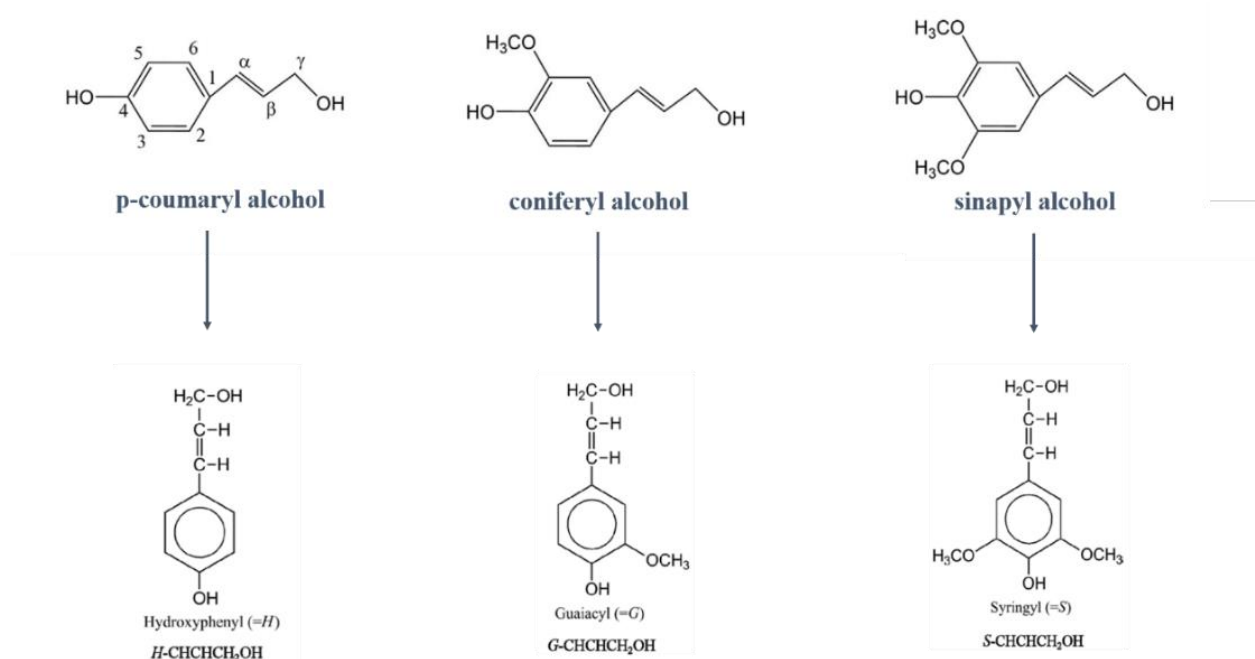


## 3 LIGNIN

### 3.1 Overview

Lignin is the most abundant vegetal polymer with a phenolic structure on the planet. Lignin plays a key role for the plant organism; provides rigidity and resistance to the stems, and plays roles in the transport of water, nutrients, and metabolites in the vascular tissue. It also plays an important role in the plant's defense system against pathogens (Bhuiyan et al, 2009).

In nature, lignin forms ether or ester bonds with hemicellulose, which in turn is associated with cellulose. Lignin is an aromatic polymer composed of 4-phenylpropane units. It has a heterogeneous macromolecular structure and contains three types of aromatic units: p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units. Figure 4 shows the three main precursors of the lignin polymer which are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Chio et al, 2019)



**Figure 4.** Precursors and basic unit in lignin molecule. Adapted from (Kim et al, 2017; Chio et al, 2019)

Like the other organic polymers, the composition of lignin in biomass depends on its botanical origin. Thus, lignin from softwood mainly has G units, those derived from hardwood have G and S units, and lignin from herbaceous plants contains H, G and S units in various proportions. Lignin represents between 16 and 25% of the dry biomass in softwood, and between 23 and 35% in hardwood (Brebou & Vasile, 2009).

### 3.1.1 Lignin Biorefinery

The main constituents of lignocellulosic materials (cellulose, hemicelluloses, and lignin) are, in theory, capable of being separated in an integral fractionation scheme, similar to oil refinery, this in order to obtain biomaterials and generate bioenergy from renewable materials. However, authors such as Zakzeski (2010) state that the high degree of crosslinking between the components is one of the main economic barriers for the development of refining technology, both due to the resistance of the lignocellulosic matrix to its degradation, and due to its insolubility in most solvents.

Currently, the main biorefinery processes of lignocellulosic materials are the production of cellulose (paper industry) and the production of bioethanol. The lignin residues from these processes are also susceptible to industrial use. Both the efficiency of the fractionation of lignocellulosic materials, as well as the added value of the products obtained, or derived from them, play an essential role in the industrial success of biorefinery processes.

#### *Pulp and paper production*

Long before the introduction of the biorefinery concept, lignocellulosic materials were already used to produce paper. Besides paper, a wide variety of other high added value products can also be obtained from cellulose such as nanocellulose, composite materials, or cellulose derivatives such as carboxymethylcellulose, acetates, fatty acids, etc.

In addition, the concept of the biorefinery not only aims to fractionation of the lignocellulosic matrix, but also to increase sustainability by improving the use of natural resources at a technical-economic and environmental level. This concept has been building up in the paper industry through the development of processes that increase the added value of the hemicelluloses and lignin fractions, and of processes that are more respectful with the environment.

Paper is a biorefinery product, in the sense that its production basically consists of separating the cellulose fibers from the lignocellulosic matrix, through mechanical and chemical processes. The content, composition and chemical structure of lignin are important parameters in the production of cellulose pulp, as they influence the consumption of reagents and the quality and final yield of the pulp. The proportion of syringyl (S) and guaiacyl (G) units in lignin has been considered an important factor in determining the maximum monomer yield from lignin depolymerization. This limit comes up from the notion that G

units are prone to C-C bond formation during lignin biosynthesis, resulting in fewer monomer-generating ether bonds (Anderson et al, 2019).

Initially, the fibers are separated by mechanical fragmentation using mills and disc refiners breaking up the cellulose fibers. Lignin does not dissolve, it just softens, allowing the fibers to settle out of the wood structure. At this point, the lignin content in the pulp is high, thus reducing its quality since its fibers are still not enough flexible and are not well bonded together. To carry out the partial dissolution of the lignin there are several chemical processes. In general, during this process, the alkyl-aryl ether bonds are depleted in the lignin, the condensed bonds are enriched, and new bonds can be formed between lignin and carbohydrates (Prinsen, 2013).

Some of the methods that have been used in the pulp and paper industry have been the soda, sulfite, kraft and organosolv processes. Moreover, recently a new method so-called LignoBoost have been developed to isolate lignin.

Soda process was the first process used for lignin isolation in 1854 by Watt and Burgess. Here lignin is extracted and degraded in an alkaline medium. The lignin produced through the soda process is soluble in water and after acidification it is isolated from the pulp liquor through a precipitation reaction (Khan et al, 2018).

Lignin from the traditional sulfite (acid) pulping process is generated as a chemically modified sulfonated lignin derivative, which is soluble in water due to having sulfonate equivalent weights in the range of 400 to 600 Da. (Glaser, 2001). In this process residual lignin in paper pulp is easily removed in the paper bleaching process. However, the paper generated by this means has much less resistance than that created by means of the Kraft process.

The Kraft process makes it possible to have a highly resistant cellulose pulp with a very large decrease in the lignin content in it of up to 90%. Its name comes from the German and Swedish Kraft, which means "strength".

This process dissolves the wood lignin in an aqueous mixture of NaOH and Na<sub>2</sub>S, better known as white liquor, at temperatures between 160° and 180°C, keeping it under these conditions for several hours (Glaser, 2001). The lignin depolymerization process in the Kraft process is the same as in the soda process; the reaction proceeds with cleavage of the  $\alpha$ -O-4 and  $\beta$ -O-4 ether bonds and results in soluble fragments of lignin. (Khan et al, 2018).

The liquor resulting from cooking, called black liquor, is subjected to a regeneration cycle. This liquor is an extremely complex mixture, which includes components such as lignin, acetic acid, formic acid, dissolved hemicelluloses, methanol, and hundreds of other components (Bajpai, 2018). The organic part is consumed and burned as fuel, generating heat that is recovered in the form of steam at high temperature, which is used for several purposes within the same process.

The unburned inorganic part is collected at the bottom of the boiler as a molten mixture, which is dissolved in a weak caustic solution, obtaining a "green liquor" that contains mainly dissolved  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{CO}_3$ . This liquor is pumped to a recausticizing plant where it clarifies obtaining a white liquor that is filtered, regenerated, and stored to be used again. All types of woods can be used for the Kraft process, although the best results are obtained with hardwoods.

Organosolv process operates at high temperature and pressure, with the addition of water as a co-solvent. This process uses organic solvents such as alcohols, organic acids, ketones, ethers, or amines (Upton & Kasko, 2016), where the bonds between carbohydrates and lignin are broken and produces cellulose pulps with a low residual lignin content.

LignoBoost is a novel technique that have been developed by Valmet Oyj used to isolate lignin on an industrial scale from the kraft pulping process. By removing up to 25% of the lignin in the black liquor, the boiler capacity is increased allowing 20-25% more pulp production. The lignin obtained can be sold for use in the manufacture of special chemicals or as fuel in the form of granules or powder (Valmet, 2019)

### **3.2 Current status**

Traditional applications of lignin mainly include its use where it plays a replacement role for a relatively low value chemical or material. The fraction of lignin outcoming from the production of cellulose can also be used by obtaining isolated lignin for applications as a solid biofuel and as a polymer in biomaterials.

On the one side, during the production of cellulose pulp, a large amount of lignin is produced in black liquors, which are usually used by combustion to co-generate energy. As an energy replacement for burning black liquor in the paper pulp industry, natural gas is used since it is a cheap fuel whose combustion generates much lower local atmospheric emissions than black liquor (Bernier et al., 2013). On the other hand, the solid residue obtained after

hydrolysis and fermentation of carbohydrates is also rich in lignin. Something similar happens in the biofuel industry, where about 40% of the lignin residue is used for lignin combustion and the remaining 60% is treated as waste (Su et al, 2020).

The recovery of the lignin fraction, beyond the use of energy by combustion to generate heat or electricity, can increase the technical-economic and environmental viability of biorefinery processes, in particular, for paper producers and bioethanol producers. It is noteworthy that the use of different types of lignocellulosic materials implies that lignin products with different compositions and properties are obtained, since the composition and structure of lignin varies with the origin of the material and consequently with the processes applied to it. Such variation is one of the greatest challenges for lignin applications, but it also represents great potential for obtaining various products.

### **3.3 Potential**

As a renewable carbon source for chemicals, lignin is today the largest untapped terrestrial source. The predominant use of lignin has so far been as a fuel source in the paper pulp industry. However, considering the great variety of functional groups that it possesses, it is convenient to opt for other applications and alternatives for its conversion and / or harnessing. The molecular structure of lignin offers the possibility of enhancing the lignin substrate in a wide variety of high added value products. Among the most outstanding uses are the obtaining of polymeric molecules, aromatics, as well as their use in the manufacture of catalysts and electronic components.

#### **3.3.1 Macro molecules**

Lignin products are synthesized through depolymerization pathways that include reducing and non-reducing catalytic fractionation as well as thermal processes.

Carbon fiber production is one of the markets that currently has the best projection (Ponnusamy et al, 2019), with an average production of 46,000 metric tons, but whose processing is expensive due to the high production price of its precursor, polyacrylonitrile (PAN) whose price varies between 15 to 20 USD / kg (Numma et al, 2019). However, the high weight carbon content in lignin, up to 60%, and its high availability has made lignin a more effective precursor of carbon fiber synthesis. However, although lignin has a lower melting temperature and a higher stabilization capacity, the generation of carbon fibers from lignin has a lower mechanical resistance compared to those generated from PAN.

Lignin can be used in the generation of polyurethane products, which is one of the most widely used polymeric compounds. The synthetic creation pathway of polyurethanes incorporates the reaction of diisocyanates and polyols (Engels et al., 2013). Lignin can be consolidated as a polyol in the synthesis of polyurethane by being structurally modified before being used, thus giving rise to the formation of polyurethanes with improved mechanical characteristics of rigidity, brittleness and anti-aging, compared to the conventional one (Ponnusamy et al, 2019).

Epoxy resins, also called polyepoxides, are a sort of reactive polymers and prepolymers that contain epoxy groups that can be based on renewables material, thus minimizing the environmental impact for its use or production. Zhang et al, (2021) prepared a lignin-based epoxy resin employing a carboxylated lignin as a co- hardener. The prepared resins showed an increase of the elongation at break, flexural strength and tensile strength with the addition of lignin up to 20 wt%. Thus, demonstrating simultaneous reinforcing and toughening effects on the epoxy resin due to the incorporation of carboxylated lignin at an appropriate amount, which can be attributed to the rigid and highly branched structure of lignin.

Likewise, lignin has a potential use in the synthesis of bio- based polymer hydrogels. Composite hydrogels combine efficient adsorption, good specific surface area and easy applicability, therefore comprising a great alternative for the reduction of heavy metal ions. This approach is being specially investigated for the elimination of these metals present in aquatic ecosystems. In their study Goliszek et al, (2021) used lignin-containing polymer hydrogels for sorption of nickel (II) ions. The incorporation of methacrylated lignin into the structure of the hydrogels 2-hydroxyethyl methacrylate and divinylbenzene, increased their sorption of nickel ions by 30 % due to the addition of lignin significantly increases the swelling ability of the hydrogels. Similarly, efficient removal of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$  ions (Fouda et al, 2021) and removal of Cr (VI) pollution from aquatic environment (Chen et al 2021) by carbohydrate biopolymers and nanocomposites based on lignin have been demonstrated.

### **3.3.2 Lignin based sub-micro and nano-structured materials.**

Interest in the use of lignin in advanced materials such as sub-micro and nano-structured materials has increased significantly. Adding sub-micro lignin particles in the preparation of other polymeric compounds, an increase in tensile strength and modulus is obtained, indicating the reinforcing effect of lignin particles within polymeric matrices (Duval &

Lawoko, 2014). These lignin-based particles also increased the thermal deflection temperature and improved the thermal resistance of the polymeric compounds (Matsakas et al, 2018).

Lignin-based nanoparticles such as poly (lactic acid) (PLA)/lignin and binary and ternary poly (vinyl alcohol)/chitosan/lignin, PLA/cellulose nanocrystal/lignin have shown excellent thermal, optical, mechanical properties, migration, antioxidant and antibacterial activities. The nanoparticle films produced have applications in many different biomedical fields, such as drug delivery, tissue engineering, and wound healing. More recently, nano and micro-lignin were added to the phenol-formaldehyde resin as an adhesive (Deng et al, 2021).

### **3.3.3 Aromatic compound**

As the most abundant aromatic biopolymer in nature, lignin can be converted into bio-BTX (butane, toluene, and xylene) by different reaction mechanisms such as catalytic fast pyrolysis process (Huang et al, 2021) and either oxidative or reductive depolymerization catalytic processes (Bourbiaux et al 2021). Today, most BTX originates from fossil-derived oils that are being replaced by lignin-based biomass. BTXs are precursors to materials such as resins, nylon fibers, polyurethane, and polyester. Productive advancement to obtain BTX from lignin may possibly expand the utilization of lignin-based waste materials.

Moreover, compounds such as catechol, ferulic acid, phenolic monomers, guaiacols, oligomers, xylenol, ferulic acid, vanillin, vanillic acid, coumaric acid, syringic acid, among others, can be extracted from lignin via thermochemical processes (Nguyen et al, 2021) or by biological means, using fungal enzymes which have high catalytic efficiencies for lignin degradation (Yaguchi et al, 2021).

### **3.3.4 Lignin-based Catalysts**

Carbon, as the basis for the manufacture of catalysts, has been used for a long time either in the form of nanotubes or graphene (Yu et al, 2014). Lignin has the potential to replace this mineral carbon as the basis for such catalysts.

Recent synthesis methodologies have eliminated the need to functionalize lignin or use organic solvents to prepare nanocomposites and catalysts simply using pH driven precipitation (Petrie et al, 2021). Core-shell lignin@Fe<sub>3</sub>O<sub>4</sub> nanostructures for lignin: Fe<sub>3</sub>O<sub>4</sub> were successfully fabricated which possessed a well-defined heterogeneous, multicore magnetic structure where kraft lignin acts as a shell, and multiple Fe<sub>3</sub>O<sub>4</sub> magnetic

nanoparticles cluster together, forming the core. The inherent magnetic and adsorptive properties of the composite showed potential in adsorption or chemical separation processes induced by low-strength, rare-earth magnets.

Similarly, Savunthari et al (2021) used nanocomposites based on lignin nanobars for the photocatalytic degradation of pharmaceutical contaminants dissolved in aqueous environments, showing a high removal efficiency by photocatalysis (99.90%) and an improved cyclic performance that allows stable catalyst operability for up to five use cycles.

### **3.3.5 Applications in electronics.**

Biomass-based materials are considered an ideal and sustainable alternative as a replacement for fossil materials in electronic components. Lignin-based materials are being developed for the manufacture of electrodes (Chaleawler & Liedel, 2017; Liu et al, 2021) for energy storage applications, and in the manufacture of capacitors and supercapacitors (Torres et al. 2016; Cao et al, 2020) which show high specific capacitance.

The results and multiple applications described above show that the development of different lignin-based materials is ecological, easy to prepare, highly efficient and reusable.



## 4 HYDROTHERMAL CARBONIZATION

### 4.1 Overview

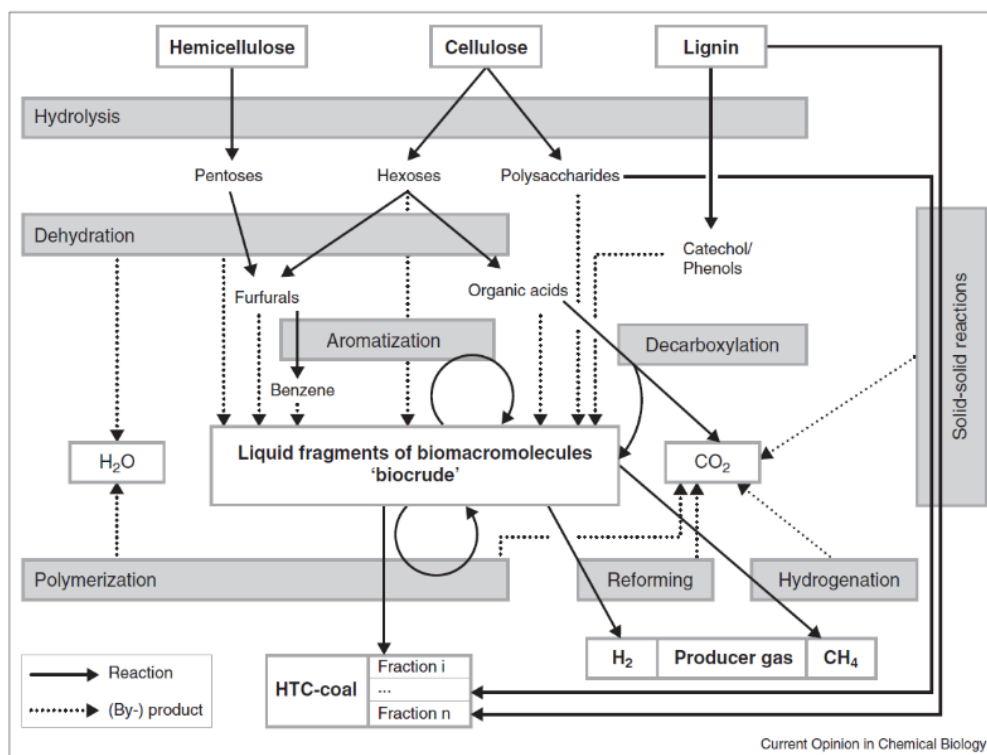
This process was described for first time by Friedrich Bergius in 1913. It is sometimes referred to as "high temperature, high pressure aqueous carbonization" or "thermal hydrolysis". It is a chemical process for the conversion of organic compounds into structural carbons which its implementation has increased in the recent years (Titirisi & Antonietti, 2009)

Basically, hydrothermal carbonization technology transforms organic mass into a solid biofuel like carbon so called biochar, that concentrates energy by increasing energy density removing carboxyl and -OH groups reducing the O/C ratio significantly. What makes this technology so interesting is that it has an optimal energy balance regardless of the humidity of the biomass, thus allowing the use of a wide range of raw materials regardless of its sector (agricultural residues, crops, waste, etc.) to be transformed into a homogeneous product.

The HTC includes processes such as hydrolysis, dehydration, decarboxylation and polymerization for which drying of the feedstock is not needed (Kumar & Ankaram, 2019). Although hydrolysis is the predominant reaction in this process, the reactions do not have a specific order since they happen at the same time and in an interconnected way. Since hydrolysis is the reaction with the lowest activation energy, it is the first to take place. In figure 5 the basic scheme of the HTC process and pyrolysis is illustrated.

Carbonization temperature dependent on the type of starting materials and its decomposition temperature; a range of 150–350 °C is typically employed. (Jain et al., 2016) under autogenous pressure (up to 2.4 MPa) in a close system.

This process allows the creation of a wide variety of structured carbonaceous materials: production of lignite substitutes which can be utilized in co-firing with low rank fossil coals, synthesis gas (mainly CO<sub>2</sub>), liquid oil precursors (rich in nutrients) and humus from the initial biomass, with a net generation of energy (Yoganandham et al., 2020).



**Figure 5.** HTC reaction scheme (Kruse et al., 2013)

The solid yield varies between 35% and 65% of the initial dry feedstock with a higher heating value (HHV) around 13–30 MJ/kg depending on the initial energy content of the feedstock. (Kirtania, 2018).

At an industrial level, today there are several companies that own and develop hydrothermal carbonization facilities in which a wide range of raw materials are used.

Among these companies it is possible to highlight:

#### 4.1.1 AVA-CO<sub>2</sub>

This Swedish company developed HTC's first industrial-size demonstration plant in 2010 with an annual production capacity of 1000 tons of CO<sub>2</sub>-neutral AVA carbon and in 2012 put into operation in Germany the world's first HTC industrial plant with an annual production capacity of 8000 tons of AVA coal (AVA-CO<sub>2</sub>, 2012). AVA along with HTCycle, a leading company in the management of agricultural waste and sewage sludge (mixed waste) through the hydrothermal carbonization process (HTC), launched in 2017 an HTC plant in Innovationspark Vorpommen in Relzow, Germany (HTCycle, 2017).

The company has a subsidiary (AVA-Biochem) focused on large-scale biochemical production synthesizing chemical compounds such as 5-Hydroxymethylfurfural (5-HMF), which opened the door to a wide range of chemical modifications, because of this it has become the base component of their other products, such as diformylfuran (DFF) or polyethylene furanoate (PEF). (AVA-Biochem, 2020).

#### **4.1.2 Ingelia SI**

This Spanish company founded in 2005 put its first HTC plant into operation in 2010, in the city of Valencia. With the development of its own patented technology, this first plant had an annual processing capacity of 6000 tons of solid waste. In 2015, a second reactor unit was installed, increasing the processing capacity to 14,000 tons per year. Ingelia along with CPL Industries in 2018 carried out the construction of an HTC reactor in England. Ingelia has exported its HTC technology to other countries such as Italy, UK, Canada, Belgium, Poland, and Portugal. (Ingelia SI, 2018).

#### **4.1.3 CPL Industries**

This British company is Europe's leading manufacturer of smokeless solid fuels, with a capacity of 500,000 tons per year. In co-operation with Nottingham University and Ingelia (Spain), and the Energy Research Accelerator (ERA), CPL Industries has developed a new hydrothermal carbonization process (CPL Industries, 2019). The plant can convert up to 30,000 tons per year of wet waste into biocoal and black pellets.

#### **4.1.4 TerraNova**

In 2010 this German company started the operation of its HTC plant in Kaiserslautern, which is mainly destined to the treatment of sludge and has a processing capacity of 8000 tons per year. In addition to the production of solid fuels, in these plants the liquids resulting from the HTC process are treated in order to extract nutrients from it to be later used in the fertilizer industry (TerraNova Energy, 2015)

## **4.2 Operational parameters**

The HTC process requires knowledge and control of process parameters such as reaction temperature, reaction time, catalyst, pressure, and the raw material itself.

### **4.2.1 Temperature**

Temperature is the most important parameter, being this widely studied. Temperature provides the heat necessary to initiate the fragmentation reactions of the chains that make up the biomass. As the reaction temperature increases, the performance of the process is improved. Depending on which temperature range is handled, the performance of liquid or solid product is favored, being more favorable for liquid products the use of moderate temperatures, and high temperatures for the generation of biochar and gas.

Generally, the production of solids is higher in a temperature range between 150 to 200 ° C. Liu et al (2013) evaluated the effect of temperature in a process that involved coconut fibers and eucalyptus leaves, finding a rapid decrease in the yield of solids as the temperature increased from 150°C to 375°C. Likewise, as the temperature increases, the percentage value of carbon in the solid product increases while the amount of hydrogen and oxygen decreases, which in turn justifies the increase in heat capacity as the temperature increases (Dinjus et al, 2011; Ruan et al, 2018).

### **4.2.2 Reaction time**

The HTC is characterized by being a slow process. Depending on the raw material or the final product that is desired, the reaction times can vary from a few minutes to several days (Sangchoom & Mokaya, 2015). Reaction time only influences hydrolysis reactions up to a certain time interval beyond which it has no specific impact on the process.

The duration of the reaction defines the composition of the product, as well as the total conversion of biomass, obtaining a greater quantity of solid product at longer reaction times. The hydrolysis rate and biomass rate degradation are relatively fast under supercritical conditions, so less time is required to effectively decompose biomass (Sasaki et al, 2003).

Inoue et al (2002) show that even with reaction times below one hour, a solid product can be obtained with a considerable calorific value, equal to or greater than lignin depending on the temperature used in the process. Reaction times directly influence the formation of hydrocarbons during the process, as well as the degree of porosity, pore volume and surface area. The longer the reaction time, the higher the parameters mentioned above.

### 4.2.3 Pressure

Pressure impacts the degradation of biomass in the hydrolysis process as long as the pressure remains above the critical pressure of the medium, significantly driving successful reaction pathways that thermodynamically favor the conversion of biomass into valuable products (Nissamuddin et al, 2017).

This can be increased either by increasing the temperature or by injecting some gaseous fluid into the reactor (nitrogen). The direction to which the equilibrium shifts at higher pressure from solid to liquid phase or vice versa are decided according to Le Chatelier's principle. The effect of pressure is to improve the formation of hydrochar since this greatly influences its formation due to the fact that high pressures lead to high temperatures generating the hasty breakdown of the biomass composition obtaining a high-quality final product.

### 4.2.4 Catalyst and pH

The hydrothermal procedure is self-catalytic since, during the degradation of the biomass, organic acids such as lactic acid, levulinic acid and formic acid are generated, causing a drop in pH and generating an acidic environment influencing the reaction behavior (Khan et al, 2019). The choice of catalyst to use depends on the product whose formation is to be favored (solid, oil or gas) as well as its characteristics and end use (porosity, capture capacity, energy storage, etc.) In their research, Reza et al (2015) found that a greater surface area, pore volume and smaller pore size were formed in an acid environment, generating an opposite effect in a basic environment.

Basic catalysts improve the oily product formation performance, but at the same time decrease the solid product formation (Nissamuddin et al, 2017). The presence of acids improves the dehydration process, which remains a dominant carbonization technique that results in a significant decrease in the oxygen content of the hydrocarbon while increasing its HHV. One aspect to consider when choosing a catalyst is not only its level of efficiency in the process, but its level of danger and/or toxicity.

One of the most widely used catalysts is KOH (Li et al, 2021; Reza et al, 2015; Sevilla et al, 2020), which is classified as "Extremely Dangerous" restricting its use at an industrial level.

### 4.2.5 Feedstock

In the HTC process, it is possible to use a wide variety of biomass, whose characteristics vary among themselves, depending on factors such as their origin or their growth time. A

higher content of cellulose and hemicellulose favors a higher yield in the formation of oil, as well as a higher content of lignin favors a better yield in the production of hydrochar (Zhong et al, 2004), this due to the Lignin does not degrade as easily compared to the other two organic polymers. Studies carried out by Sevilla & Fuentes (2009) and Funke & Ziegler indicate an optimal degradation of hemicellulose (hydrolysis) at temperatures close to 180°C and of cellulose and lignin above 200°C.

### **4.3 Potential and constrains**

One of the fundamental advantages of HTC is that it presents as an easy, environmentally friendly, and scalable process to produce coals, as well as nanostructured hybrid materials for practical applications capable of replacing some of the traditional petrochemical processes. Some of the processes in which the carbon obtained via HTC can be used are the generation of nanostructured materials, catalysis, water purification, energy storage or acting as a CO<sub>2</sub> scavenger from the atmosphere. Likewise, there is the possibility of cooperating with small commercial electric and thermal power plants in co-firing processes.

Regarding the generation of nanostructured metal oxides, the carbon spheres from HTC can be used as templates for production of new materials. An example is the simple and scalable synthesis in one step to obtain hollow metal oxide spheres. These have been prepared from the charcoal from the enzymatic hydrolysis of lignin by HTC (Mao et al, 2018).

The solid material produced can also be used as a structural base for catalysts. The hybridization of the functional groups of biomasses from inorganic materials included in the HTC process can generate catalytic systems of interest. If the HTC takes place in the presence of noble metal salts, these can be reduced in situ thanks to the aldehyde groups of carbohydrates and produce intermediates, resulting in carbon loaded with metallic nanoparticles. An example of this, is the preparation of Pd nanoparticles within the carbon matrix, creating a medium with hydrophilic polar oxygenated groups which shows an excellent performance (Tiriciti & Antonietti, 2009).

A widely used property of activated carbons is their adsorption capacity. Unlike activated carbons, HTC carbons treated at 180°C do not present microporosity, but nevertheless present a large number of oxygenated groups located on the surface, which enhance the adsorption (Titirici et al, 2012). This property can be used to capture CO<sub>2</sub> helping to mitigate GHG emissions, since it is this gas that contributes the most to climate change. It is also

possible to use it in applications such as the storage of methane or hydrogen, the latter being currently one of the main obstacles that hinder the commercial use of hydrogen in the fuel cell system. Excellent results have been obtained in storage with activated hydrochar due to its optimal pore size (0.8–1.1 nm).

Hydrothermal carbons and their nanocomposites have also been used extensively so far as electrodes in Li + or Na + ion batteries, supercapacitors and fuel cells. Wu et al, (2020) successfully synthesized hierarchical porous carbons (HPC) from hydrothermal lignin pretreated with ZnCl<sub>2</sub> to be used as electrode material for a double-layer electrical condenser. This material has a high energy density of 10.48 Wh/kg and an excellent cycle life with a slight decrease in specific capacitance (approximately 3.04%) after 10,000 cycles, concluding that the hierarchical pore structure facilitates the transfer of ions that conducts to good performance.

There are also possible applications of HTC carbon in agriculture. Although charcoal and hydrochar have similar chemical structures, hydrochar retains nutrients better in the soil and provides better carbon storage. The fact that a previous drying of the raw material is not needed allows the use of a large number of different types of biomasses such as animal manure, use of wastewater, urban solid waste and residues from the agricultural industry (Titirici et al, 2012). Nevertheless, must be careful when using the material produced by HTC (whether liquid or solid), as this could affect the soil microbiota due to its acidic nature.

## **5 HYDROTHERMAL CARBONIZATION OF LIGNIN**

The previous chapters describe in detail the characteristics, previous and current applications, as well as the potential use of both the material to be used and the procedure to be carried out. In this section the thermal process and the variation of its operational parameters during the hydrothermal carbonization of lignin will be described.

### **5.1 Material**

The Kraft Lignin was collected from UPM's Kaukas pulp mill located in Lappeenranta, Finland.

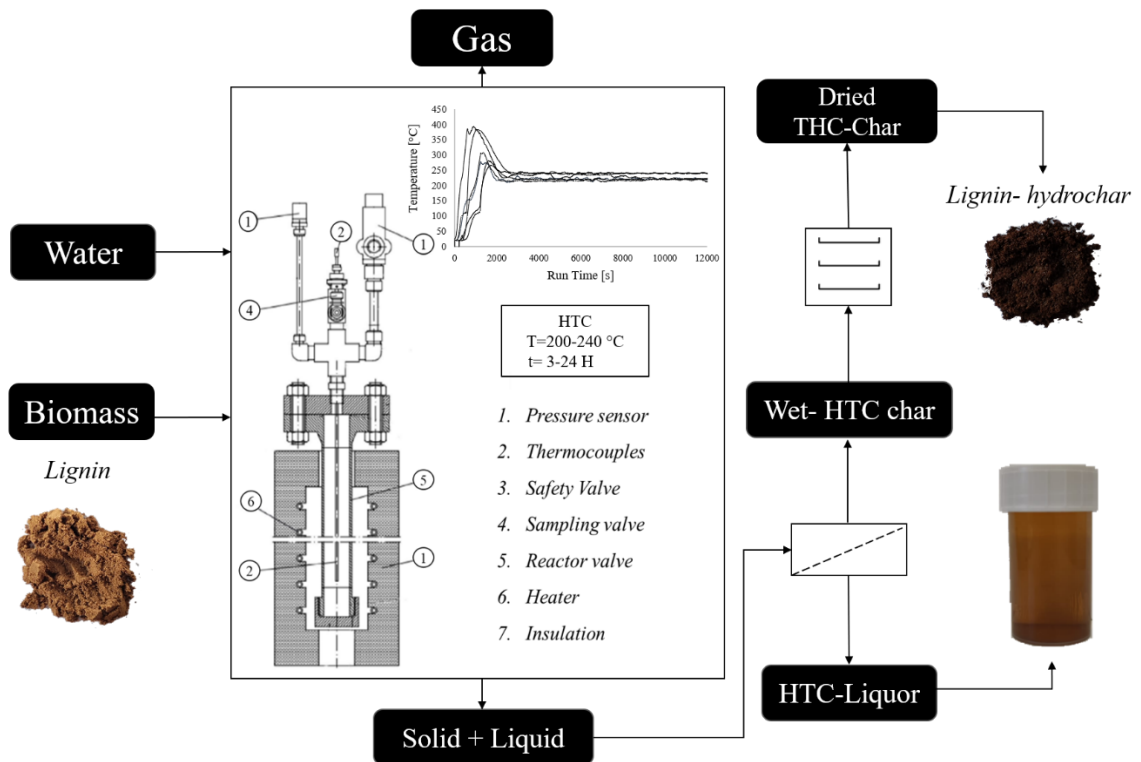
### **5.2 HTC reactor**

The hydrothermal carbonization was performed in the laboratory facilities of Lappeenranta-Lahti University of Technology LUT, Finland. The process was divided in x stages: feedstock preparation, HTC treatment, separation of the liquid and solid products and hydrochar characterization.

The treatment was carried out in a stainless-steel batch reactor designed in LUT University. Figure (6).

The reactor has an inner volume of approximately 1L (705 mm height and 42 mm inner diameter) with a flange connection at the top and screw closing at the bottom. The insulating layer and the sheet steel cover prevent heat losses during the process. The insulation in the upper part of the reactor is reinforced using glass wool. The temperature of the process is controlled by mean of four thermocouples: two inside the cylindrical reactor and 2 outside. The upper thermocouple inside the reactor is located at 245 mm from the top, and the lower one is at 645 mm. The other two sensors are located on the outer surface of the reactor and on the heating surface.





**Figure 6.** HTC experimental unit

A pressure sensor and a pressure relief valve (set point pressure 40 bar, maximum temperature 300 °C) were installed at the top of the installation for pressure measurements and safety purposes. For the control and measurement of the operational parameters, was employed the National Instruments LabVIEW software. By means of proportional-integral-derivative (PID) controller, the required pressure and temperature levels within the reactor were maintained during the process. The control system recorded every three seconds the temperature and pressure data.

### 5.3 Methodology

For this work, the main parameters to be evaluated are the temperature, the residence time, and the concentration of the recirculated process water in the HTC treatment (Table 1).

**Table 1.** Operational parameters of HTC treatment.

Variable	Unit	Temperature			Time				Recirculation		
		200	220	240							
Temperature	[°C]				240				240		
time	[h]	6			3	6	12	24	6		
Mass ratio	-	1:9			1:9				1:9		
Concentration	[%]	0			0				40	60	80

In each experiment, the lignin sample was previously weighed and subsequently dispersed in water and stirred manually until obtaining a solution as homogenized as possible. For each experiment 10 wt/v of biomass in water was prepared and placed into the reactor.

After the correct sealing of the reactor, the temperature was gradually increased to the established set-point value and maintained for the desired time. The temperature and the reaction time vary according to each experimental stage.

Upon completion of the HTC process, the heater is shut down and the reactor temperature continues to be monitored. Once the reactor reaches the temperature of the room this is opened, and the mixture of solid and liquid products are carefully extracted from it in order to avoid any loss of material. The products were separated using a vacuum flask and a Büchner funnel with Whatman glass microfiber filter paper (grade GF/A).

Solid product (Hydrochar) was subsequently dried overnight in an oven (oven reference) at the temperature of  $105\pm 2$  °C and milled in a (reference of the mill) until obtain a uniform powder. The particle size was not determined. The PH was measured to the liquid product and later was stored in a fridge. Each experiment was repeated at least twice, and the average experiment data were taken for further analysis.

## **5.4 Analytical Methods**

Proximate analysis, ultimate analysis, ash content and measurements of heating values were carried out both on the raw lignin and on the hydrochar generated after the hydrothermal carbonization treatment. Each analysis was repeated at least twice, and the average experiment data were taken for further analysis.

The analyzes were performed following the appropriate procedural standards for each case.

### **5.4.1 Proximate Analysis**

#### ***Moisture content***

The Sartorius 7093 express moisture analyzer is used to measure moisture content. The equipment has an electric balance on which a gram of sample is placed, which is heated for eight minutes in an air atmosphere until it reaches a constant mass. At the end of the test, the equipment itself provides the percentage value of the moisture content of the sample.

### ***Ash content***

The ash content of the lignin samples is determined according to the SFS EN 14775: 2009 standard (SFS., 2010a).

### ***Volatile matter***

The volatiles content is determined according to the 15148: 2009 standard (SFS., 2010c).

### ***Fixed Carbon***

Fixed carbon is the solid combustible residue left after heating a sample and expelling volatile matter. The fixed carbon content is determined by subtracting the sum of the percentages of volatile matter and ash from one hundred percent.

## **5.4.2 Higher heating value**

The measurements of the HHV were made in the Parr 6400 calorimeter, following the "Solid biomass" standard EN 14918 (SFS, 2010b). Once the material has been ground, a pellet is prepared with a manual press and subsequently weighed. The pellet is disposed inside a stainless-steel capsule, and this is carefully placed inside the capsule holder. A cotton thread is used as an auxiliary fuse to ignite the sample. The thread is wound on the heating cable, folded over itself, twisted to form a single strand and the pellet is placed on it. The thread will ignite, drop into the sample cup, and ignite the pellet. Increasing the temperature level of the water jacket surrounding the inner cylinder of the calorimeter allows the determination of the higher calorific value.

## **5.4.3 Elemental Analysis**

The organic elements of the samples, i.e. carbon, hydrogen, nitrogen, oxygen and sulfur, were measured in accordance with the standards ISO 16948 [1] and ISO 16994 [2]. The elemental analysis was performed with a LECO CHN628 Series Elemental Determinator coupled with a 628S Sulphur Add-On Module. Prior to the analysis, standard samples (ethylenediaminetetraacetic acid for CHN and coal for S measurements) were analyzed to verify the experimental error within  $\pm 1\%$  for the elements. The results are presented on a dry basis as the mean of duplicate determinations. The oxygen content was calculated by difference on a dry basis.

#### **5.4.4 FT-IR**

Fourier-transform infrared spectroscopy (FTIR) analysis for solid samples was performed with a Frontier MIR/FIR spectrometer (PerkinElmer Inc.) coupled with a universal diamond crystal ATR module in the range of 400–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

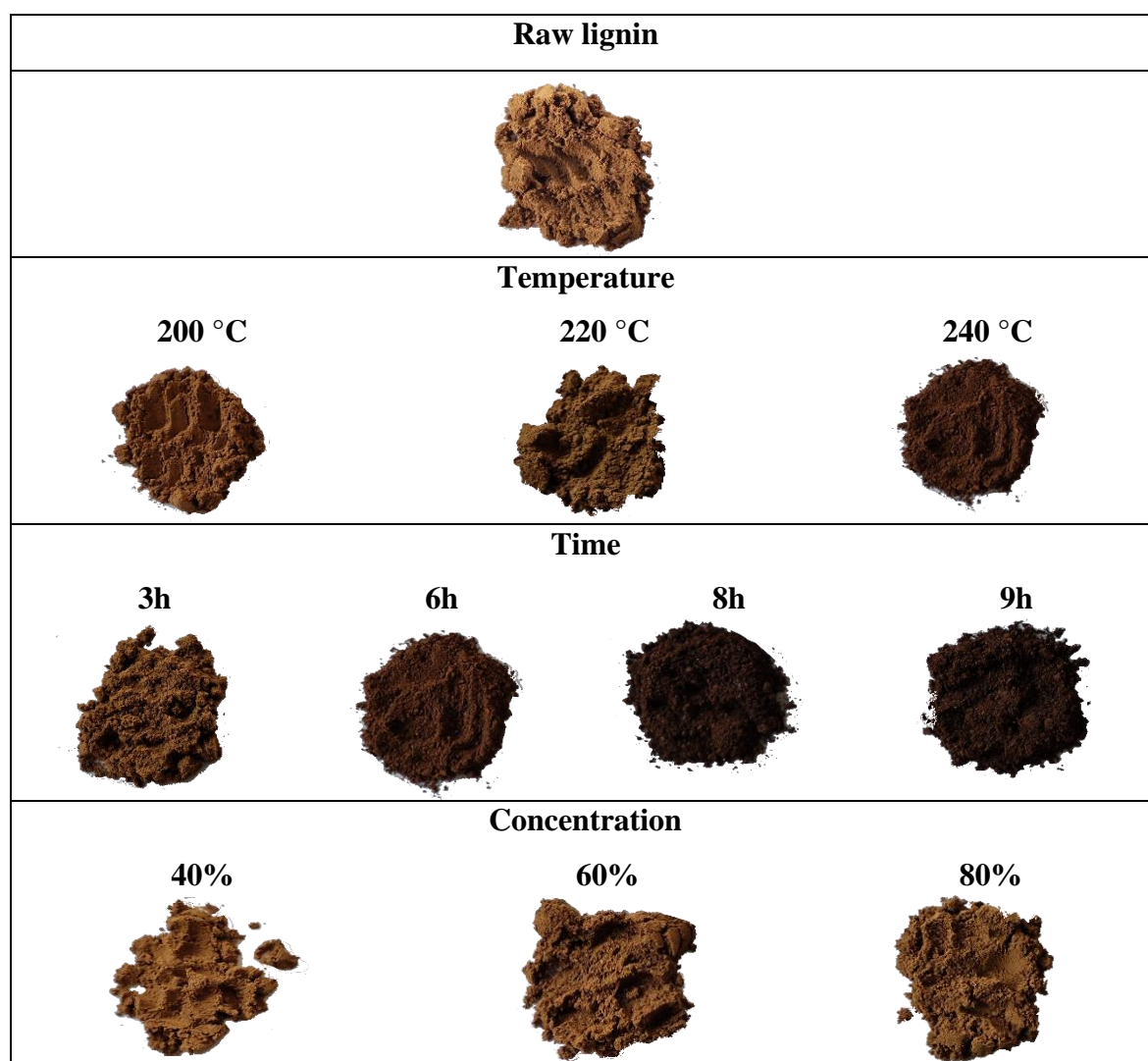
#### **5.4.5 Thermogravimetric Analysis (TGA)**

TGA was performed with STA 449C thermogravimetric analyzer (Netzsch Instruments, Germany). About 10 mg of the sample were placed inside  $\text{Al}_2\text{O}_3$  sample holder. The sample was heated from room temperature to 900  $^\circ\text{C}$  at rate of 20  $^\circ\text{C min}^{-1}$ . High purity nitrogen was applied for inert atmosphere and compressed air for combustion conditions. A constant gas flow rate of 250  $\text{mL min}^{-1}$  was maintained in both cases (Sermyagina et al., 2021).

## 6 RESULTS AND ANALYSIS

### 6.1 Effect of HTC temperature, reaction time and concentration of recirculated process water

Kraft lignin was hydrothermally carbonized, this with the aim of induce a degradation of the material, thus generating components that would undergo polymerization to carbonaceous material. The experimental results shown that HTC treatment generates a hydrochar with somewhat enhanced heating properties compared with the raw lignin. In general, while increasing the temperature increase the HHV and the FC, likewise while decrease.



**Figure 7.** Untreated raw lignin and hydrochars after HTC.

The experimental results show that the HTC treatment produces a hydrochar with slightly improved energy properties compared to crude lignin. In general, as the temperature increases, high heating (HHV) and fixed carbon (FC) values increase, as volatile matter (VM) is reduced and part of the inorganic material dissolves in the aqueous phase. Moisture content (MC) is also influenced by hydrothermal treatment. The change in color of the material after the hydrothermal treatment can be considered as an effect on one of its qualitative properties that can be easily appreciated, indicating that there was indeed a change in the biomass. Figure 7 shows the raw and dry lignin after and before having carried out the HTC treatment under the analyzed reaction parameters. The color of the sample changes with increasing severity of the process; increase of temperature and residence time. No significant qualitative change was seen as the concentration of the recirculated process water increases.

The raw lignin underwent to proximate and ultimate analysis prior to the heat treatment, to have a comparative reference base for the samples after the HTC process. The results of these analysis can be appreciated in Table 2. The higher and lower heating values parameters are presented on dry basis, as well as the values of the results of volatiles and ash analysis.

**Table 2** Raw lignin properties

<b>Property</b>	<b>MC</b>	<b>VM</b>	<b>FC</b>	<b>Ash</b>	<b>HHV dry</b>	<b>LHV dry</b>
Unit	[wt%]	[wt%]	[wt%]	[wt%]	[MJ/kg]	[MJ/kg]
Raw Lignin	8.64	70.93	27.90	1.17	26.98	25.64

### **6.1.1 Proximate analysis**

The hydrochar generated by HTC treatment have a lower moisture content than the raw biomass. The moisture content of the solid samples was approximately 1wt%, except for the sample L-40% which presented a MC near of 2 wt%, which however remains been low, representing an 87% reduction in moisture content after HTC treatment. Moisture content is presented in Appendix IV. This low affinity of lignin for moisture is due to its hydrophobic structure. Likewise, lignin with higher impurities presents higher MC, indicating that the impurities contain hydrophilic compounds (Sameni et al, 2014).

The proximate analysis of treated samples is presented in Table 3. Volatile matter of treated samples can be found in Appendix II.

**Table 3.** Samples properties before HTC treatment.

Variable	Unit	Temperature			Time				Recirculation		
		200	220	240	240				240		
Temperature	[°C]										
time	[h]	6			3	6	12	24	6		
Mass ratio	-	1:9			1:9				1:9		
Recirculation	[%]	0			0				40	60	80
ID	-	L-200-6	L-220-6	L-240-6	L-240-3	L-240-6	L-240-12	L-240-24	L-40%	L-60%	L-80%
VM	[wt%]	65.77	64.95	63.27	63.78	63.27	61.60	67.28	68.04	67.84	67.28
FC	[wt%]	33.70	34.71	36.41	35.90	36.41	37.99	32.41	31.51	31.81	32.36
ASH	[wt%]	0.53	0.34	0.32	0.32	0.32	0.40	0.30	0.45	0.35	0.36
MC	[wt%]	1.1	0.96	1.04	1.06	1.04	0.97	0.99	1.91	1.22	1.04

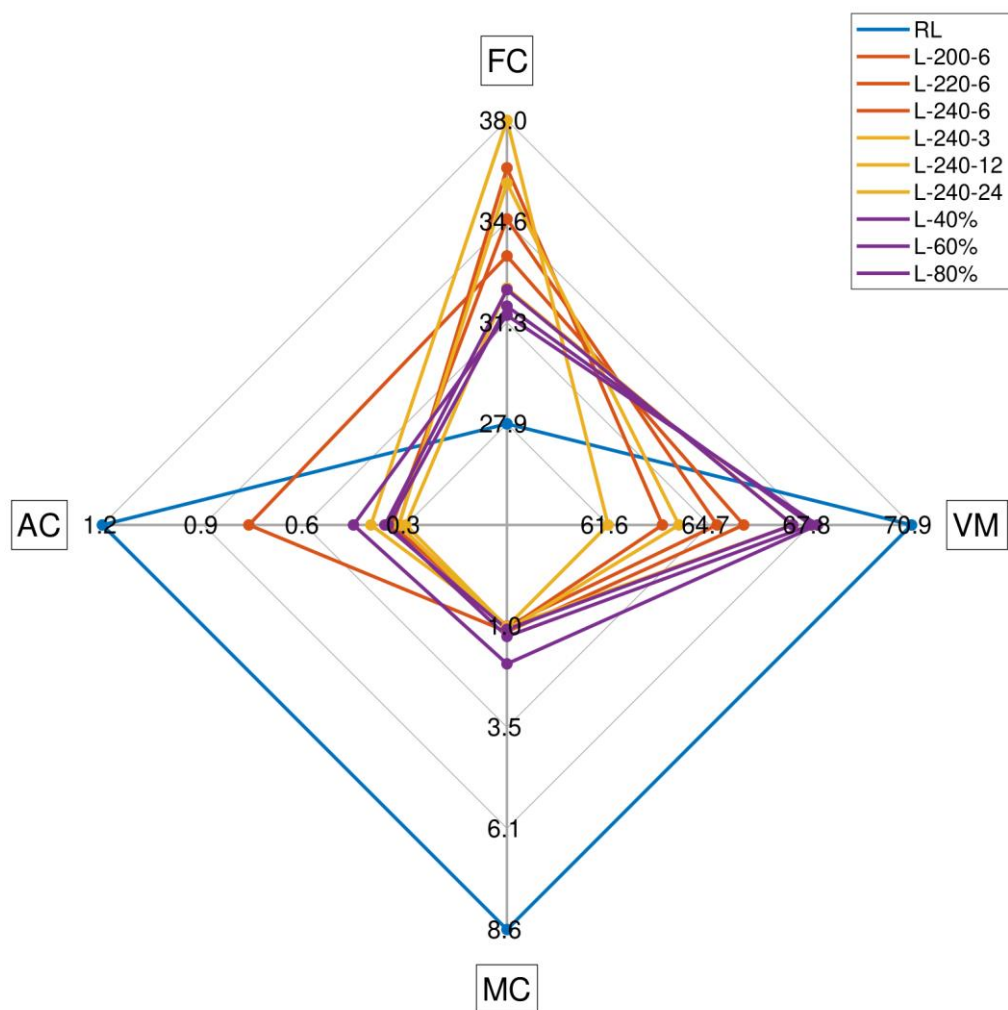
As abovementioned, the reaction time and the temperature at which it is carried out, are the two variables that most affect the characteristics and composition of the samples once the HTC process is performed. The spider chart, Figure 8 shows graphically the change of the properties listed in Table 3 and how these vary according to the operational parameters.

By setting the reaction time and taking temperature as the treatment variable, the VM content decreased as temperature is increased, thus obtaining a lower amount of volatiles for the L-240-6 sample which was 63.27 wt%, indicating a 10.8% reduction in volatile material content. This reduction of the VM is the result of devolatilization/depolymerization reactions that takes place during the HTC treatment (Mendoza et al, 2021).

Regarding the reaction time, a maximum volatile reduction was obtained for the L-240-12 sample, having a VM content of 61.60 wt%, which represents a decrease of 13.15%. However, by increasing the reaction time further, setting it to 24 hours, a considerable increase in its content was observed, rising to 67.28 wt% indicating that could be a re-adsorption of those materials that were previously degraded to the aqueous medium.

Authors such as Cai et al. (2016), Rodriguez et al. (2019), and Li et al. (2021) have studied the adsorption capacity of hydrocarbons generated from hydrothermal processes, indicating that these have a high adsorption strength due to the formation of micropores, even without the use of activating agents such as sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) or potassium hydroxide (KOH).

A similar adsorption/desorption effect can be seen in the recirculation samples where the decrease of VM in the samples is almost nil compared to the initial sample, with these having almost the same volatile matter content of 68% for the three cases in those in which the process water was recirculated.



**Figure 8. Spider** Chart of Proximate Analysis Properties for RL and HTC Hydrochars

On the other side, the amount of fixed carbon has a slight increase as the temperature and the reaction time increase. A maximum increase of 36% was obtained, going from 27.9 wt% to 37.9 wt%, corresponding to raw lignin and sample L-240-12 respectively. This relationship between the decrease in the content of volatile material and the increase in the content of fixed carbon, improve the combustion properties of the hydrochar, since during the burning process there is a more stable flame, and the combustion speed is decreased. FC values can be found in Appendix V.



Concerning ash content (AC) (the inorganic residue remaining after the water and organic matter have been removed by heating) is presented in Appendix III. Even though, crude lignin has a low AC value of only 1.17 wt% per se, when it is putting forward to HTC treatment its content can be reduced between 0.32 and 0.3 wt%, which means a reduction of 75% of the ash content. This low ash content in lignin is due to its strong polymeric structure does not allow inorganics to bind to its main structure.

These low AC characteristics in conjunction with the low MC make this hydrocarbon, so far, viable when considering this material as renewable energy source. The above, is supported due to this hydrochar could be stored for long periods with a stable MC without major problems and it would also have an easy handling of its combustion residues (Toufiquir, 2011).

### 6.1.2 Ultimate analysis

Lignin, like the other polymers that make up the lignocellulosic biomass, is mainly composed of C, H, O, N and S. The ultimate analysis is presented in Table 4.

**Table 4.** Elementary composition of samples after HTC treatment

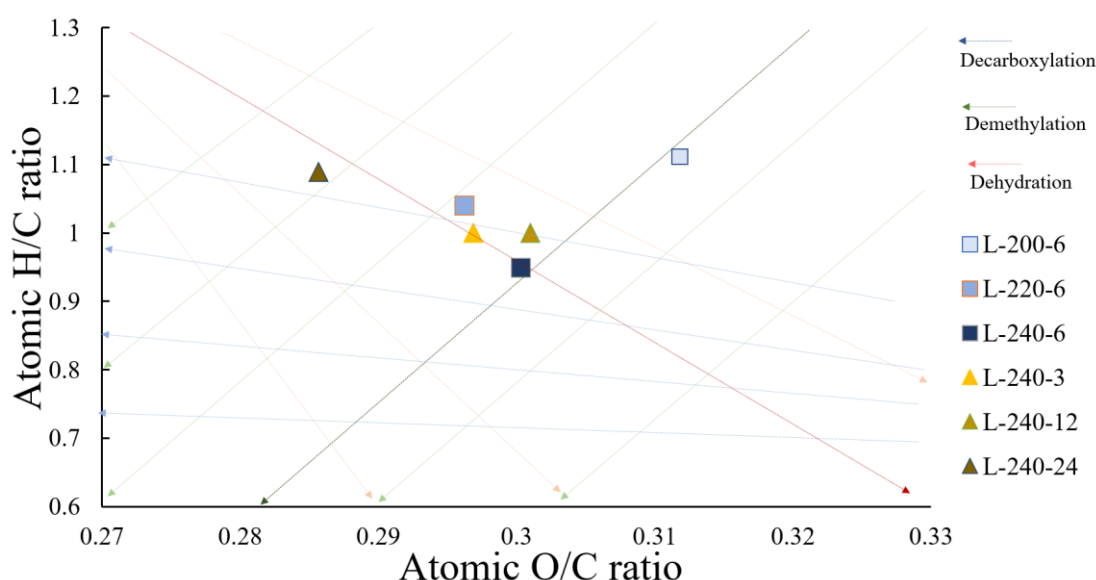
NR-Due to some technical problems, it was not possible to measure the elements to the samples L-40%, L-60 & and L-80%, reason why those values are not present in the table.

Sample ID	Elementary [wt%]						
	C	H	N	S	O	H/C	O/C
RL	65.71	6.14	0.16	2.34	25.64	1.12	0.29
L-200-6	65.68	5.98	0.2	2.12	26.02	1.11	0.32
L-220-6	65.87	5.22	0.18	2.22	26.02	1.04	0.3
L-240-6	65.99	5.71	0.19	2.17	26.42	0.95	0.29
L-240-3	65.68	5.94	0.19	2.2	26	1.09	0.3
L-240-6	65.99	5.94	0.19	2.17	25.7	0.95	0.29
L-240-12	66	5.16	0.2	2.16	26.49	0.94	0.3
L-240-24	66.28	6.01	0.22	2.24	25.24	1.09	0.29

In all the samples analyzed, carbon was the main constituent whose value it is slightly increased as the severity of the process conditions increased, obtaining a maximum of 66.27 wt%. The second element present to a greater extent was oxygen, varying between 25-26 wt%. Regarding the content of nitrogen and sulfur, this remains practically unchanged by HTC treatment, which agrees with the results of previous studies for lignin (Watanabe et al., 2018). The sulfur content is not affected by the hydrothermal treatment and remains at a value of 2 wt%. Kraft lignin has an average sulfur content of between 1.5 to 3 wt%. This

element is found in lignin as sulfate ions, elemental sulfide, as absorbed sulfide, and as organically bound sulfur (Svensson, 2008).

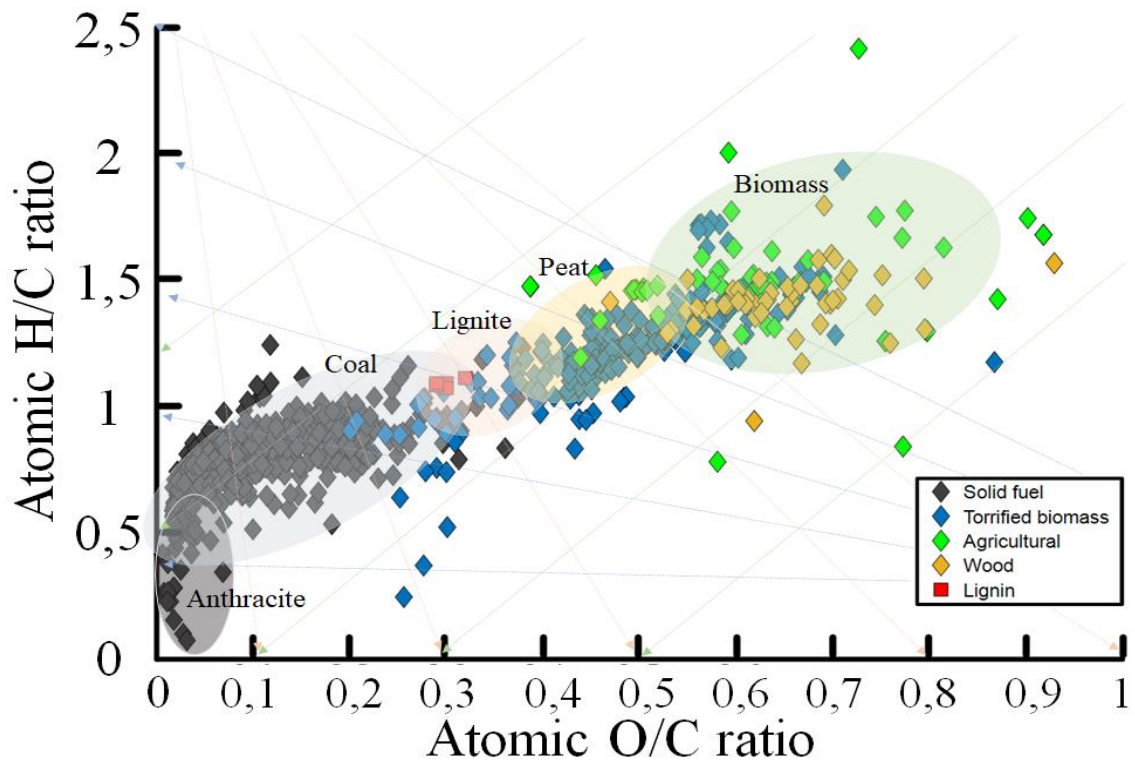
The atomic ratios hydrogen to carbon (H/C) and oxygen to carbon (O/C) are frequently used in the characterization of fuels with respect to their thermochemical conversion (Sermyagina, 2021). Likewise, the van-Krevelen diagram represented in Figure 9, is used to graphically analyze the changes in the atomic ratio of the generated hydrochars. By increasing the temperature of the HTC process, the rate of atomic ratios was reduced following a dehydration and decarboxylation trend. A tendency to decarboxylation with increasing residence time was observed.



**Figure 9.** van-Krevelen diagram for HTC hydrochars.

Moreover, the values obtained for the produced hydrochar are compared with data available in the literature for solid fuels, torrefied biomass, and agricultural (Mendoza, 2021b). This comparison can be seen in Figure 10. It is observed that the hydrocarbon values of lignin are in the range of solid fossil fuels, an intermediate point between carbon and lignite.

From this graph it is also possible to conclude that high moisture and ash content in materials greatly affect their combustible capacity, this because of have high ratio values of H/C and O/C (wood and agricultural waste without any treatment) is inversely proportional to the potential use of the material as fuel.



**Figure 10.** van-Krevelen diagram of HTC produced hydrochars and different solid fuels.

### 6.1.3 Mass Yield

Reaction temperature seems to be the variable that most significantly affects mass yields (MY %) of hydrochar samples generated after HTC treatment, and this can be calculated as:

$$MY = \frac{M_{hc}}{M_{rl}} * 100\% \quad (1)$$

Where:

$M_{hc}$  → mass of dry hydrochar [g]

$M_{rl}$  → mass of dry solid raw lignin [g]

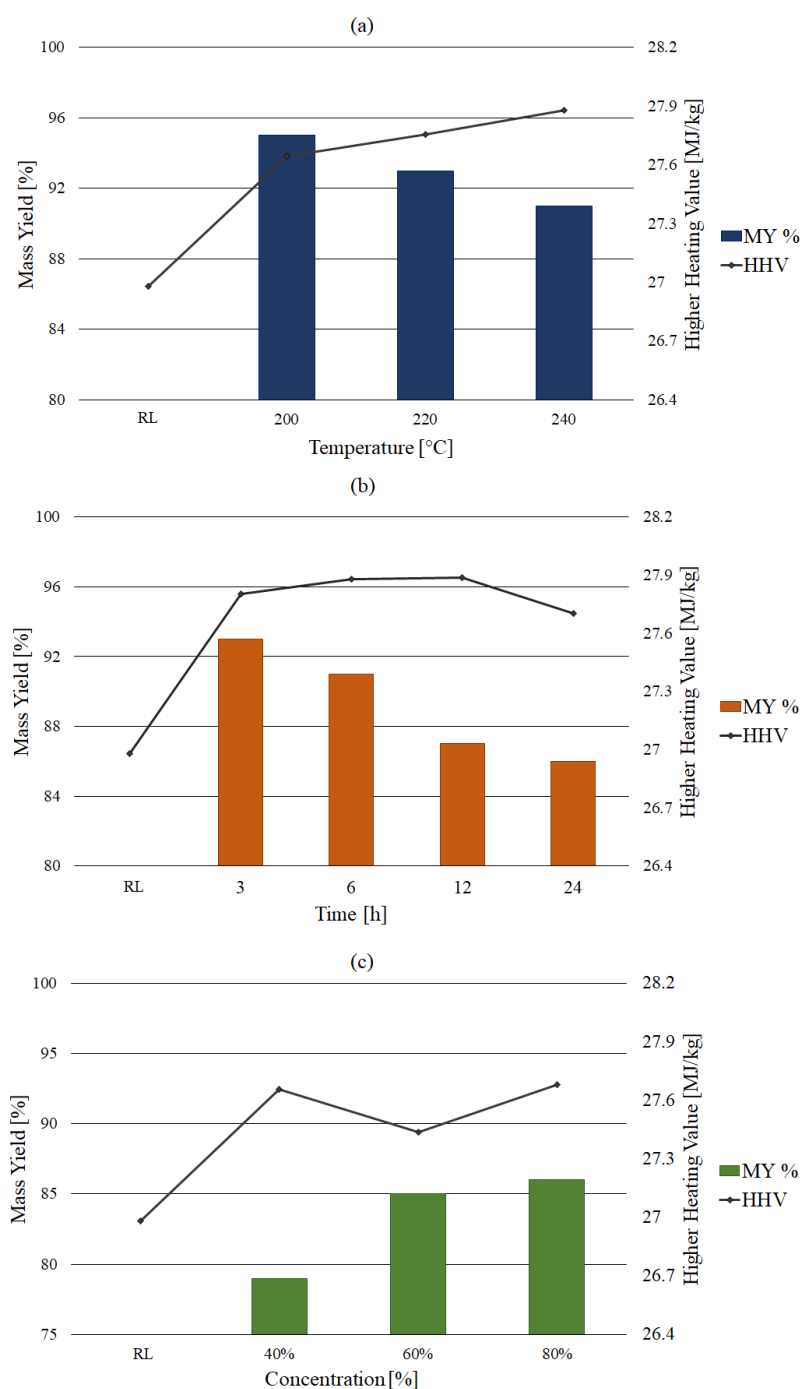
Mass yield results can be found in Appendix I, and its behavior is graphically shown in Figure 11.

The MY obtained in this work was better than expected compared with previous findings, where the MY of lignin in hydrothermal treatments without the use of catalysts was 61% (conditions of 240°C for 22h) (Wikberg et al., 2015) and 79.32% (conditions of 150-280 ° C for 30 min) (Kim et al, 2016).

As time and temperature increased between the ranges 3-24h and 200-240°C, the mass loss increased as well from 5% to 9% with respect to temperature and from 7% to 14% as reaction time increased. However, for the recirculation case, the MY tends to increase, rising from 79% for the L-40% sample to 86% in the L-80% sample. This increasing of the mass yield could indicate that part of the organic compounds that were previously dissolved and are in the aqueous phase e.g., phenolic derivatives, could polymerize again to form a solid product during further thermal process. Similar results were obtained by Wang et al. (2019), when analyzing the recirculation effects of the process water on solid and liquid products of the hydrothermal carbonization of microalgae, obtaining an increase in the mass yield as the number of recirculations increase.

Although in this study only a single recirculation was carried out, the residual water concentration was varied with respect to pure water used in the HCT treatments. This makes it possible to compare, in some sense, the increase in the concentration of the residual water, with the number of recirculations, since in both cases there is a tendency to have a greater amount of organic material dissolved in the process water, which is the material that in effect will be repolymerized, thus increasing the mass yield.

This idea is also supported by analyzing the amount of fixed carbon in this specific case, since these values also increases as the concentration of residual water increases in the recirculation process.



**Figure 11.** Mass and energy yields of hydrochar as a function of: (a) temperature, (b) time and (c) PW concentration

#### 6.1.4 Heating value and Energy yield

Concerning those parameters considered of vital importance when evaluating a material with a possible use as fuel, one of the most important is its HHV, which could be defined as the amount of heat released when said fuel is burned. In other words, these heating values somehow describe the quality as fuel of the produced hydrochar.

In appendix VI, the HHVs for crude lignin and for the samples obtained from the different HTC treatments can be found. Likewise, Figure 11. shows graphically the relation between HHV and the operational parameters.

Overall, HTC treatment tends to increase the HHV of the treated samples. The percentage value of this increase depends largely on the nature and composition of the biomass that is being used, and how the treatment affects its composition.

Raw lignin initially has an HHV of 26.98 MJ/kg, which slightly increases throughout hydrothermal process. This increase is due to the higher carbon and lower oxygen content and hence slightly increased energy density of the produced materials (Wikberg et al., 2015)

Regarding temperature, a larger increase in HHV was obtained in the hydrocarbon of the sample L-240-6 whose value increased by 3.33% reaching 27.88 MJ/kg. Concerning time, a significant change in HHV is not appreciated as it increases, on the contrary, the values of the samples corresponding to L-240-6 and L-240-12 are practically the same, these being 27.88 and 27.89 MJ/kg, respectively. There is a decrease in this parameter for higher times, sample L-240-24, this is related to the increase in volatile material and decrease in the fixed carbon present in this sample.

Likewise, to explain these values, the variations in HHV of the products degraded by the HTC process must be reviewed. Although mass spectroscopy was not carried out in this work, there have been previous investigations such Wikberg et al. (2015), where it is shown which products have been degraded to a greater extent from pure kraft lignin once the hydrothermal process is carried out and in turn, it can be seen which compounds increase their concentration in the generated hydrochar. The increase or decrease in the concentration of these components in the hydrochar causes its HHV to vary. Following the aforementioned case, after HTC treatment the concentration of guaiacol whose HHV is 28.91 MJ/kg increased and the concentrations of products such as vanillin, homovanillin or coniferyl with lower HHV, decreased as result of the demethylation and dealkylation reactions.

Any deposition of these compounds or intermediates (with relatively low HHV) on the surface of the hydrochar particles generated by the HTC treatment would be expected to decrease its overall HHV. Even though the hydrochar generated has a low content of ash and moisture, and notwithstanding that it presents a reduction in the values of volatile matter under certain parameters, the increase in calorific values is very small in all samples, which

indicates that the hydrothermal process may not be an effective approach to producing solids from kraft lignin with the aim of use them as fuel.

The previous argument can also be supported by analyzing the energy yield (EY, %) values. This value is the product of two factors: energy densification (EDF) and MY. Regularly, as the HHV increases, the MY decreases, resulting in an energy densification of the material (more energy contained in a reduced amount of mass). The EY can be calculated according to the following equations:

$$EDF = \left( \frac{HHV_{hc}}{HHV_{RL}} \right) \quad (2)$$

$$EY = MY * EDF \quad (3)$$

Where:

$HHV_{hc}$  → higher heating value of dry solid hydrochar [MJ/kg]

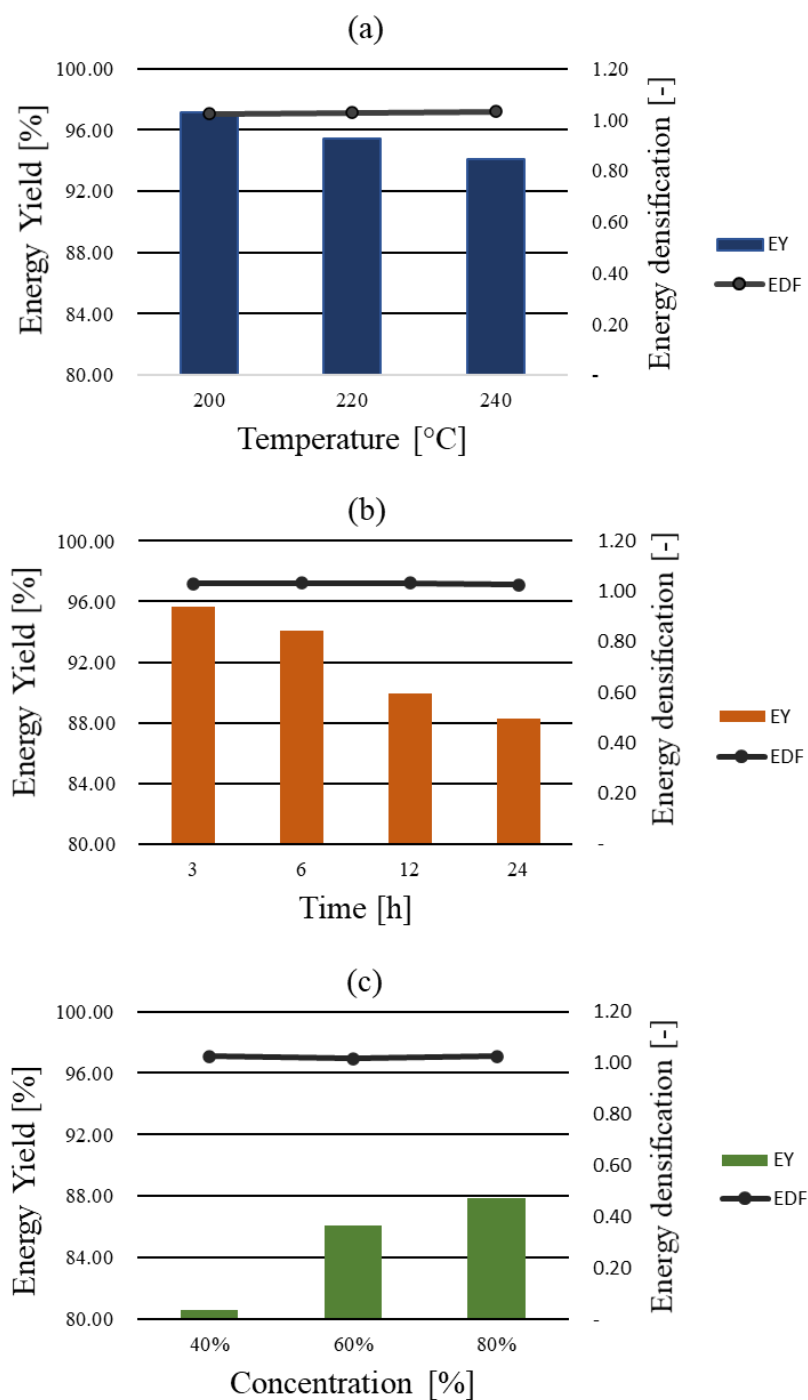
$HHV_{RL}$  → higher heating value of dry raw lignin [MJ/kg]

Regarding to the temperature and reaction time, in both sample groups high percentage values of energy yield are appreciated, with a maximum decrease between these of 3% and 8% for the temperature and time samples respectively, going from 97.13% to 94.11% for temperature samples and from 95.69% to 88.28% for time samples.

The high MY and the small increase in the HHV indicate that the energy densification achieved during the HTC process was low in the hydrochars produced from lignin. This can also be appreciated by looking the EDF line on the EY graph, Figure 12. The EDF line is practically a constant value line in 1.03 for the 3 study cases, which indicates that the difference between the HHV of the crude lignin and the hydrochar produced is almost none.

Regarding the samples L40%, L60% and L80%, and similar to reported by Uddin et al. (2013) and Arauzo et al. (2020), an opposite trend is seen, i.e., the energy yield value tends to increase as the number of recirculations or the concentration of dissolved components in the process water increases.

This is due to, although to a small extent, there is an increase in HHV as well as the mass yield. In other words, although the fuel properties of the hydrochar generated are improved, it in turn has a lower loss in its net mass throughout the hydrothermal carbonization process.



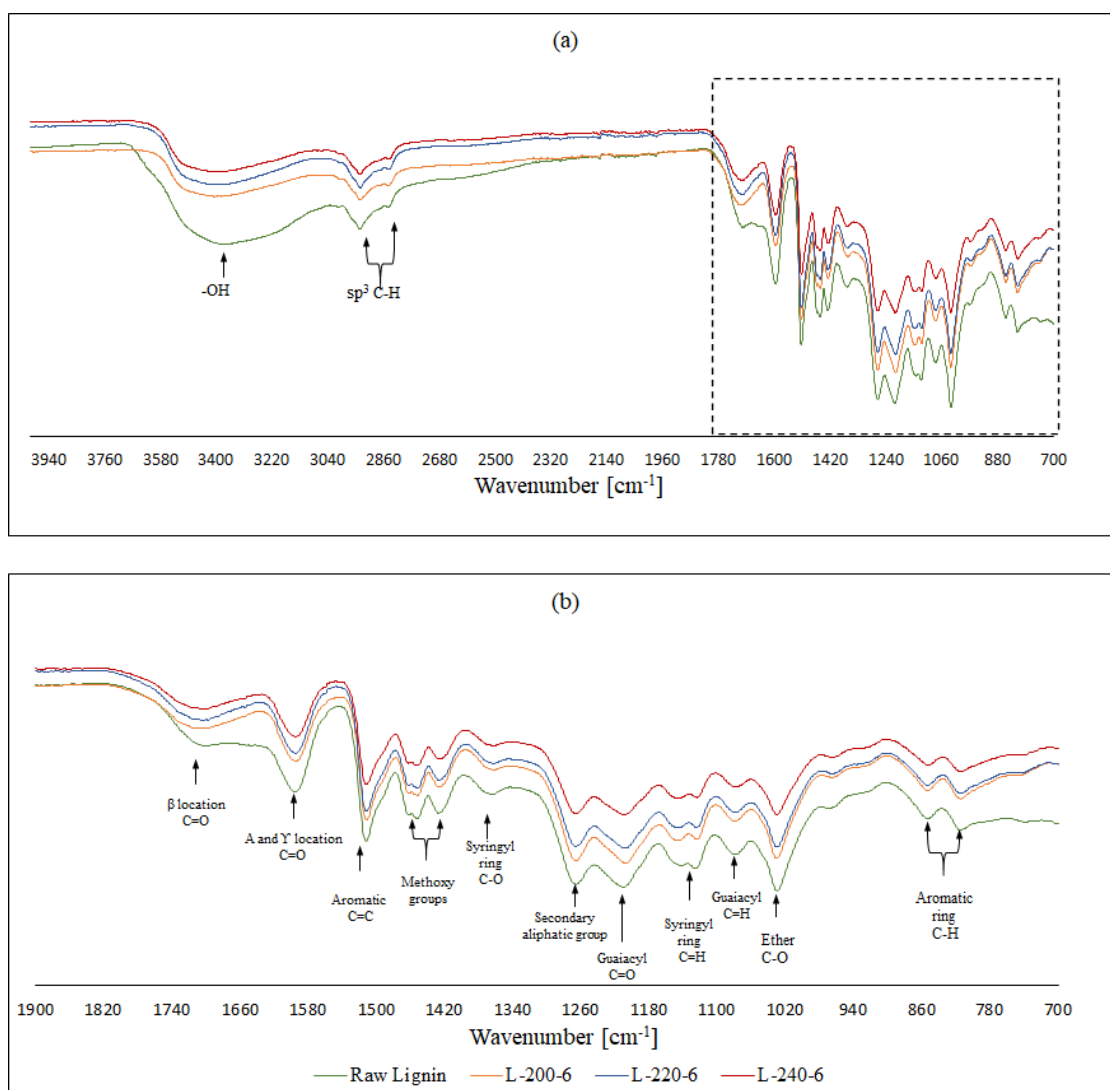
**Figure 12.** Energy yield of hydrochar as a function of: (a) temperature, (b) time and (c) PW concentration.



## 6.2 FT-IR Analysis

Fourier transform infrared (FTIR) spectra show the functional groups of the raw lignin components and the biofuels generated from it, Figure 12. The FTIR spectrum of each component showed variation in the intensities of the different peaks, which indicates changes in the composition of the functional group of the raw material as a function of the temperature, time, or concentration of the process water.

The spectrum of raw lignin is characterized by having a -OH band between 3500 and 3200  $\text{cm}^{-1}$ , this is due to the stretching vibration peak of the hydroxyl groups in the alcohol and phenol residues that exist in lignin. The small peaks at 2935 and 2842  $\text{cm}^{-1}$  are due to  $\text{sp}^3$  C-H stretching, typical vibrations of methoxy groups.



**Figure 13.** Attenuated total reflectance-Fourier transform infrared spectroscopy of raw lignin and hydrochar samples. (a) measurement of raw lignin and samples on temperature function, (b) between 1900 and 700  $\text{cm}^{-1}$ .

The absorption peaks at 1705 and 1603  $\text{cm}^{-1}$  correspond to carbonyl peaks conjugated to aromatic rings, existing at the  $\beta$  position and also at the  $\alpha$  and  $\gamma$  positions of the phenylpropane unit (Kim et al., 2017). The band at 1511  $\text{cm}^{-1}$  indicate the presence of aromatic C=C and the two bands at 1450 and 1425  $\text{cm}^{-1}$  are attributed to methoxy groups (Kim et al, 2016).

The peaks at 1359 and 1076  $\text{cm}^{-1}$  indicate the stretching vibration peak of C-O and C-H groups in the syringyl ring, respectively. Likewise, bands at 1206 and 1076  $\text{cm}^{-1}$  expose the C-O and C-H groups in the guaiacyl ring (Roman et al, 2012). Moreover, vibration peak for the secondary aliphatic groups appear at 1262  $\text{cm}^{-1}$  and ether peak is at 1028  $\text{cm}^{-1}$ . Lastly, the two peaks located at 855 and 813  $\text{cm}^{-1}$  correspond to aromatic C-H bond.

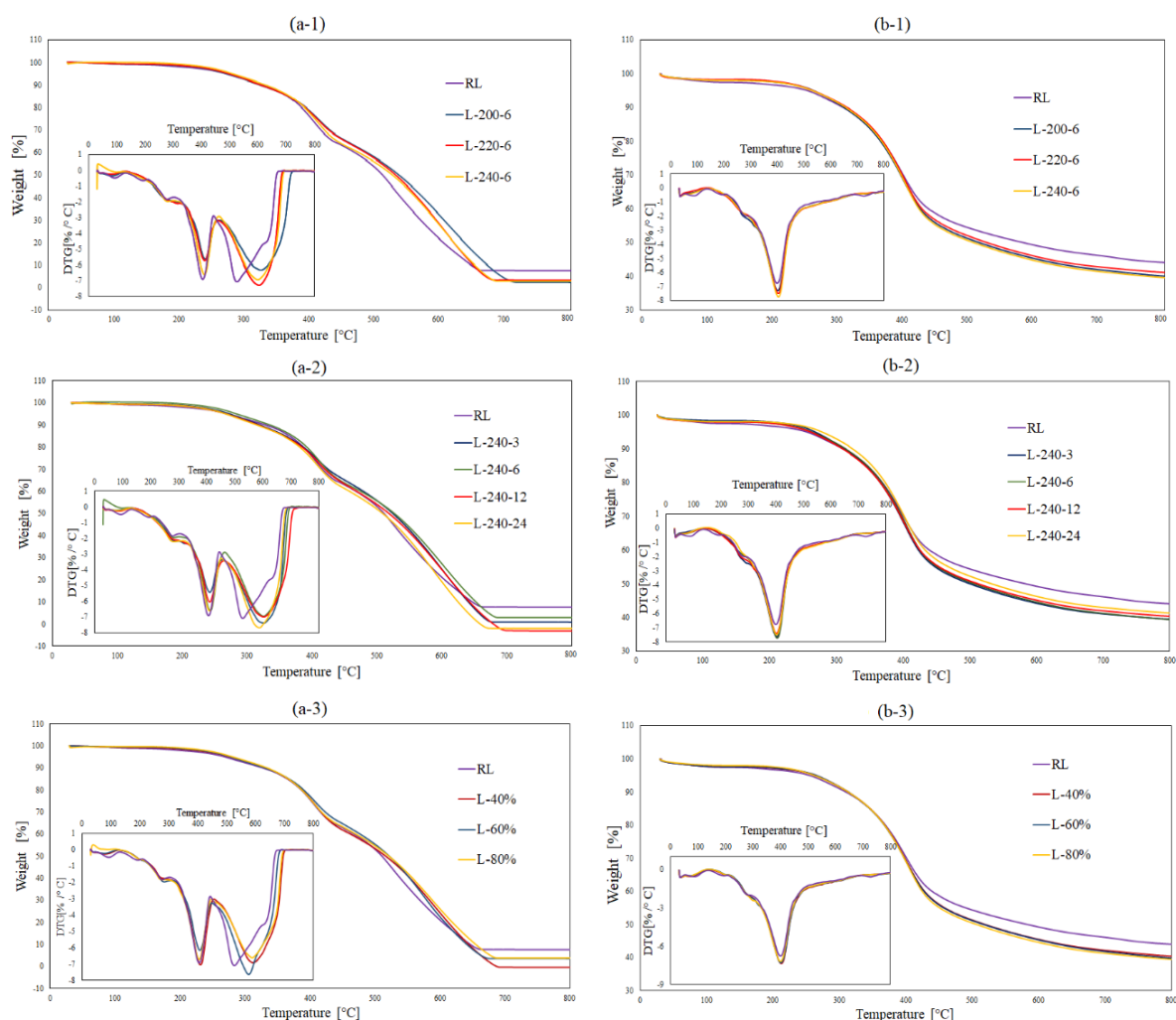
The decrease in intensity of most of the bands indicates the reduction of these functional groups in the hydrocarbon due to dealkylation and demethylation caused in the HTC process.

### 6.3 Thermogravimetric Analysis

The thermal stability and degradation profile of raw lignin and the produced hydrochar samples are shown in Figure 13. For both the air and nitrogen atmosphere, there is a small initial mass loss up to 200°C in crude lignin. This small loss of mass can be attributed mainly to the loss of light volatiles and the evaporation of moisture. For all hydrochar samples produced, the loss of mass up to this point only represents 1%, this due to the low moisture content and the partial loss of volatiles resulting from the HTC treatment.

Having its initial structure intact and without breaking of its bonds, the release of volatiles and other components in crude lignin under an inert atmosphere is not as efficient compared to hydrochar samples. This is reflected in the fact that the crude lignin reaches the thermal stability faster compared to the hydrochar samples generated and has a lower loss of mass. Under a  $\text{N}_2$  atmosphere, the primary weight loss occurs beyond 200°C, this due to above this temperature the lignin softens, and its particles fuse (Kim et al., 2017). At this point, the guaiacyl and syringyl components are removed thus changing the structure of the lignin. A small shoulder between 280 and 290°C in the inert atmosphere DTG curves is shown, corresponding to the removal of hemicellulose components remaining in the lignin (Atta-Obeng et al, 2017). The only sample where this shoulder is not present is for L-240-24 indicating that under this HTC treatment conditions the hemicellulose components were completely degraded.

Under an inert atmosphere all the samples show the main degradation takes place at temperatures between 200 and 500°C with a maximum weight loss at approximately 400°C. In general, and in accordance with previous lignin studies (Sangchoom & Mokaya, 2015), a residue of ca. 40% of non-volatilized matter at 800°C remains in all samples, because of the formation of highly condensed aromatic structures, which are likely to be the structures that form carbon when lignin is heated under oxidizing conditions. Additionally, in the TGA graph the sample L-240-24 shows the higher thermal stability compared with the other samples. Nevertheless, is sample L-240-6 that one which shows a higher release of volatile material. No significant difference is observed in any of the recirculation samples.



**Figure 14.** TGA of raw lignin and its generated hydrochar samples after HTC treatment. (a) Air atmosphere, (b) N<sub>2</sub> atmosphere.

When the samples are heated under an oxidizing condition the degradation took place at temperatures between 200 y 690 °C for most of the samples. Two main stages of thermal degradation can be identified besides the initial drying. The first stage is a moderate and stable release of volatile compounds (Sermyagina et al., 2021), which leads to a mass loss of between 37 to 40% where the maximum loss occurs between 400 and 420°C.

The second stage presumably is the release of higher molecular weight compounds, the char formation, and its subsequent combustion. In this second stage the maximum rate of weight loss occurs at temperatures between 580 and 600 °C for hydrocarbon samples, however this occurs much earlier in pure lignin, having its maximum degradation rate at 527 °C. This early degradation of the raw lignin under an oxidizing atmosphere in this stage, shows that raw lignin has a lower thermal compared to the hydrocarbon samples. At 700°C practically all the samples have reacted completely, generating the almost total loss of the remaining mass from the first stage. Just the sample L-200-6 required a temperature further of 700°C for its completely reaction. Although the behavior in the first stage for samples L-200-6 and L-220-6 is virtually the same, the first sample needs a higher temperature to achieve its complete degradation. For all the samples, their residual mass is practically 0%, since these samples have a very low level of inorganic compounds.

## 7 CONCLUSIONS

Bioenergy is projected to be one of those renewable energies that will most influence and help achieve the objectives of generating energy in a clean, sustainable, and environmentally friendly way. Bioenergy greatest advantage is being able to make use of a wide and heterogeneous variety of materials covering different types of feedstocks such as those derived from the agricultural and forestry industry, as well as the use of waste in those industries where their disposal streams have a high content of lignocellulosic biological material which is simply discarded or its potential energy use does not go beyond its incineration, as is the case of lignin in the pulp and paper industry.

Furthermore, due to the development of new technologies, especially focused on the use of these materials as a future replacement for fossil fuels or products derived from them, it is increasingly a reality and is here where the hydrothermal carbonization process has a special role in achieving the optimal use of the available biomass. HTC is projected as a promising method in the production of solid fuels from biomass regardless of its moisture content since a prior drying process is not necessary to carry out this treatment.

This work focused on the hydrothermal carbonization of lignin, and how some operational parameters of the treatment such as temperature, time and concentration of the recirculated process water could affect the performance of the process focused on the solid product. The hydrocarbon obtained showed improvements in all its properties, having a lower percentage of volatiles and humidity, as well as increasing its fixed carbon value. Likewise, the mass yield obtained is higher than that reported in earlier studies, being mainly influenced in this study by the increase in time and temperature. Nevertheless, as the concentrations of the recirculated process water increased, the mass yield showed a contrary trend increasing as the concentration increased.

Regarding some of hydrochar characteristics, a greater release of volatiles was obtained for samples L-240-6 and L-240-12 where there was a decrease of 10.8 and 13.15% respectively. Likewise, this last sample presented the best behavior in terms of the increase in fixed carbon, achieving an increase of 37.9%. Regarding the ash content, all samples had an average reduction of 75%, some of them reaching up to 0.3 wt%. The moisture content for all the hydrocarbon samples was relatively low, with an average of 1 wt%.

It is worth mentioning that despite the improvement of the previously named characteristics, the analysis of elements shows slight changes in the elemental composition of hydrocarbons. The analysis of the atomic ratios by means of the van-Krevelen diagram (Figure 9) indicates a greater decarboxylation tendency with increasing temperature and a greater dehydration tendency with increasing reaction time. Furthermore, in figure 10 it is possible to see that the hydrocarbons generated by HTC treatment have characteristics like those of coal and lignite, indicating their favorable use as solid fuel.

Regarding heating value, this had a slight increase throughout the hydrothermal treatment, being influenced to a greater extent by the rising in temperature, this having a maximum increase at a temperature of 240°C and a residence time of 6 hours. After this period, the values stabilize and beyond 12 hours it shows a decrease in its value. This decrease in HHV together with the increase of the MY under these control parameters was attributed to possible repolymerization and/or absorption of those materials that had previously been degraded to the aqueous medium.

In general, there was a good performance in the mass yield, the release of volatiles and an increase in the fixed carbon of the solid product. Likewise, pure lignin and hydrocarbons have the potential to be used as solid fuels according to the analysis carried out to the elemental ratios by means of van-Krevelen diagram.

However, the fact that a significant increase in the caloric power of the hydrocarbons produced has not been obtained compared to raw lignin, making the energy densification factor practically constant both in the variation of temperature, time and concentration, allow us to conclude that hydrothermal carbonization by itself might not be the most optimal treatment to treat lignin if the approach sought is to improve its properties, seeking to generate hydrochar with a considerable increase in its caloric properties.

## 8 RECOMENDATIONS

In the application of hydrothermal treatment in order to improve different characteristics of the biomass used, in previous investigations a variety of catalysts have been used with the aim of increasing or decreasing the pH of the reaction medium and improving or accelerating its reactions. Utilize these catalysts in the hydrothermal carbonization of lignin could not only improve its performance as a solid fuel but could also cause reactions and yields to lean more towards the formation of one or another product (liquid or solid).

Likewise, it would be of great interest not only to test the typical catalysts such as  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$ , which despite showing high effectiveness are considered "extremely dangerous" but use more "ecofriendly" catalysts such as  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$  and thus be able to make a comparison in the performance that these would have on the structure and morphology of lignin.

Since the samples showed adsorption or repolymerization behavior at reaction times greater than 12 hours, a study on the morphology and structure of these hydrocarbons would allow to know how their surface characteristics are, determining these hydrochars as possible base for adsorbing agents.

As mentioned in the main discussion of the present study, in this research a GC/MS was not carried out, which would allow us to know accurately which aromatic components of the lignin are being degraded. In the same way, a complete characterization of the liquors produced by hydrothermal carbonization will allow a better understanding of the reaction mechanisms by knowing which components have been degraded to the aqueous medium.

Having more information on the characteristics and properties of the solid and liquid product resulting from the hydrothermal carbonization of lignin, it will be much easier to determine which could be the possible applications of both the hydrocarbons produced under the conditions studied in this research, as well as the liquors, which due to their change in color once the treatment is finished, is estimated to be rich in aromatic compounds that have been degraded from the main structure of lignin.

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## Appendix I. Mass Yield

Table I. Mass yield of HTC hydrochars

Sample ID	L-200-6		L-220-6		L-240-6	
Experiment	A	B	A	B	A	B
Solid mass in [g]	25	25.26	25.37	25.17	25	25.25
Solid mass in dry [g]	25	25	25	25	25	25
Liquid volume [ml]	225	225	225	225	225	225
Solid mass out dry [g]	23.29	24.36	23.45	23.42	22.17	23.60
Mass yield [%]	93	96	92	93	89	93
Average Mass yield [%]	95		93		91	

Sample ID	L-240-3		L-240-6		L-240-12		L-240-24	
Experiment	A	B	A	B	A	B	A	B
Solid mass in [g]	25.24	25.28	25	25.25	25.28	25	25	25
Solid mass in dry [g]	25	25	25	25	25	25	25	25
Liquid volume [ml]	225	225	225	225	225	225	225	225
Solid mass out dry [g]	23.48	23.43	22.17	23.60	22.24	21.51	21.54	21.44
Mass yield [%]	93	93	89	93	88	86	86	86
Average Mass yield [%]	93		91		87		86	

Sample ID	L-40%		L-60%		L-80%	
Experiment	A	B	A	B	A	B
Solid mass in [g]	5.55	5.55	7.22	7.22	7.23	7.23
Solid mass in dry [g]	5.55	5.55	7.22	7.22	7.22	7.22
Liquid volume [ml]	50	50	65	65	65	65
Solid mass out dry [g]	4.39	4.34	6.21	6.01	6.18	6.18
Mass yield [%]	79	78	86	83	86	86
Average Mass yield [%]	79		85		86	

## Appendix II. Volatile matter

Table II. Volatile matter of raw lignin and HTC hydrochars

Sample ID	Experiment	Crucible mass [g]	Sample mass [g]	Crucible+ ash [g]	Volatile	Volatile average
Raw Lignin	A	53.0816	1.0254	53.3864	70.28%	70.93%
	B	47.7991	1.0248	48.0903	71.58%	
L-200-6	A	47.8092	1.0131	48.1514	66.22%	65.77%
		53.1214	1.0138	53.4702	65.59%	
	B	51.3176	1.0770	51.6894	65.48%	
		48.6600	1.0326	49.0135	65.77%	
L-220-6	A	33.8070	1.0539	34.1772	64.87%	64.95%
		33.6824	1.0180	34.0395	64.92%	
	B	34.2180	1.0420	34.5837	64.90%	
		39.1453	1.0655	39.5170	65.11%	
L-240-6	A	47.8076	1.0304	48.1843	63.44%	63.27%
		53.1105	1.0125	53.4815	63.36%	
	B	40.7092	1.0137	41.0819	63.23%	
		37.5571	1.0183	37.9333	63.06%	
L-240-3	A	33.6810	1.0775	34.0748	63.45%	63.78%
		34.2175	1.0121	34.5797	64.21%	
	B	42.0373	1.0318	42.4072	64.15%	
		37.1902	1.0290	37.5677	63.31%	
L-240-6	A	47.8076	1.0304	48.1843	63.44%	63.27%
		53.1105	1.0125	53.4815	63.36%	
	B	40.7092	1.0137	41.0819	63.23%	
		37.5571	1.0183	37.9333	63.06%	
L-240-12	A	47.8067	1.0451	48.2054	61.85%	61.60%
		51.3083	1.0322	51.6966	62.38%	
	B	34.2158	1.0528	34.6242	61.21%	
		36.3208	1.0190	36.7185	60.97%	
L-240-24	A	37.5554	1.0405	37.9040	66.50%	67.28%
		35.5843	1.0733	35.9377	67.07%	
	B	39.1424	1.0210	39.4757	67.36%	
		34.2172	1.0327	34.5456	68.20%	
L-40%	A	40.7101	1.0064	41.0325	67.97%	68.04%
	B	35.5862	1.0133	35.9093	68.11%	
L-60%	A	37.1908	1.0680	37.5327	67.99%	67.84%
	B	37.5574	1.0110	37.8840	67.70%	
L-80%	A	36.3203	1.0100	36.6490	67.46%	67.28%
	B	42.0376	1.0573	42.3854	67.10%	

### Appendix III. Ash content

Table III. Ash content of raw lignin and HTC hydrochars

Sample ID	Experiment	Crucible mass [g]	Sample mass [g]	Crucible+ ash [g]	Ash	Ash average
RL	A	14.8730	1.0048	14.8846	<b>1.15%</b>	1.17%
	B	16.0263	1.0197	16.0383	<b>1.18%</b>	
L-200-6	A	15.7215	1.0224	15.7278	<b>0.61%</b>	0.53%
		15.6884	1.0288	15.6939	<b>0.53%</b>	
	B	160,285	10,604	160,331	<b>0.43%</b>	
		140,561	10,586	140,619	<b>0.55%</b>	
L-220-6	A	15.6896	1.0393	15.6931	<b>0.34%</b>	0.34%
		15.3879	1.2085	15.3926	<b>0.39%</b>	
	B	224,209	10,392	224,239	<b>0.29%</b>	
		150,257	10,988	150,295	<b>0.35%</b>	
L-240-6	A	22.4206	1.0343	22.4237	<b>0.30%</b>	0.32%
		22.4206	1.0291	22.4236	<b>0.29%</b>	
	B	7.4507	1.0228	7.4533	<b>0.25%</b>	
		15.6729	1.1094	15.6778	<b>0.44%</b>	
L-240-3	A	15.4635	1.0740	15.4667	<b>0.30%</b>	0.32%
		14.8711	1.0388	14.8750	<b>0.38%</b>	
	B	15.7130	1.0270	15.7160	<b>0.29%</b>	
		15.3746	1.0204	15.3779	<b>0.32%</b>	
L-240-6	A	22.4206	1.0343	22.4237	<b>0.30%</b>	0.32%
		22.4206	1.0291	22.4236	<b>0.29%</b>	
	B	7.4507	1.0228	7.4533	<b>0.25%</b>	
		15.6729	1.1094	15.6778	<b>0.44%</b>	
L-240-12	A	15.1796	1.1294	15.1841	<b>0.40%</b>	0.40%
		15.4774	1.1467	15.4813	<b>0.34%</b>	
	B	15.1754	1.0554	15.1797	<b>0.41%</b>	
		15.5561	1.0836	15.5612	<b>0.47%</b>	
L-240-24	A	13.6100	1.0766	13.6135	<b>0.33%</b>	0.30%
		7.4515	1.0687	7.4547	<b>0.30%</b>	
	B	15.7105	1.0067	15.7134	<b>0.29%</b>	
		14.0534	1.0151	14.0565	<b>0.31%</b>	
L-40%	A	15.0269	1.0003	15.0315	<b>0.46%</b>	0.45%
	B	15.7127	1.0021	15.7171	<b>0.44%</b>	
L-60%	A	15.4641	1.0059	15.4678	<b>0.37%</b>	0.35%
	B	15.5573	1.0237	15.5606	<b>0.32%</b>	
L-80%	A	14.0566	1.0243	14.0607	<b>0.40%</b>	0.36%
	B	13.6096	1.0125	13.6129	<b>0.33%</b>	

## Appendix IV. Moisture content

Table IV. Moisture content of raw lignin and HTC hydrochars

Sample ID	Experiment	Moisture	Moisture Average
Raw Lignin	A	8.6%	8.6%
	B	8.7%	
L-200-6	A	1.1%	1.1%
		1.1%	
	B	1.1%	
		1.1%	
L-220-6	A	0.9%	1.0%
		1.0%	
	B	1.0%	
		0.9%	
L-240-6	A	1.3%	1.0%
		1.3%	
	B	0.8%	
		0.8%	
L-240-3	A	1.0%	1.1%
		1.0%	
	B	1.3%	
		1.0%	
L-240-6	A	1.3%	1.0%
		1.3%	
	B	0.8%	
		0.8%	
L-240-12	A	1.0%	1.0%
		1.0%	
	B	0.9%	
		1.0%	
L-240-24	A	1.1%	1.0%
		1.1%	
	B	0.9%	
		0.9%	
L-40%	A	1.85%	2%
	B	2%	
L-60%	A	1%	1%
	B	1%	
L-80%	A	1%	1%
	B	1%	

## Appendix V. Fixed carbon

Table V. Fixed carbon of raw lignin and HTC hydrochars

Sample ID	Experiment	Fix Carbon	Fix Carbon Average
Raw Lignin	A	28.57%	27.90%
	B	27.24%	
L-200-6	A	33.17%	33.70%
		33.87%	
	B	34.09%	
		33.69%	
L-220-6	A	34.79%	34.71%
		34.69%	
	B	34.81%	
		34.54%	
L-240-6	A	36.26%	36.41%
		36.35%	
	B	36.51%	
		36.50%	
L-240-3	A	36.25%	35.90%
		35.41%	
	B	35.56%	
		36.36%	
L-240-6	A	36.26%	36.41%
		36.35%	
	B	36.51%	
		36.50%	
L-240-12	A	37.75%	37.99%
		37.28%	
	B	38.38%	
		38.56%	
L-240-24	A	33.18%	32.41%
		32.63%	
	B	32.36%	
		31.49%	
L-40%	A	31.58%	31.51%
	B	31.45%	
L-60%	A	31.65%	31.81%
	B	31.98%	
L-80%	A	32.14%	32.36%
	B	32.57%	

## Appendix VI. Higher heating value

Table VI. Higher heating values of raw lignin and HTC hydrochars

Sample ID	Experiment	HHV calorimeter	HHV Average	HHV dry basis	LHV dry basis	EDF	EY %
Raw Lignin	A	28.57	27.90	26.98	26.31	-	-
	B	27.24					
L-200-6	A	33.17	33.70	27.65	26.34	1.02	97.13
		33.87					
	B	34.09					
		33.69					
L-220-6	A	34.79	34.71	27.76	26.51	1.03	95.40
		34.69					
	B	34.81					
		34.54					
L-240-6	A	36.26	36.41	27.88	26.74	1.03	94.11
		36.35					
	B	36.51					
		36.50					
L-240-3	A	36.25	35.90	27.80	26.50	1.03	95.68
		35.41					
	B	35.56					
		36.36					
L-240-6	A	36.26	36.41	27.88	26.63	1.03	94.11
		36.35					
	B	36.51					
		36.50					
L-240-12	A	37.75	37.99	27.89	26.76	1.03	89.92
		37.28					
	B	38.38					
		38.56					
L-240-24	A	33.18	32.41	27.70	26.39	1.03	88.28
		32.63					
	B	32.36					
		31.49					
L-40%	A	31.58	31.51	27.66	-	1.02	80.61
	B	31.45					
L-60%	A	31.65	31.81	27.44	-	1.02	86.05
	B	31.98					
L-80%	A	32.14	32.36	27.68	-	1.02	87.87
	B	32.57					