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School of Energy Systems

Degree program in Sustainability Science and Solutions

BH60A5000 Master's Thesis

ANALYSIS OF LIQUORS FROM BIOMASS HYDROTHERMAL CARBONIZATION TO
DETERMINE FEASIBILITY OF FURTHER ENERGY AND/OR MATERIAL RECOVERY

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ABSTRACT

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Hydrothermal Carbonization is a promising and relatively novel biomass conversion technology which can transform highly humid biomass into useful coal-like solids that can be utilized for energy applications and also as feedstock for bio-products manufacture. However, the aqueous byproduct of the process may be subject of concerns from the sustainability perspective given the possible high costs of treatment and environmental affectations, especially when the technology is scaled up.

Despite few authors have examined in detail the HTC liquors, the research on HTC technology has focused primarily in the optimization and improvement of the hydrochar. This work is intended to analyze the composition of the liquid phase resulting from the HTC treatment of various biomasses at different temperatures, compare with data obtained by other researches and study the possible treatment pathways for the HTC liquors. Implementing recirculation of the liquids and anaerobic digestion stand out as solutions that would reduce the environmental impacts associated while improving the efficiency of the overall HTC process.

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*To my parents Martha and Francisco,
for their uninterrupted and restless fight.*

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LIST OF SYMBOLS

[°C]	Celsius Degrees
[mg]	Milligrams
[g]	Grams
[kg]	Kilograms
[L]	Liters
[wt%]	Percentage in weight basis
[h]	Hours
[kJ]	Kilojoules
[MPa]	Mega-Pascals

ABBREVIATIONS

GHG	Green House Gases
TOC	Total Organic Carbon
IC	Inorganic Carbon
TC	Total Carbon
TN	Total Nitrene
TP	Total Phosphorus
COD	Chemical oxygen demand
NVR	Non-Volatile Residues

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1 INTRODUCTION

1.1 General Introduction



Figure 1 Doomsday Clock (Bronson, Eden et al. 2018)

The ‘*Doomsday Clock*’ is an iconic symbol that represents metaphorically how close humankind is from its total collapse or irreversible global catastrophe, symbolized in the clock by midnight. The time in this clock is set by a board of scientists and analysts of the ‘*Bulleting of the Atomic Scientists*’ magazine, including 15 Nobel laureates (Bever 2018), accordingly to global events and/or the decisions and behavior of world’s leaders and governments.

This widely known icon was created in 1947 just after WWII. Back then, the clock was set at 7 minutes to midnight by the magazine’s board based on the concern and panic that had spread within the scientific community towards the nuclear weapons dangers. Since then and until 2007, the clock had been moved forward and backwards only in accordance to the access of nations to massive destruction weapons and the willingness of their governments to use them. The further the clock has ever been set from midnight was 17 minutes, it occurred in 1991 when cold war ended (Bronson, Eden et al. 2018).

In 2007, for the first time, climate change effects were considered by the magazine’s board as a potential cause of global disaster along with the latent nuclear menace. As a result, the clock was moved 2 minutes ahead from its previous point and set at 5 minutes to midnight. After that, the minutes hand of the clock was moved slightly back due to global climate-change-related activity and initiatives like UNFCCC conference in

Copenhagen 2009 for example, along with other reasons. However, during the last 4 years the clock has been moved constantly forward until reaching 2 minutes to midnight in January of 2018, same position it was in 1953 when USA and URSS developed and tested Hydrogen bombs (Bronson, Eden et al. 2018).

Two minutes is the closest point in which the clock has ever been from midnight. The Bulletin of the nuclear scientist board agreed to set this new time considering -within other reasons- that the response of governments to climate change has been insufficient. Additionally, the board considered the withdrawn of USA from Paris agreement and the global warming denial by some powerful leaders and policymakers (Bronson, Eden et al. 2018).

The ‘Doomsday Clock’ is relevant to the context of this thesis given the fact that it is a graphical representation that illustrates the standpoint of scientific community towards climate change and geopolitical situations, which is expressed in terms of the level of risk at which humanity’s existence is. Therefore, it is a way to explain the huge urgency and importance of even the smallest actions executed to mitigate climate change.

A clear majority of the scientific and academic community around the world agrees in identifying the accumulation of anthropogenically-generated Green House Gas (GHG) Emissions as the main cause of global warming. NASA claims that more than 97% of scientists that have recently published articles on climate change ensure that global warming is highly likely originated by mankind activities(NASA 2018b).

Thanks to the analysis of gases trapped in ancient ice, scientists are able to track the concentrations of gases in the atmosphere back to hundreds of thousands of years ago (NASA 2018). According to IPCC, the anthropogenic emissions have been growing since pre-industrial revolution times and the current concentration of CO₂ in the atmosphere is the highest in 800.000 years at least (WGIII IPCC 2015). Figure 2 shows the historical concentrations of CO₂ established by NASA, as noticed, the levels of CO₂ in the atmosphere have grown faster than ever during the last couple of centuries.

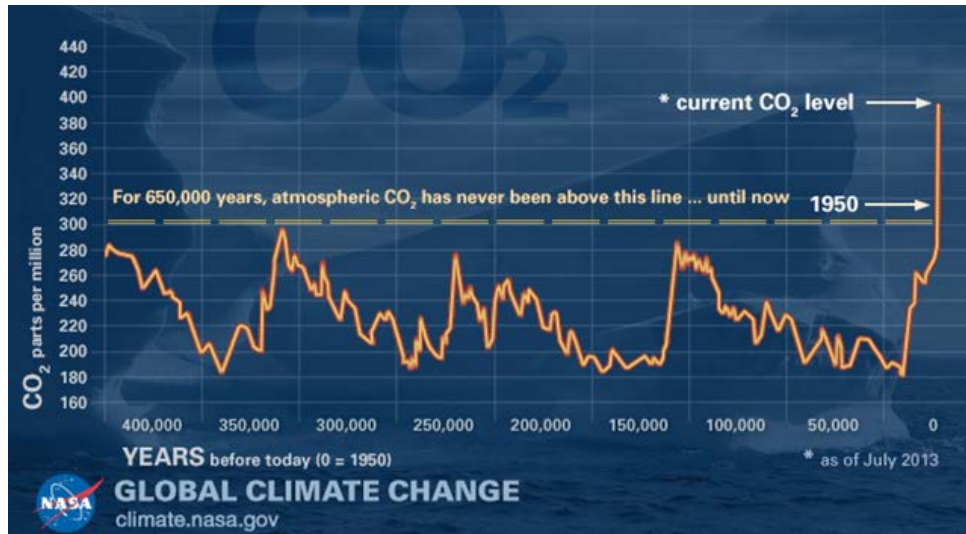


Figure 2 Historical Concentration on CO_2 in the Atmosphere (NASA 2018a)

As settled, this extremely high concentration of CO_2 in the atmosphere has caused a rise of the global average temperature which in 2012 had increased between 0.65 and 1.06 $^{\circ}\text{C}$ in comparison to 1880. Moreover, each one of the last three decades has been warmer than the previous one and the temperatures are the highest registered since 1850 (WGIII IPCC 2015). Figure 3 shows the increment of the temperature anomaly since 1850, the steep increasing trend in the last 50 years is evident.

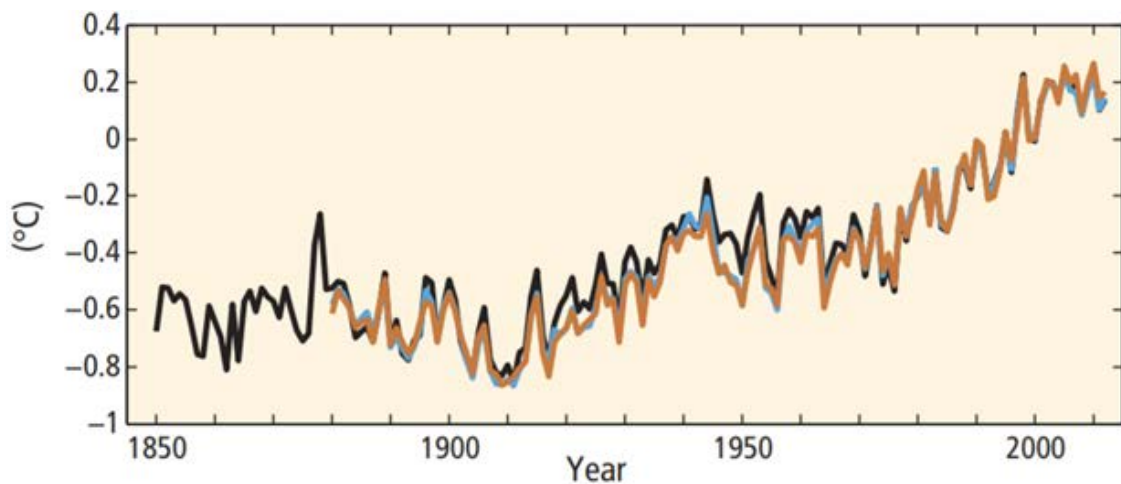


Figure 3 Globally Averaged Combine Temperature Anomaly (WGIII IPCC 2015)

The signs of climate change are visible and generally the affectations are relatively stronger on poor populations around the world, especially in tropical areas. The manifestations include erratic weather patterns, more extreme weather events like storms and hurricanes, more droughts and heat waves, stronger rain seasons, etc. This causes

damages in residential areas and infrastructure such as roads and water and electricity supply facilities; it also triggers public health issues and affects crops causing food prices increases, diminishing food security. These changes are expected to continue and become more drastic in the upcoming years (Karl, Melillo et al. 2009).

Figure 4 shows the contributions of the main economic sectors to GHG emissions in 2010, as seen the sectors with highest GHG emissions are Heat and power production along with Agriculture, forestry and other land uses (AFOLU). With roughly equal contributions, the emissions from these two sectors along with 'other energies' sector account for nearly 60% of the total GHG emissions. The indirect emissions shown in the figure refer to the sectors that consume the Heat and Electricity generated, hence, the emissions of the energy sector are allocated.

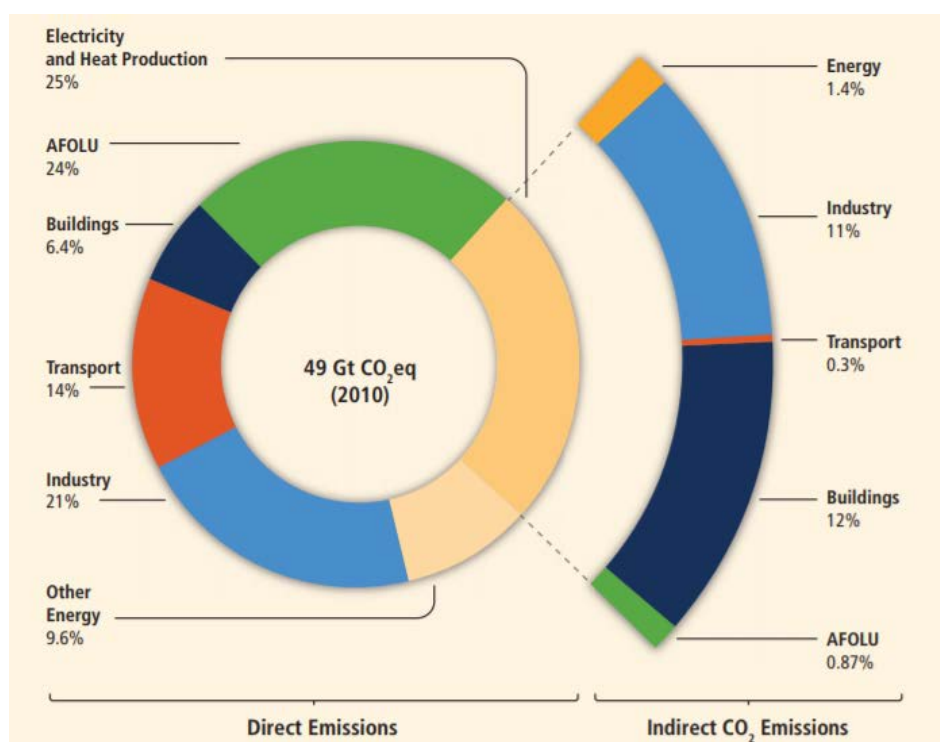


Figure 4 Contributions of Economic Sectors to GHG Emissions (WGIII IPCC 2015)

As a result, the energy sector is the focus of the efforts to combat climate change. An accelerated implementation of renewable and sustainable energy technologies is essential to slowdown global warming fast enough to limit the global rise of temperatures below 2 °C, as established by the goals set by Kyoto Protocol and Paris Agreement.

But the truth is that energy sector still relying on fossil fuels (oil, coal, natural gas) and currently Renewable energy Resources (RES) only account for 15% of the global primary energy supply. However, nowadays renewable energy technologies such as wind, hydro, solar PV, geothermal and bioenergy make possible to provide energy at competitive prices in comparison to fossil fuels (IRENA 2017).

The root of the problem is highly complex, it involves political, economic, social and technical factors that hinder the access to renewable and sustainable primary energy resources and their development.

From the technical perspective, the availability of the renewable resources is probably the main issue, especially in the case of wind, geothermal and hydro, which are only accessible in specific geographical locations, not only because natural reasons, but also because of policies, regulations and public acceptance. Furthermore, except for geothermal, these RESs are significantly dependent on weather conditions. On the other hand, PV is certainly available worldwide but also intermittently due to weather circumstances and naturally because of nights.

Biomass as energy resource is widely available, easily storable, considered carbon neutral or even carbon negative if CCS (Carbon Capture and Storage) is employed. Heat and power from biomass can be generated in accordance to the demand and biomass is sustainable when exploited under given restrictions and controls. For these reasons, the utilization of bioenergy is essential to meet world's climate goals.

However, biomass for heat and power generation also involves challenges. For example, hazardous emissions, low energy and bulk density, fouling and sintering risks, high moisture content, etc.

With the aim of overcoming the technical challenges, biomass energy conversion technologies other than direct combustion have been developed during the last couple of decades. The approaches include pyrolysis, gasification, torrefaction and hydrothermal carbonization. In general, these technologies are able to increase the energy density of the biomass by producing derived solid and/or gaseous fuels which can be fired in regular fossil fueled boilers or engines. In consequence the overall efficiency would be higher in comparison to conventional biomass fired or cofired boilers, while reducing GHG and other hazardous emissions if compared to fossil fuels burning.

Hydrothermal Carbonization (HTC) is thermochemical conversion process that occurs at mild temperature in an aqueous medium, under high autogenous pressures. It differentiates from other technologies mainly due to its remarkable flexibility and its capability of transforming into coal-like fuel or 'hydrochar' highly humid biomass materials with up to 90% of moisture content, without any previous treatment. Therefore, the feedstock could include several kinds of biomass such as sewage sludge, agricultural wet wastes, algae, food processing wastes, etc. (Lucian, Fiori 2017). The hydrochar can be employed for heat and power generation and also as feedstock for products manufacture.

HTC treatment delivers three different products, solid phase or hydrochar, liquid phase called 'HTC liquors' and gaseous phase. Since the main objective of the treatments is to produce hydrochar with higher calorific value and density than the untreated raw biomass, the development and research of HTC treatment has been focused mainly in optimizing the properties of the solid phase.

Nevertheless, some researchers have determined the composition of the HTC liquors after treating different kind of biomasses, in order to find possible applications for these liquids, such as biofuels production or bioproducts manufacture.

More attention should be paid to HTC liquors, as the technology is scaled-up, the water footprint of the conversion process might become considerable, which could jeopardize the sustainability of the energy and/or materials produced through this technology. As an example, in Ingelia SL. HTC plant, one of the currently existing HTC commercial plants, the liquors are treated using inverse osmosis to obtain purified water that can be utilized for crops irrigation or simply incorporated to a watershed (Ingelia 2018). However, this method involves the consumption of energy which would reduce the overall efficiency of the process. One feasible solution could be to carry out energy recovery processes on the HTC liquors, increasing the overall efficiency of heat and/or power generation as a result. However, this requires the collection and analysis of data from laboratory and commercial plants, given that further energy recovery may not be always feasible, other solutions such as material recovery should be studied, this would drive the HTC process onto a circular economy /model.

1.2 Objective of the thesis

This work has three main objectives: First, to identify main components and physical characteristics of the hydrothermal carbonization liquors resulting from the treatments performed at LUT of different biomasses commonly found in South America treatment, results of analyses available in the literature and data collected from an HTC industrial Plant. Second, to determine the feasibility of different pathways of HTC liquors treatment, including energy and materials recovery. And finally, to recommend the adequate treatment pathways in order to exploit possible attributes and/or reduce the environmental impacts.

In order to accomplish the main objectives, a sequence of intermediate goals or milestones have to be reached. In first place, HTC treatment procedures are going to be performed in the different Biomasses, parameters of the treatments are going to be changed in order to study the incidence on the final results. Subsequently, the HTC liquors obtained will be subject of a series of chemical and physical tests in order to obtain the values for the relevant physicochemical characteristics. And finally, the data obtained is going to be analyzed from energy recovery and environmental perspectives

1.3 Scope of the Thesis

The chemical and physical analyses of this thesis are limited to hydrothermal carbonization of Coffee wood, Coffee parchment, Bamboo and Eucalyptus, species commonly found in Latin America. The treatment parameters such as temperature and residence time will be described in section 6.3. However, the literature review part does not have a specific focus, composition of different kinds of biomasses will be analyzed.

The solid and gaseous products of hydrothermal carbonization as well as their composition, characteristics and possible utilization are not going to be object of study in this thesis. Solely the liquid part is going to be analyzed.

Likewise, this thesis is focused in studying the feasibility of water treatment, material and energy recovery of HTC liquors; in the case of material recovery, only its utilization as soil enhancement substance is going to be studied.

2 BACKGROUND

2.1 Biomass and Bioenergy

The European parliament, in the directive 2009/28/EC, defines biomass as *“The biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste”* (Piebalgs 2009).

Generally speaking, biomass denotes the organic matter originated or derived from living or recently death organisms, plants or animals; this definition excludes fossilized organic matter and soils (EESI 2018). In the energy context, biomass refers to the matter described above as well as municipal and industrial waste that can be utilized as combustible material or feedstock for fuels production (Fantini 2017).

The energy stored in biomass materials is called ‘bioenergy’, this energy is seized through different technologies such as direct combustion and fuels refining (Biofuels). Direct combustion stands as the most utilized and mature technology, biomass can either be treated to reduce size and improve quality and then fed into boilers or transformed to increase its energy density prior combustion (palletization). Biomass can be mixed with fossil fuels (co-firing) in low rates without any adaptation of the fossil fuel fired boilers, while for higher mixing rates adaptations could be needed or even different boiler designs.

Besides combustion, other technologies have been developed to harness energy from biomass. These technologies such as pyrolysis, gasification, torrefaction and HTC have arisen as solutions to technical and logistic challenges involved in bioenergy utilization, especially in combustion. This is going to be covered more in detail in section 2.4.

2.1.1 Classification of Biomass

The definition of biomass gathers a large range of substances, they can be classified according to different criteria, some authors classify biomass in accordance to its source into the following groups:

- Forest: All the products or byproducts of forestry activities. Trees, wood, bark, logging residues, thinning residues, sawdust, timber slash and mill scrap, etc. (Fantini 2017).
- Agriculture: Not edible materials that remain after harvesting and processing at farms food and/or energy crops products (Alternative Energy Tutorials 2018). Roots, stems, food grain, bagasse, corn stalks, wheat straw, seed hulls, nutshells, rice straw, etc.
- Urban and suburban Waste: All biologically-originated waste materials produced within municipalities or settlements. MSW, sewage sludge, refuse-derived fuel, food waste, waste paper, urban wood waste, waste cooking oil, trap grease, etc. (EESI 2018).
- Energy Crops: Agricultural products intended for bioenergy production exclusively. Switchgrass, miscanthus, willow, algae, poplars, corn, sugarcane, soybean, canola, oil palm, etc.
- Industrial Waste: Effluent of waste from industrial activity like food, paper, manufacture of goods, etc.
- Biological: waste from farms, slaughterhouses, fisheries. Animal waste, tallow, fish oil, manure, etc.(Fantini 2017).

Figure 5 Shows an illustration of the variety of biomass sources. As depicted, biomass can be obtained as a direct product or byproduct of a large range of human activities.



Figure 5 Sources of Biomass (Alternative Energy Tutorials 2018)

The European committee of standardization classified biomass feedstocks according to their origins in the following categories (Fantini 2017):

- **Woody Plants:** Characterized by over ground perennial stems coated by a bark layer. These plants contain wood, which consists of packed fibers of cellulose and lignin.
- **Herbaceous Plants:** In these plants the stem dies down when the growing season finishes, they do not contain wood, instead their structure consists of loosely bounded fibers of lignin and cellulose, therefore, the lignin content is much lower than in woody plants.
- **Aquatic Plants:** Plants that grow under water such as algae.
- **Wastes:** This category includes all kind of wastes like animal waste, RDF, sewage, etc.

2.2 Historical Role of Bioenergy

Biomass, mostly in the form of wood, is the oldest primary energy resource used by mankind, its usage can be tracked back at least 300 thousand years, when primitive humans began using fire for cooking and heating. The mastery of fire allowed our ancestors to create safer and larger settlements and it improved their adaptability to rough weather conditions. Moreover, the usage of fire led to early methods of crafting and materials transformation (Bithas, Kalimeris 2016). Hence, the ability of controlling fire, fueled by biomass, was a key aspect in human evolution. Furthermore, according to the “Cooking hypothesis”, proposed by Richard Wrangham, the harnessing of fire dates back to 1.8 million years ago and it was likely the main cause of the human evolution from ‘Homo Habilis’ to ‘Homo Erectus’ (Miller 2017).

During the first phase in the evolution of energy resources, biomass was the only primary energy source used to satisfy human needs, this period is known as ‘Organic Energy Economy’ (Bithas, Kalimeris 2016). The Organic Energy economy era ended in 1769 with the invention of the steam engine, which was the main precursor of the industrial revolution. Then, technological developments enabled advances in coal mining, boosting the utilization of coal as fuel. Due to its higher energy density, coal surpassed Biomass becoming the main primary energy resource in the 19th century (Zou, Zhao et al. 2016).

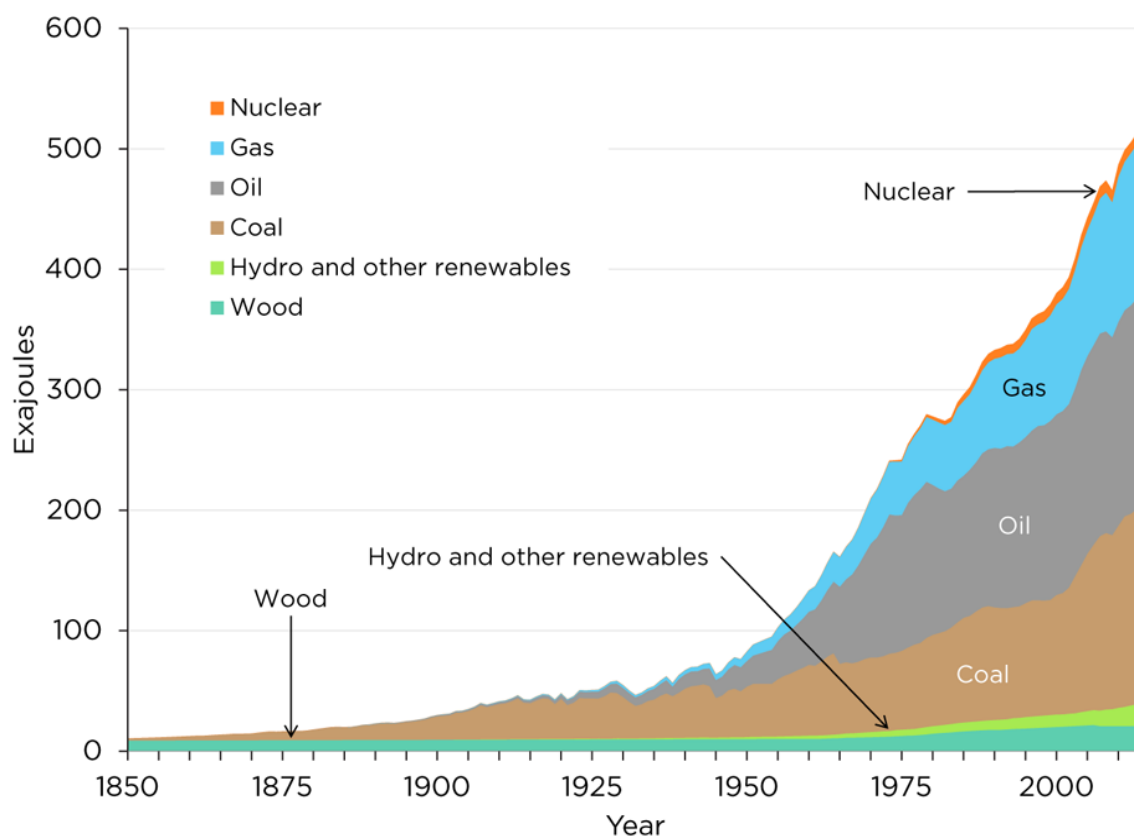


Figure 6 Evolution of World Primary Energy Consumption from 1850 to 2014 (BP 2017)

Figure 6 Shows the evolution of the shares of primary energy resources in world's energy mix consumption since the industrial revolution to nowadays. As described, the utilization of biomass as energy source has not increased significantly in comparison to fossil fuels (Coal, Oil, Gas) which utilization has grown drastically and steadily. According to the graph, oil and coal remain as the most consumed primary energy sources. This fact can be also noted in Figure 7, which shows Oil and Coal with contributions to global energy consumption of 38% and 21% respectively, biomass accounts for a 14%, considering heat and power generation as well as transportation fuels. Therefore, biomass still as the most relevant renewable energy source.

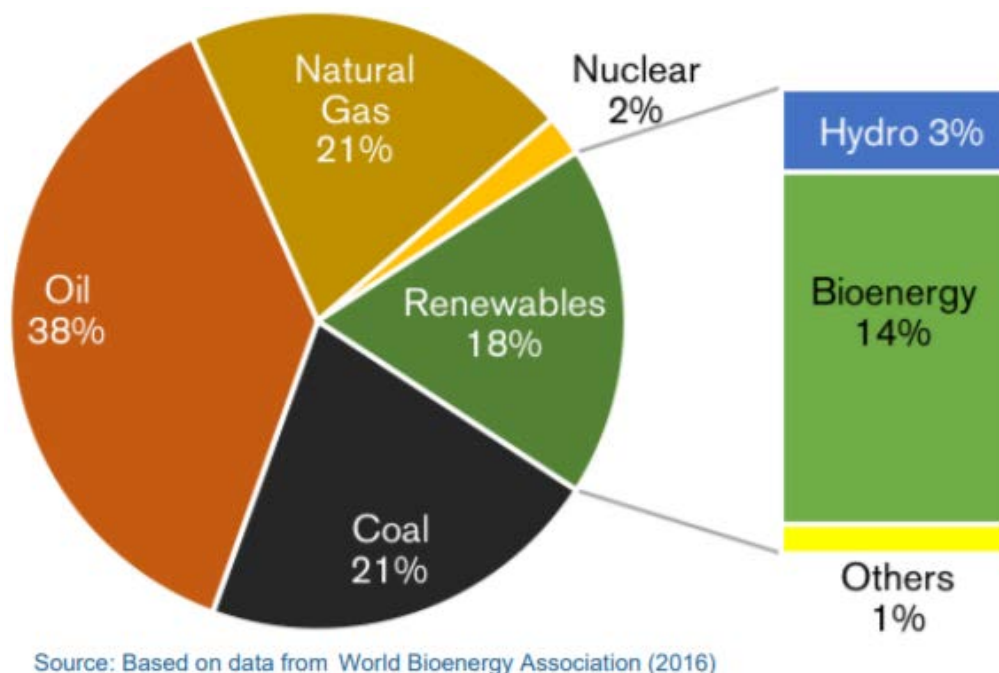


Figure 7 Shares of World's Final energy Consumption in 2013 (Kummamuru 2016)

2.3 Biomass in Modern Energy Systems

Given the world's targets regarding climate change mitigation adopted in Kyoto Protocol, as well as the necessity of improving the equality of energy supply globally in an increasingly energy intensive world, biomass has recovered the prominence it lost against fossil fuels during the industrialization. Nowadays Biomass represents a very valuable option as primary energy source as well as feedstock for products manufacture (bioproducts). As stated before, bioenergy accounts for 14% of the world's energy consumption (see Figure 7), which makes it the Renewable Energy Source (RES) with the largest share in global energy mix. In addition, bioenergy is the most flexible RES, since biomass can be directly used as a fuel for heat and power generation or refined and converted into different energy carriers, such as gaseous, liquid or solid biofuels (World Energy Council 2016). Figure 8 depicts the contribution of different forms of bioenergy to its share in world's total energy supply, as shown, fuelwood still holds the biggest contribution with 68%, followed by charcoal and black liquor with 10% and 7% respectively.

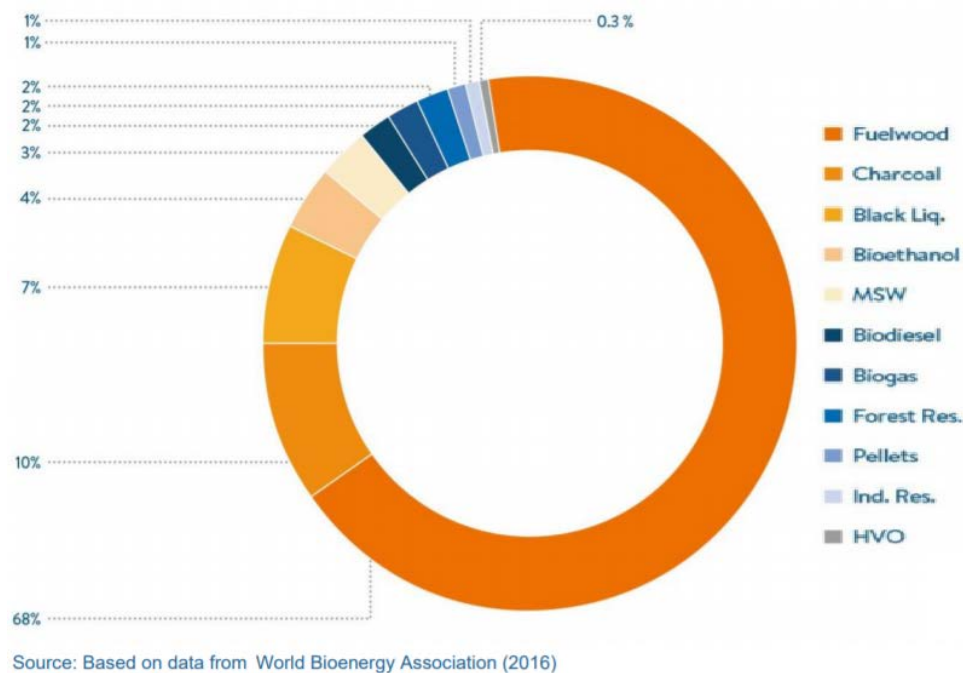


Figure 8. Utilization of Biomass Resources in World's Energy Supply 2013 (Kummamuru 2016)

In addition to its flexibility, bioenergy is also a relevant resource due to its abundance. The estimated amount of energy from biomass that can be sustainably exploited worldwide is 100 EJ/a, which is equivalent to around 30% of the total global energy consumption (Parikka 2004). Moreover, the development of new and more efficient technologies could rise this potential significantly. Nevertheless, it is important to point out that Biomass despite being renewable and abundant, is a finite energy resource, therefore its exploitation must follow some guidelines and constraints.

The utilization of bioenergy is dominated by heat and power generation sectors. Currently the highest growth of bioenergy markets occurs in European Union, North America and Southeast Asia. Advanced biomass combustion and cofiring technologies have reached maturity becoming highly efficient and reliable. Moreover, the utilization of biomass wastes for power generation has become also more efficient and new technologies with high potentials are being developed such as gasification, torrefaction and Hydrothermal Carbonization. All of this has resulted in competitive costs of energy (IEA Bioenergy 2007).

2.4 Sustainability of Bioenergy

2.4.1 Climate Change Mitigation

In terms of its contribution to climate change mitigation, bioenergy is subject of constant debate and complex analysis, especially regarding the use of forest biomass for heat and power generation. When considering forest bioenergy as a replacement for fossil fuels like coal and natural gas, the reductions are calculated between 55% and 98% in GHG emissions per kWh of electricity, if there is no change of land use. These reductions depend on feedstocks, fertilizers, harvesting technologies and logistics (European Climate Foundation, Södra et al. 2010).

Bioenergy is generally defined as Carbon neutral, this is because the CO₂ emissions released to the atmosphere during the combustion of biomass were earlier removed from it by the biomass during its growth; in addition, if more biomass grows after harvesting, then the CO₂ emissions are going to be absorbed again. Therefore, there are not net carbon additions to the atmosphere. Nevertheless, this re-absorption process requires periods of time or “Carbon Payback Periods” that could take hundreds of years, creating “Carbon Debt” (Erbach 2017).

Bioenergy exploitation must be carried out under policies and restraints that have to be established by governmental authorities. In the European Union for instance, the European Commission considers the GHG emissions from bioenergy equal to zero in the energy sector, but considered and added to the agricultural, forestry and land use sectors. These emissions are to be estimated taking into account the lifecycle of biomass production, including fertilizers, energy consumption of machinery, transport, land use change, etc. (Erbach 2017).

The reduction of GHG emissions resulting from the usage of bioenergy can differ drastically, in fact, using biomass could even have prejudicial effects on climate change mitigation. As a result, the EU renewable energy directive establishes the sustainability criteria that must be satisfied by bioenergy plants in order to consider them as contributive to the renewable energy targets (Erbach 2017), these requirements are:

- The GHG emission reduction should reach at least 35% in relation to the emissions of fossil fuels. This minimum limit increased to 50% in 2018. In addition, new power plants should reach 60% reduction.
- Land which are considered carbon stock like wetlands and forests, cannot be transformed to areas dedicated to produce biofuels.
- Highly biodiverse areas cannot be used for biofuels production.

Brazil, the world's biggest producer of sugarcane-based ethanol(Hofstrand 2009), could be considered as an example case of bioenergy production controls in Latin-America, this country implemented the so called "Agro-ecological zoning" with areas assigned to sugarcane production which can be expanded within these zones without restrictions. The lands belonging to the zones have been either used for agricultural production or they are degraded. In addition, the Amazon regions cannot be used for bioenergy feedstock production (Euroelectric 2011).

2.4.2 Water Use

The water footprint of bioenergy is substantial in comparison with other energy resources due to the high water-demand of cultivation, growing and transformation processes of biomass. However, the difficulties and possible impacts of bioenergy regarding water use are similar to any agricultural and/or forestry activity (World Energy Council 2016). The potential impacts include, degradation of water habitats due to the releasing of nutrients (eutrophication) and emissions of particles, acidic compounds and chemicals (European Climate Foundation, Södra et al. 2010).

The impacts of bioenergy production on water resources differ depending of the kind of biomass being grow and the bioenergy system used, as well as the geographical location. Biomass for energy should be produced considering the availability and quality of the water and the seasonal changes(World Energy Council 2016). Bioenergy production should not compete with food production for water resources (IEA Bioenergy 2007).

2.4.3 Socio-Economics

One of the key socio-economic aspects that encourage bioenergy development is the creation of jobs. The production of bioenergy feedstocks in large scale requires the utilization of semi-automatic methods for farming and skilled manpower, in addition to

the personnel needed for plants operation. Furthermore, bioenergy production promotes the development of adjacent industries different of farming and plant operations, such as freight and logistics (World Energy Council 2016).

When bioenergy replaces fossil fuels for heat and power generation, capital that used to be spent abroad in the import of fuels can then be invested within the region. Hence, the development of local economy is boosted creating a favorable scenario for entrepreneurship. Furthermore, the wealth is distributed more equitably which builds up social growth.

Locally produced bioenergy feedstock for heat and power generation also improves the energy independency and energy security of the regions. What is more, this could lead to better energy supply coverage and consequently, reduction of the energy poverty (World Energy Council 2016). Access to energy is one of the drivers of social development around the world.

On the other hand, the production feedstock for bioenergy (forestry and energy crops) could lead to rises of food prices. This might result beneficial for food producers while extremely negative for poor people. Moreover, Biofuels production in large scale also may cause agricultural “Land-Grabbing”. These negatives effects are more notorious in developing countries (Erbach 2017).

The use of agricultural residues for energy production represents a big opportunity for bioenergy. In first place, the bioenergy feedstock production would not affect food prices and second, it increases the revenues of farmers (World Energy Council 2016).

2.5 Technologies for Energy Conversion of Biomass

Biomass can be converted into usable forms of energy through different technologies. These technologies are divided into three main groups: thermo-chemical, bio-chemical and mechanical methods. Within the thermo-chemical transformation methods, we find; combustion, pyrolysis, gasification, torrefaction and hydrothermal carbonization. Meanwhile the bio-chemical methods include anaerobic digestion and fermentation (Yılmaz, Selim 2013).

The selection of the appropriate conversion technology depends on variables such as the kind of biomass feedstock, its quantity, quality and physical characteristics;

environmental requirements, economic constraints, the preferred form of energy and its final use (McKendry 2002).

In this section the most significant conversion technologies will be shortly described. However, hydrothermal carbonization will be covered in more detail in section 3.

2.5.1 Direct Combustion

Combustion or burning of biomass is the most utilized conversion technology to transform the chemical energy contained in biomass into useful heat that can be further transformed into mechanical work and electricity by using Rankine Cycle through boilers, steam turbines and generators.

Figure 9 depicts an overview of the transformation process of biomass into heat and power through combustion. While growing, the biomass absorbs CO_2 from the atmosphere, nutrients from the ground as well as sun light, these are transformed into chemically stored energy throughout photosynthesis, this chemical energy is then released during the combustion process along with CO_2 , particulate material and other gas emissions (Mandø 2013).

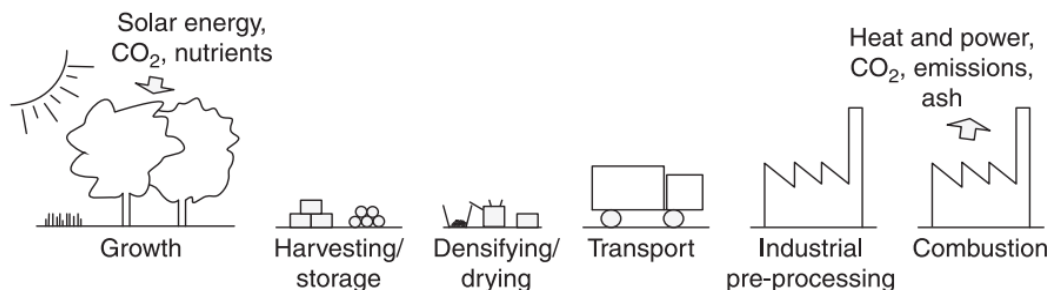


Figure 9 Transformation of Biomass into Heat and Power (Mandø 2013)

In principle, it is possible to burn any type of biomass, but in reality, in most of the cases, it results impractical to burn biomass with moisture content above 50%, wet biomass must be pretreated to reduce moisture content or using another more suitable conversion technology could be considered.

The physical characteristics and chemical composition of biomass bring about technical challenges, such as:

- Biomass firing is not entirely clean, flue gases may contain from particulate matter to dioxins and furans. Hence, pollution control systems are needed.

- Biomass is bulky and possess lower energy density compared to fossil fuels. Therefore, large volumes are needed, this complicates transport and logistics. It also means that the boilers must be larger than fossil fueled boilers. Nevertheless, densifying solutions like pelletizing and briquetting are effective to solve these issues, but they consume energy and increase costs.
- Bioenergy power plants require large handling and storage facilities.
- Biomass usually requires pretreatment to reduce moisture content and impurities before combustion.
- Biomass also may present sintering and fouling risks, which limits the steam temperatures and subsequently lowers the overall efficiency of the thermal power plants.

BFB (Bubbling Fluidized Beds) and CFB (Circulating Fluidized Beds) boilers are mature technologies that in part solve the issues related to biomass combustion while increasing the efficiency. Co-firing biomass is also a valuable solution, the mix of selected types of fuels can solve disadvantages that they would have when fired separately (Hupa, Karlström et al. 2017) .

2.5.2 Torrefaction

Torrefaction, which is considered a mild pyrolysis(Chen, Kuo 2010), is a thermo-chemical process that transforms biomass materials into a solid fuel similar to coal which have improved characteristics as a fuel compared to the raw biomass(BTG 2018). The final product does not possess the typical fibrous nature of biomass which makes it easy to grind and hence suitable for coal-fired boilers; torrefied product is also pelletizable without binders (Basu 2013); for instance, studies reported a reduction of energy consumption between 50% and 85% during size reduction of torrefied biomass in comparison to its raw feedstock(Bergman, Kiel 2005). Furthermore, the biological degradation and the water-absorption capacity of torrefied materials are substantially lower than the original biomass(BTG 2018).

The process consists in heating the biomass in an inert or very low-oxygen environment up to temperatures between 200 °C and 300 °C. The temperature increasing rates should not be higher than 50 °C/minute in order to optimize the solid yield. Throughout the

process biomass partly degrades, hemicellulose degradation occurs at temperatures above 200 °C, while the cellulose degrades at temperatures higher than 275 °C. Lignin softens within 80 and 90 °C and starts degrading gradually at 250 °C (Basu 2013).

Figure 10 describes in a simplified manner the stages involved in torrefaction process. As it is shown, torrefaction initiates with the evaporation step in which the moisture content of the biomass evaporates. Also, at the end of the drying step light organic compounds present in the biomass are volatilized. Subsequently, at temperatures around 180 °C lignin becomes amorphous while volatiles and tars are released, these compounds burn providing the necessary heat for the prolongation of the process. Finally, the breakage of the chemical bonds between hydrogen, oxygen and carbon takes place; the thermal degradation of the biomass happens and turns into torrefied biomass (Shoulaifar 2016).

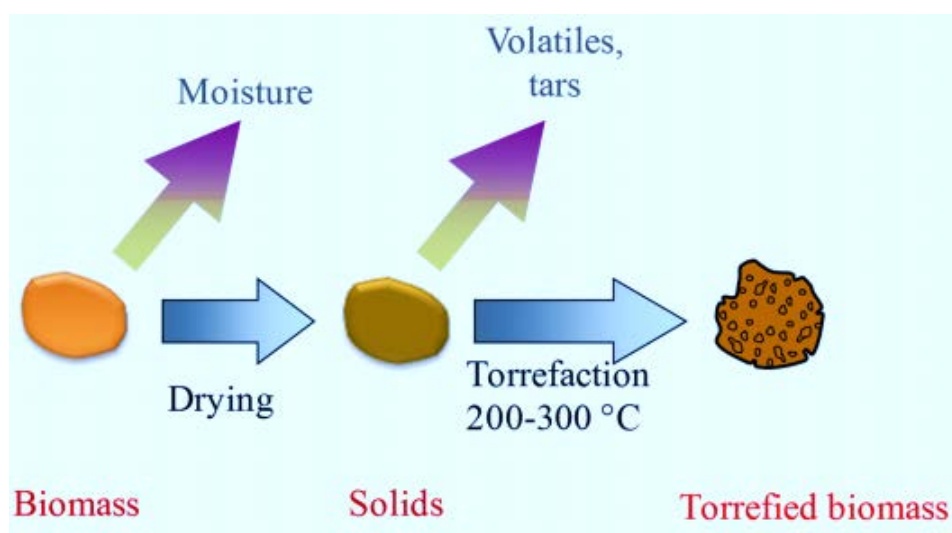
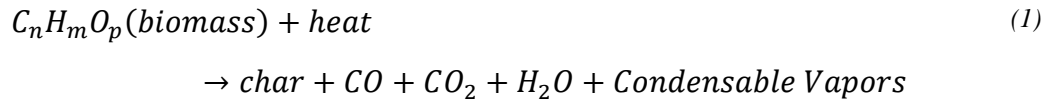


Figure 10 Torrefaction stages (Shoulaifar 2016)

The moisture content of biomass before the treatment should be as low as possible given that drying is the most energy consuming part of the process (Basu 2013). If the feedstock is rather wet, the evaporation stage would spend a big amount of energy while the temperature of the biomass would remain constant along the stage.

Besides the enhanced solid fuel, torrefaction also results in liquid and gaseous byproducts. Liquids than contain lipids, waxes, alcohols, furans and phenols; while the gases consist of CO, CO₂ and CH₄. Part of the energy content of the raw biomass is contained by the torrefaction gasses. The generic reaction of torrefaction is given in Equation (1) (Basu 2013).



2.5.3 Pyrolysis

Pyrolysis is another thermo-chemical conversion method of biomass. It can be described as a degradation of biomass by heating it in a non-oxidant environment, similarly to torrefaction. This conversion method produces three different outcomes, solid (char), liquid phase (bio-Oil) and Gas (Fernandez-Lopez, Avalos-Ramirez et al. 2016).

Figure 11 represents the pyrolysis process in a biomass particle. As shown, the preliminary product of the process consists of condensable gases and char. Subsequently, these condensable gases decompose into non-condensable gases, liquid and char.

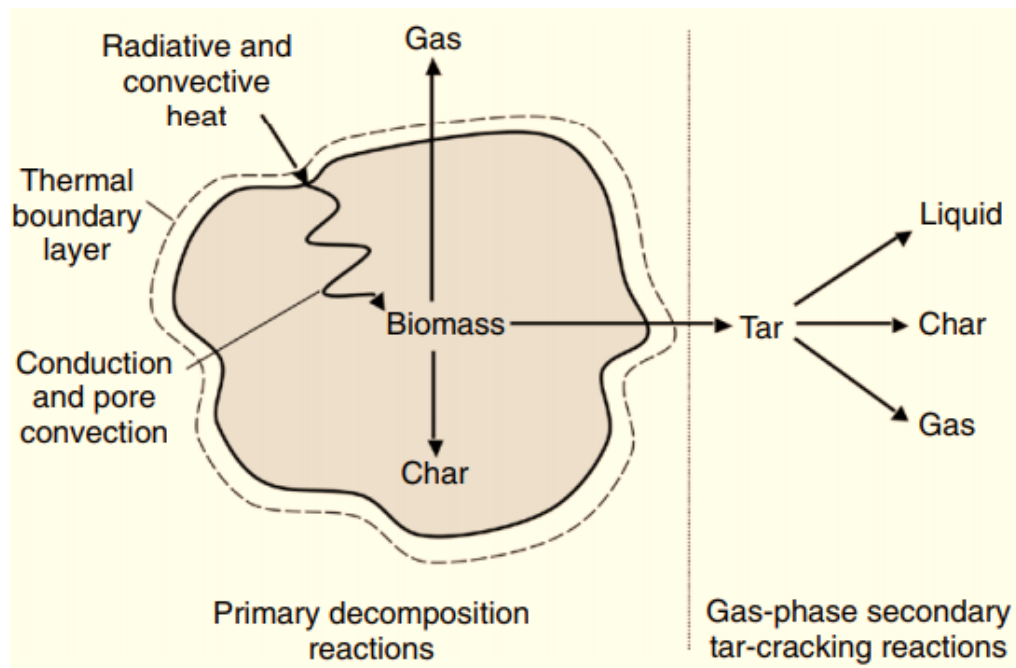


Figure 11 Pyrolysis process of a Biomass Particle (Basu 2013)

The final Products of pyrolysis vary in accordance to implementation parameters such as final temperature called pyrolysis temperature, heating rate and residence time. At pyrolysis temperatures below 450°C and low heating rates, the main product of pyrolysis is biochar. While treatments conducted with final temperatures above 800°C and quick heating produce mainly non-condensable gases (Zafar 2018). However, the main

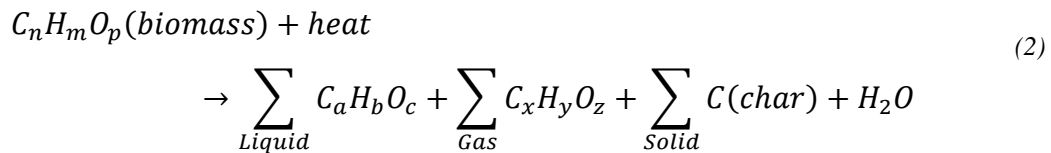
objective of pyrolysis is the obtention of liquid product or Bio Oil (Basu 2013) which occurs at intermediate temperatures and rather high heating rates(Zafar 2018).

The typical substances present in the pyrolysis products are(Fernandez-Lopez, Avalos-Ramirez et al. 2016, Basu 2013) :

- Solid: Mainly char or carbon (85%), the lower heating value (LHV) of the biochar is around 32 MJ/kg, drastically higher than the untreated biomass.
- Liquid: Tars or bio oil has a water content of up to 20%. It contains a mixture of heavier hydrocarbons.
- Gas: CO₂, CO, C₂H₂, CH₄, C₂H₄, C₂H₆, C₆H₆, H₂, H₂O

Pyrolysis is divided according to heating times into two categories, slow pyrolysis and fast pyrolysis. Fast pyrolysis is the most commonly used. Slow pyrolysis produces primarily char with oil and syngas as byproducts, while fast pyrolysis produces mainly bio-oil and syngas (Basu 2013).

Pyrolysis is represented by the reaction described in Equation (2) (Basu 2013).



2.5.4 Gasification

Gasification is a thermo-chemical method that converts solid and/or liquid organic material into syngas and solid byproducts. The syngas usually contains CO, H₂, CH₄ (45%-50%), CO₂, C₂H₆ (ethane), C₃H₈ (propane), tars and possibly, traces of H₂S, HCl and N₂. Whereas, the solid fraction is a mixture of mostly carbon, unchanged organic fractions and ash (Molino, Chianese et al. 2016).

Gasification is commonly described as incomplete combustion. Basically, biomass is combusted with an air supply lower than the stoichiometric requirement. The difference between gasification and combustion lies in the fact that combustion breaks the chemical bonds in the matter to release energy in the form of heat, while gasification packs the energy into those chemical bonds in the syngas (Basu 2013).

The process consists of four stages which in sequential order are (Molino, Chianese et al. 2016), (see Figure 12):

- Oxidation: This is the only exothermic part of the process, it provides the necessary heat for the subsequent stages.
- Drying: The moisture content of the feedstock is evaporated; an entire drying is considered when the temperature of the biomass reaches 150°C.
- Thermal decomposition (pyrolysis): In the stage the cracking of the chemical bonds occurs forming molecules with lower weight.
- Reduction: The gases and the chars resulting from previous stages react with each other forming the final syngas. This stage is endothermic in overall, nevertheless, exothermic reactions occur during the reduction.

The reduction temperature is a crucial factor for the whole gasification process. At higher temperatures the undesired solid residue of the process decreases.

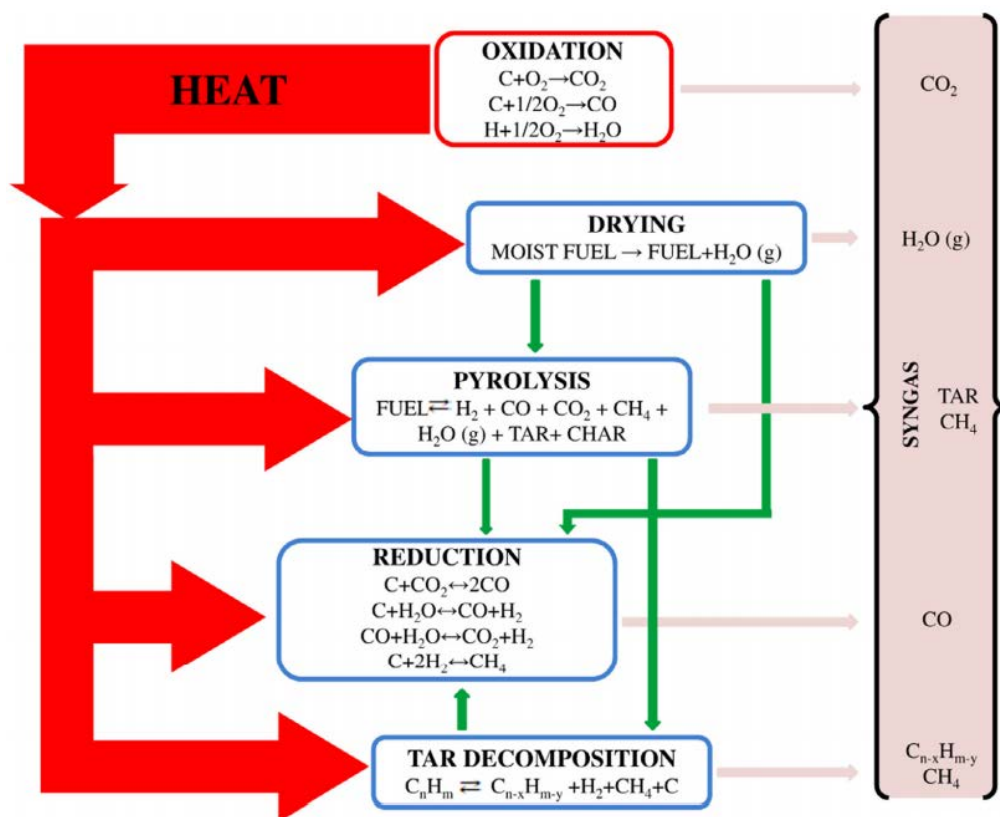


Figure 12 Main stages of gasification (Molino, Chianese et al. 2016)

As it occurs in torrefaction and pyrolysis, the moisture content of the feedstock biomass plays a crucial role in the treatment. The vaporization of each kilogram of water contained in the biomass consumes 2242 kJ of energy during the drying stage of the process, this energy can only be recovered partially by using condensing heat exchangers which decrease the flue gas temperature below the dew point, extracting sensitive heat from the steam obtaining water from the product gases, but with limitations due to the low temperature difference (Levy, Bilirgen et al. 2011). Therefore, for energy applications most gasification systems do not use biomass with moisture content above 20% (Basu 2013).

Pre-drying systems could be implemented for gasification of biomass with high water content. However, this involves the consumption of energy, resulting in the reduction of the overall process efficiency.

2.5.5 Anaerobic Digestion (AD)

AD is a bio-chemical method for biomass conversion. By definition, AD is a natural mechanism in which organic matter (biomass) is decomposed in the absence of oxygen by anaerobic microorganisms. The end product of the process is biogas which contains between 40% and 70% of CH₄, the remaining part consist mainly of CO₂ with traces of NH₃ (ammonia), H₂S (hydrogen sulphide), and H₂.

The biogas can be directly used for energy purposes or treated to remove the CO₂ and other impurities improving its fuel characteristics; then, the almost pure CH₄ can be fed into the natural gas network or used for heat and power generation in small or large scale.

When AD process is completed, the remaining solid matter or digestate can be used as soil enhancer after removing impurities like glass or plastics. Digestate can also be led to further energy recovery processes.

There are two main temperature ranges at which AD processes are carried out:

- **Thermophilic:** AD systems operate between 50°C and 60 °C, thermophilic AD processes are characterized by rapid biochemical reactions and quick microorganism's growth rates. Therefore, thermophilic AD has a higher methanogenic potential at lower retention times (3-5 days in average); in addition, the high temperatures improve the elimination of pathogens. However, these

systems require appropriate isolation in order to keep the temperature within the optimal range: also, these systems have a higher energy consumption due to heating (Gavala, Yenal et al. 2003, DeBruyn, Hilborn 2007).

- Mesophilic: AD systems operate between 35°C and 40°C, the retention time are longer (15 – 20 days) to allow the low temperature bacteria decompose the organic matter (DeBruyn, Hilborn 2007).

In general AD of biomass occurs in four phases:

- Hydrolysis: macromolecules contained in cellulose, starch, other carbohydrates, fats and proteins are broken by hydrolysis into monomers, fatty acids, amino acids and sugars. This process could take from few hours for basic carbohydrates to few days in the case of proteins and lipids. Its important to mention that the hydrolysis of Lignin and Lignocellulose occurs slower and only partially (Abbasi, Abbasi et al. 2012, Boontian 2014).
- Acidogenic: The products from the first phase are fermented by anaerobic bacteria to produce short chain organic acids, such as volatile fatty acids like lactic, butyric acid, propionic acid, acetate and acetic acid, along with alcohols, hydrogen and CO₂. (Abbasi, Abbasi et al. 2012, Boontian 2014).
- Acetogenic: Homoacetogenic Bacteria transforms the fermented Acidogenic products into acetic acid CO₂ and H₂. Short chain organic acids and alcohols are transformed into acetate. Methanogenic bacteria grow (Boontian 2014).
- Methanogenic: Methanogenic organisms produce methane from the products of the third phase under severe anaerobic conditions (Abbasi, Abbasi et al. 2012)

AD is a flexible process and a wide variety of feedstocks can be used, for example marine algae, animal manure, biodegradable fraction of municipal and industrial waste, forestry and agricultural crops residues, sewage, etc.

Nevertheless, the process is affected by several factors like the content of water and nitrogen of the substrate, pH, C/N ratio, organic loading rate and temperature. Therefore, the design of optimal AD processes should take these parameters into account (Boontian 2014). In addition, the presence of some specific microorganisms is essential as well as proper conditions for their survival (Abbasi, Abbasi et al. 2012).

The initial value of pH is an essential factor to consider in anaerobic digestion processes. This parameter could be determinant for the growth of the microorganisms that take part in the process at all stages. According to Zhang, Mao et al. 2015, the optimal initial pH value is 6.5 to 7.5, moreover, initial pH values around 8 have a better methane production but with longer retention times (Zhai, Zhang et al. 2015). The methanogenic bacteria involved in methane forming process produce higher yields at pH between 6.8-7.2 (Boontian 2014). The variation of pH between the AD stages should also be considered, for example, high content of proteins and fat in the feedstock could lead to a drop in pH value after the early phases (Zhai, Zhang et al. 2015)

The C/N ratio values are also determinant for AD, high nitrogen content could produce toxicity, while low nitrogen content at high C/N ratios could slow down the digestion process. The ideal C/N ratio value is between 25 and 30 (Boontian 2014)

2.5.6 Comparison between Thermo-Chemical Conversion technologies

As established along this section, the different thermochemical and biochemical biomass conversion technologies offer several pathways to overcome the challenges inherent to biomass as a source of energy. The solution suitability depends on the biomass feedstock and the end product desired.

Table 1 Shows a crossed comparison between the different biomass conversion pathways, showing the end products yielding and the treatment parameters.

Table 1 Comparison Between Biomass Conversion Treatments

Process	Process Conditions and Parameter							Approximate Product Yield [wt%]		
	Temperature [°C]	Range	Heating Rate	Residence Time	Pressure	Medium	Cooling Rate	Char	Liquid	Gas
Slow Pyrolysis	~400		Slow	Hours to weeks	Low	Low or no O ₂	Slow	35	30	35
Fast Pyrolysis	~500		Fast	Seconds	Variable	Low or no O ₂	Rapid	12	75	13
Gasification	>800		Fast	10-20 seconds	Variable	Lightly reducing atmosphere	-	<10	5	>85
Torrefaction	200 - 300		Moderate	Several Hours	Atmospheric	Low or no O ₂	None	70	0	30
HTC	180-360		Moderate	No vapor residence time. Processing time: minutes to several hours	High Autogenous (up to 2.4 MPa)	Water	Slow	50 - 80	5-20	2-5
Anaerobic Digestion	Thermophilic: 50 -60 Mesophilic: 35 - 40 Psychrophilic: 15 – 25 [1]		NA	Thermophilic:3-5 d Mesophilic: 15-20 d (or more) [1]	~Atmospheric	Low or no O ₂	NA	Digestate: ~94 (96% H ₂ O, 4% solids) [2]		~6 [2]

*Source: Data obtained from (Child 2014) unless specified otherwise

[1] (DeBruyn, Hilborn 2007)

[2] Wet Anaerobic Digester (Møller, Christensen et al. 2010)

3 HYDROTHERMAL CARBONIZATION

3.1 Overview

Hydrothermal carbonization (HTC), also known as wet torrefaction, is a relatively novel thermo-chemical biomass conversion technology. As torrefaction, the primary end product of HTC treatment is an enhanced coal-like material which is known as hydrochar, biochar or HTC-char within other designations. Nevertheless, HTC treatment also produces an aqueous byproduct called HTC liquors or liquid phase along with non-combustible gases (Hoekman, Broch et al. 2013).

The hydrochar typically holds between 55% and 90% of the mass of the original biomass and between 80% and 95% of its energy content. Given the enhanced fuel properties of hydrochar which are similar to low ranked coal, this material is usually regarded as solid biofuel. Nevertheless, other applications such as water purification and carbon sequestration within others have been subject of studies (Hoekman, Broch et al. 2013, Yan, Hastings et al. 2010).

Even though HTC and torrefaction both aim to transform several kinds of biomass into more energy dense and uniform solid materials, these two technologies differ in other important aspects. The main differentiator regards the required quality of the feedstocks. As stated in section 2.5.2, for torrefaction the moisture content of the biomass is a huge constraint as it affects the efficiency of the process. Meanwhile, HTC treatment offers the capability to directly carbonize biomass materials with up to 96% of moisture content (Schneider, Escala et al. 2011). Therefore, the feedstock can include manures, green waste, peat, algae, organic waste, agricultural waste and sewage sludge etc.

Also, the required process time of torrefaction and HTC are different. In HTC, the heat transfer is more effective given the aqueous environment; hence, HTC occurs faster than torrefaction at similar temperatures (Hoekman, Broch et al. 2013).

Another important aspect that distinguishes HTC from torrefaction is its aqueous phase products or HTC liquors. These liquids are byproducts that could contain potentially valuable substances like sugars or organic acids that can be further exploited (Hoekman, Broch et al. 2013)

Nevertheless, given that for HTC process is performed inside pressurized vessels, HTC is expected to be more expensive than torrefaction. (Hoekman, Broch et al. 2013)

3.2 Evolution of HTC technology

This section covers briefly the evolution of the technology since its origin to current commercial applications.

Hydrothermal carbonization concept dates back to 1544 when it was described by the German physician and botanist Valerius Cordus, and later on in 1592 by Balthasar Klein (Northrop, Connor 2016). Nevertheless, the first approach to the current HTC technology was made by the German chemist Friedrich Bergius during the first quarter of the twentieth century.

Bergius's experiments were intended to obtain hydrogen by using the reaction $C + 2H_2O \rightarrow CO_2 + H_2$ at appropriate temperature and pressure in order to avoid the formation of CO. Bergius experimented with temperatures below 600°C, the oxidation of the coal occurred when it was reacting with liquid water at 200 bar, delivering CO₂ and H₂, but the oxidation velocity was not enough for commercial applications. However, when Bergius used peat instead of coal in the experiments, he observed that CO₂ formed in high quantities and that the solid remains of the process were similar to natural coal. These results encouraged the further study of the decomposition of plant constituents. Bergius understood the process as similar to the natural transformation of biomass throughout millions of years into coal (Titirici, Funke et al. 2015).

Before Bergius, other researchers had tried to transform woody biomass into coal by heating it. However, those attempts resulted in the decomposition of the cellulose. The key for the success of Bergius experiments was keeping the biomass precursor in liquid water at high pressure, which allows the transformation of the biomass at relatively low temperatures (200 °C) preventing the super-heating and subsequently decomposition of the cellulose (Titirici, Funke et al. 2015). Friedrich Bergius along with Carl Bosch were awarded with the Nobel prize of chemistry in 1931 in recognition to their effort and contributions to the creation and development of chemical high-pressure methods (Nobel Media 2014).

Bergius's work was soon followed by other researchers. Berl and Schmidt for instance performed similar experiments modifying the temperature between 150°C and 350°C using different kinds of biomass in 1932. In 1953 J.P. Schumacher worked in the analysis of the effect of the pH on the resulting products of HTC treatment (Titirici, Funke et al. 2015).

3.3 State of the Art

Nowadays, HTC is subject of constant research aimed to optimize the process and expand the applications and benefits that this technology offers. Hence, private companies have implemented HTC commercial applications that deserve to be briefly described.

3.3.1 AVA-CO₂

AVA-CO₂ was founded in Zug, Switzerland in 2009, with the primary goal of converting waste products/biomass into bio-carbon by HTC. With this purpose, in October 2010 in Karlsruhe, Germany, AVA-CO₂ revealed the first industrial scale HTC plant in the world. The plant (HTC-0) had a 14000 liters reactor with a processing capacity of 8400 ton/a of biomass in a continuous process. HTC-0 produces around 2660 ton/a of hydrochar, operating at temperatures between 220°C and 230°C and pressures between 2.2 MPa and 2.6 MPa. The biomass feedstock includes organic fraction or MSW, sewage sludge and garden wastes (Kan, Strezov 2015, Business Wire 2010).

The process begins with the mix and preheating of the feedstock in a mixing tank at 160°C and 1.0 MPa, where biomass is combined with high and low-pressure steam and recirculated liquors. The resulting slurry is then fed into the reactor tank where the reactions are facilitated by stirring and catalysts. The product is then directed through a buffer tank where the liquid-solid separation occurs, and heat is recovered (Kan, Strezov 2015, Child 2014). Figure 13 describes the process plant.

AVA-CO₂ HTC-PLANT: THE PROCESS UNITS

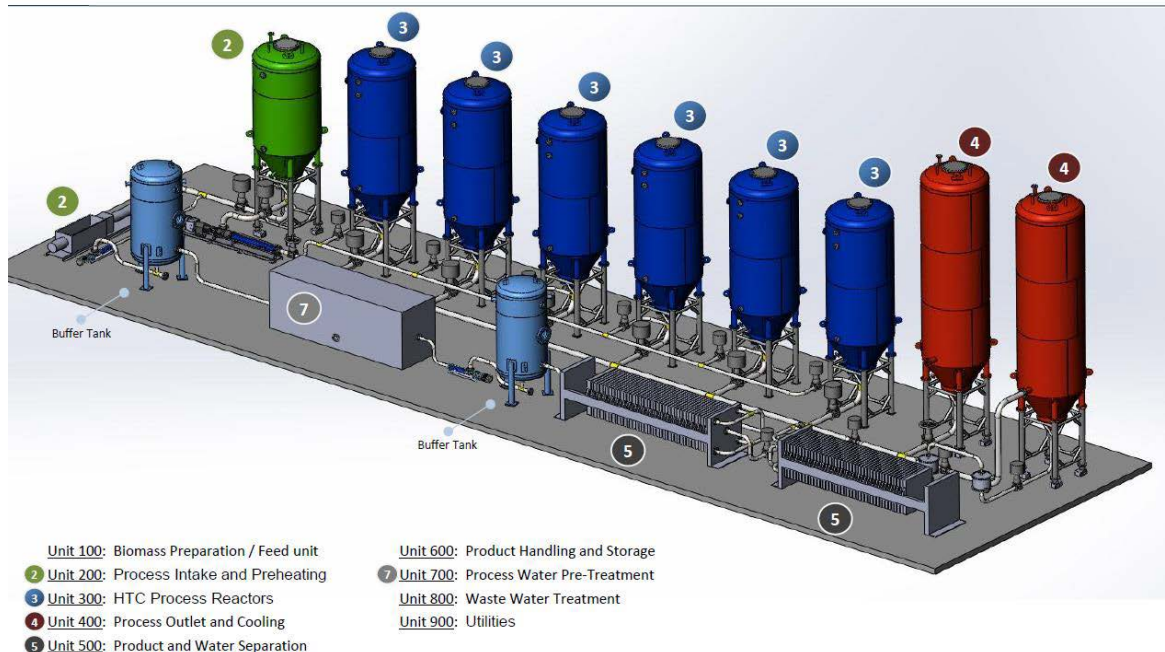


Figure 13 AVA-CO₂ Process Plant (Child 2014)

In 2010 AVA-CO₂ opened a subsidiary, AVA-Biochem aiming to produce bio-based chemicals in large scale though its patented Hydrothermal Processing (HTP) technology. In 2016 the production of bio-chemicals became the main focus of the company and the HTC plant for conversion of waste into bio-char was sold to International Power Invest AG (API), a holding company specialized in renewable energy (Mortato 2018).

3.3.2 SunCoal Industries

In 2008 and located in Ludwigsfelde, Germany, SunCoal industries launched a pilot HTC plant in consisting of six central units. This pilot plant uses the patented CarboREN technology with the aim of producing a dry, solid and high energy-biofuel named SunCoal, which has properties similar to brown coal. The plant utilizes a large range of biomass materials, such as wood, leaves and grass (Kan, Strezov 2015).

The CarboREN technology involves development in the energy management and the water handling, feeding and withdrawal systems (Kan, Strezov 2015). The process starts with reception and storing of the feedstock, which is sorted accordingly to its composition. Subsequently, the biomass its crushed to a particle size of 60 mm and impurities are

removed. Then, it is preheated by mixing it with low pressure steam and recirculated liquors. After, in a continuous reactor with a stirring system, the temperature is increased to 260°C and the pressure to 20 bar where the reactions occur. The feeding of the HTC reactor is done from the top of it while the slurry is removed from the bottom. The HTC slurry is then cooled, depressurized and dewatered by using membrane filter press. The produced SunCoal can be utilized in heat and power generation. Figure 14 depicts the CarboREN process.

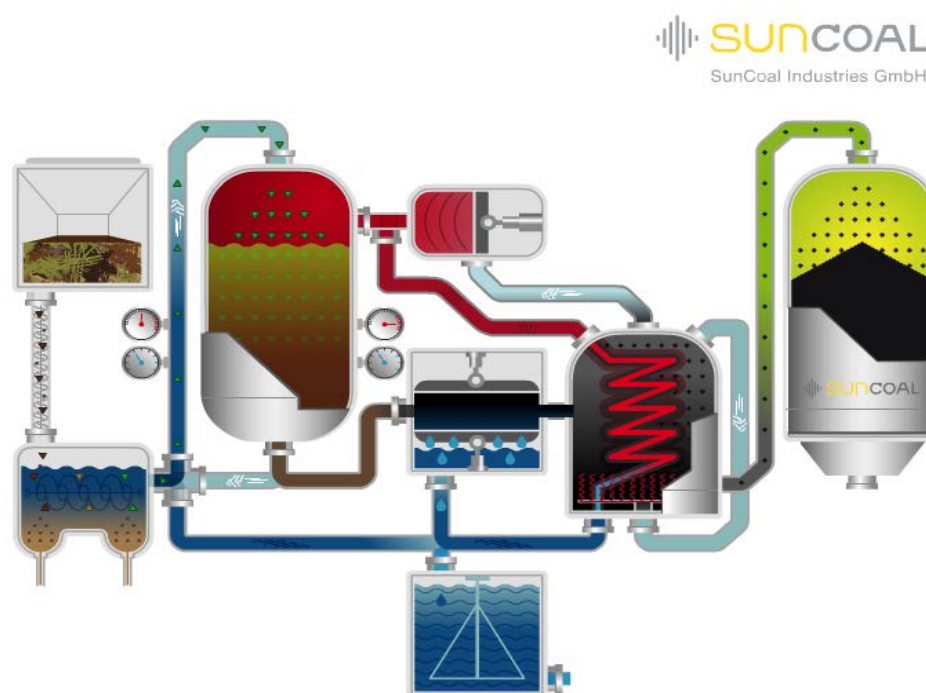


Figure 14 Schematics of CarboREN process (Child 2014)

3.3.3 Ingelia S.L

In September of 2010, in Valencia, Spain, Ingelia S.L completed the installation of its first industrial-scale HTC plant with a capacity of 6000 ton/a of raw biomass in a continuous process. The plant is in service since 2012, it operates at temperatures between 180°C and 220°C in a pressure range from 1.7 MPa to 2.4 MPa, it includes patented control of temperature and inverted flow reactor and can process organic fraction of MSW, sewage sludge agricultural and forestry residues and food production waste (Kan, Strezov 2015, Ingelia 2018)



Figure 15 Ingelia SL, Náquera Pilot Plant (Hitzl, Corma et al. 2015)

3.3.4 Valmet HTC

Valmet offers HTC technology as a solution for sludge management problems at mills of pulp and paper production industry. This sludge represents a challenge for the industry given the high transportation cost and its very low efficiency during incineration (Sjöblom 2018), Valmet HTC technology is being developed in partnership with SunCoal and is based on their technology (Valmet 2018).

Valmet HTC technology treats the sludge at 200°C under a pressure of 2.0 MPa, this reduces the mass of the sludge in 70% with an energy consumption of 25% of the required for thermal drying process (Sjöblom 2018).



Figure 16 Valmet HTC Technology (Valmet 2018)

3.3.5 TerraNova Energy

TerraNova offers technological solution for sludge treatments, in which both energy and phosphorus is recovered. The process consists of stirred reactor in which the sewage is carbonized at 200°C and pressures between 20 and 35 bar, with the addition of catalyst. The solid product which is similar to lignite is used in cement plants or waste incinerations plants. Meanwhile, the HTC liquids is directed to a secondary treatment where nutrients -mostly phosphorus- are removed to be utilized as high performance fertilizers (TerraNova Energy).

Figure 17 shows a schematic of a sludge treatment plant that would integrate anaerobic digestion as sludge treatment and HTC as treatment for the digestate.

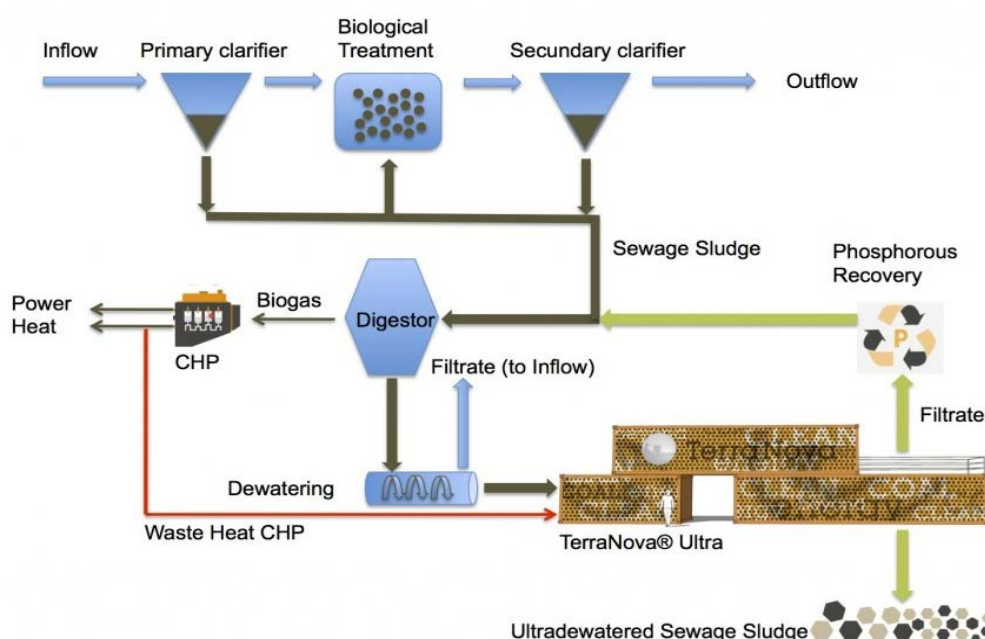


Figure 17 TerraNova Ultra Integrated to a Sludge Treatment Plant (TerraNova Energy)

3.4 HTC Process

Hydrothermal Carbonization process occurs in an aqueous environment at relatively low temperatures, usually in the range between 180°C and 350°C and under considerable autogenous pressures which can reach 2.4 MPa. Liquid water at the mentioned temperatures behaves as a non-polar solvent and the solubility of organic materials in it increases severely. Figure 18 describes briefly the HTC process showing common values of the treatment parameters.

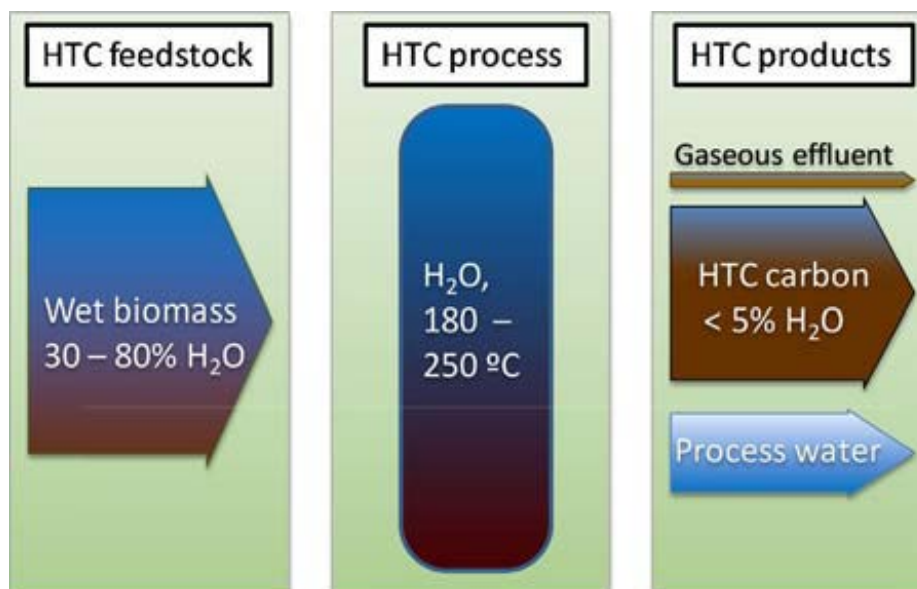


Figure 18 Schematic Simplified Description of HTC Process (Hitzl, Corma et al. 2015)

The HTC process requires external heat supply until the activation point, after this point the process is exothermic and self-sustaining. The activation occurs above 180°C, the sugar blocks contained in the biomass will supply the necessary thermal energy to continue the process; in principle, the energy balance of the whole process could be positive. However, the energy released and thus the energy balance depends on the kind of feedstock for the treatment and its parameters, such as residence time, final temperature and pressure (Dea Marchetti 2013).

The transformation of biomass during the HTC process is rather complex, it consists of diverse chemical reactions occurring in parallel, these reactions commonly include: Hydrolysis, dehydration, decarboxylation, condensation, polymerization and aromatization (Kan, Strezov 2015).

However, HTC process usually begins with Hydrolysis at around 180°C when water reacts with extractives and hemicellulose, whereas the reaction of water with lignin and cellulose occurs above 200°C. During hydrolysis the ether and ester bonds are broken creating several products such as oligosaccharides from cellulose and hemicellulose, as depicted in Figure 19. Complete hydrolyzation of lignin and cellulose is unlikely which indicates that these reactions lead to solid formation (Child 2014, Reza, Andert et al. 2014).

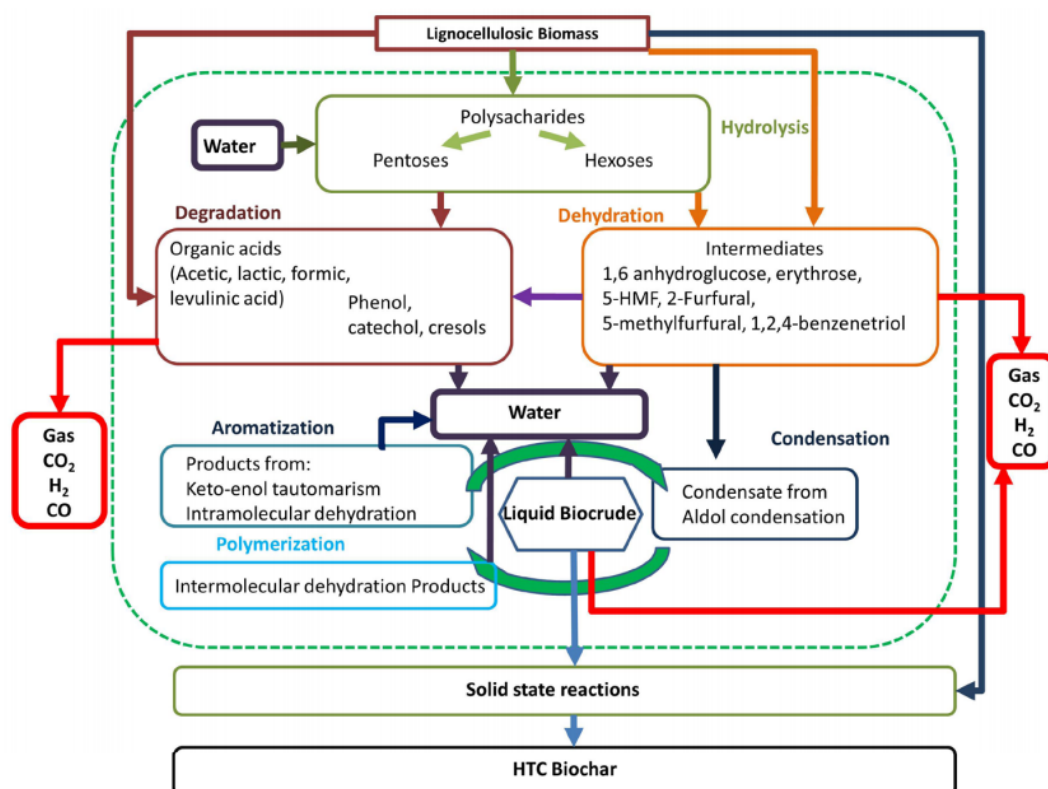


Figure 19 HTC Chemical Reaction Pathways for lignocellulosic (Reza, Andert et al. 2014)

Next, soluble extractables experience degradation reactions, mostly dehydration and decarboxylation. Through this mechanisms, oxygen and hydrogen are removed, lowering O/C and H/C ratios in comparison to the original biomass, which means energy densification. Meanwhile, condensation, polymerization and/or aromatization may happen, the produced precipitates that form most of the HTC liquors and are referred as total organic carbon (TOC) (Kan, Strezov 2015, Child 2014).

Apart from the above described reaction pathways, other mechanisms have been proposed to be involved in HTC process, these reactions are: demethylation, de-methanation, pyrolytic reactions and Fisher-Tropsch type reaction (Child 2014, Kan, Strezov 2015). The HTC process consists mainly in dehydration and decarboxylation reactions which makes it exothermal (Kan, Strezov 2015). Figure 20 describes the HTC process more in detail, explaining the mechanisms of transformation and the intermediate and final products of the main constituents of lignocellulosic biomass.

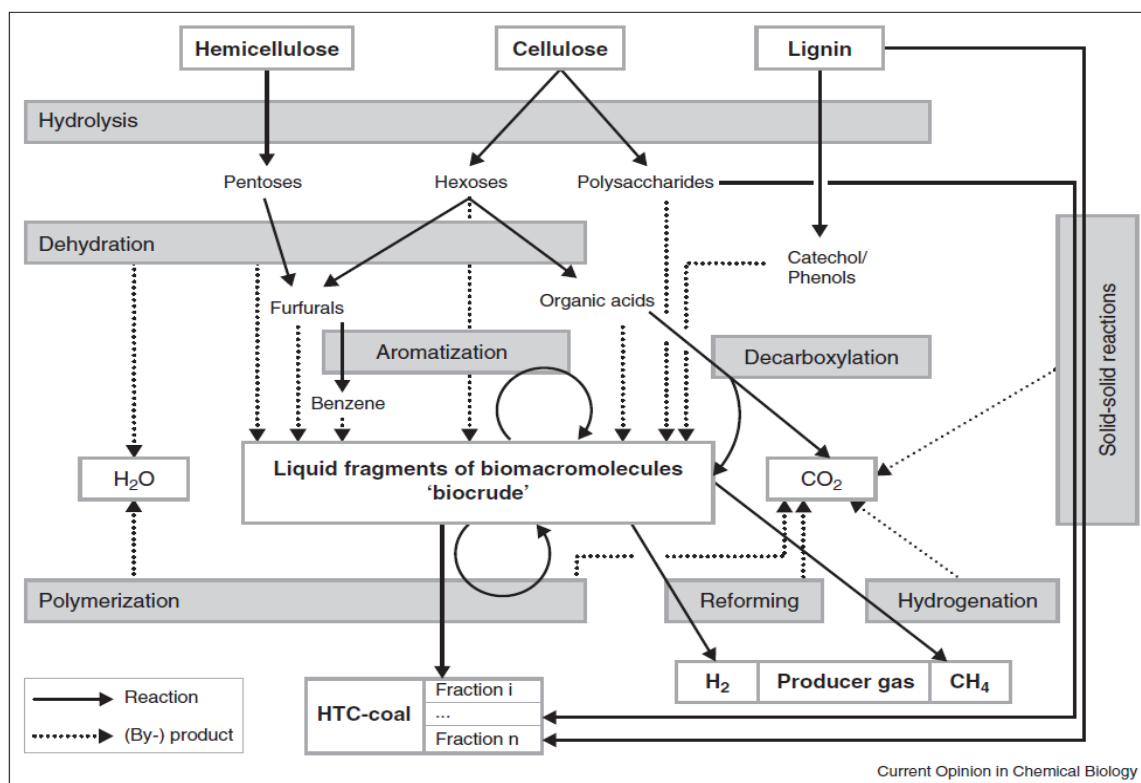


Figure 20 Schematic of HTC Reaction (Kruse, Funke et al. 2013)

A small part of the lignin contained in the original biomass reacts at temperatures as high as 260°C and forms phenol and phenolic derivatives. The inorganic components remain inert during HTC at temperatures between 200°C and 260°C, but the degradation of polymeric components may transfer inorganics from the solid to the liquid phase (Reza, Andert et al. 2014).

There are many factors that affect the characteristics and properties of the end products of the HTC process, according to Kan, Strezov (2015) some of these factors are:

- Composition and constitution of the raw biomass. For example, the aromaticity of biochar produced from bark is higher than in hydrochar obtained from the HTC treatment of sugar beet, this is caused by the lignin residues present in the bark hydrochar.
- Operating Temperature: The HTC reaction rate depends largely on the temperature of the process. The rates of paralleled reactions like hydrolysis and polymerization can be improved as the operating temperatures are increased.

- Operating Pressure: As the pressure increases, more compounds can be extracted from the biomass in the subcritical zone.
- Reaction times: When the reaction time is longer, thy hydrochar yield is expected to grow due to the longer polymerization reaction times.
- Addition of catalysts: an example of this is addition of catalysts based on metals, which can affect the shape of the carbon nano-materials obtained at low-pressure.

3.5 HTC products

As stated previously, HTC process has three outputs, hydrochar (solids), HTC liquors (liquid) and gases. These products are formed in different rates and compositions, the ratios depend on the biomass feedstock and the parameters of the HTC treatment.

Figure 21 shows the typical ratios of formation of HTC products for treatments performed at temperatures between 180°C and 250°C and pressures close to 20 bar.

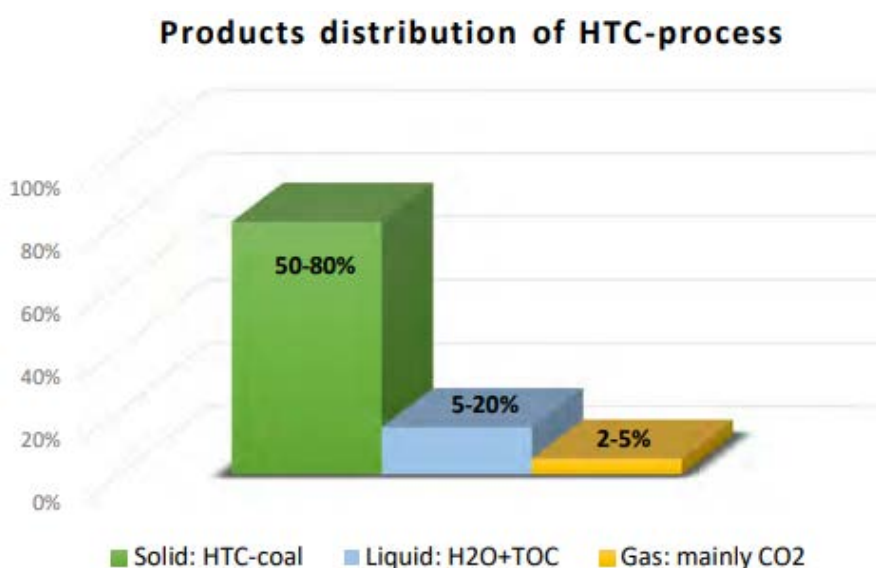


Figure 21 Typical HTC Products Ratios (Dea Marchetti 2013)

As an illustrative example, Figure 22 shows the balance of recovered mass obtained by Broch, Jena et al. (2013) after the experimental HTC treatments of lipid extracted algae from spirulina and whole spirulina (micro algae) in comparison to the mass recovered from the HTC treatments of Loblolly Pine and sugarcane bagasse. The HTC processes where performed at 175°C and 215°C. The graph shows the composition (C-H-N-S-O-Ash) of the

raw biomass and the hydrochar as well as the yield of hydrochar, aqueous co-products (ACP) and gases. As noted, the content of matter that remains after complete evaporation of water, which is known as non-volatile residues (NVR), increases as the temperature increases in the treatment of algae, whereas has the opposite behavior for lignocellulosic biomass. However, the solid yield also decreases.

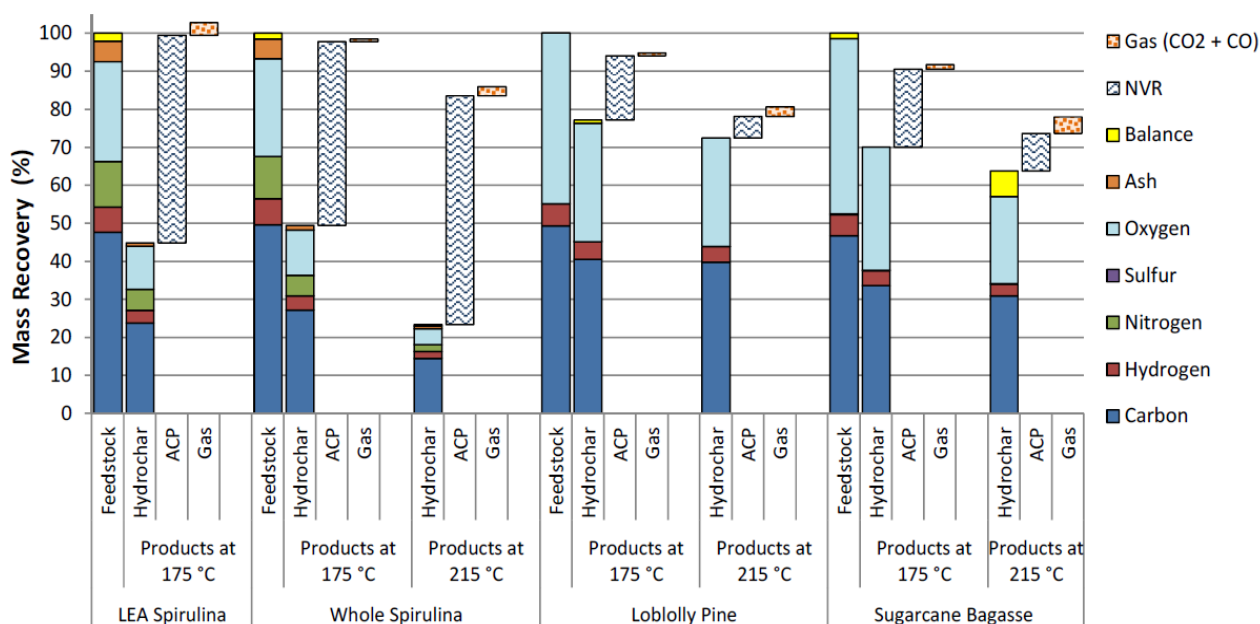


Figure 22 Mass Balance after HTC treatment of different Biomasses (Broch, Jena et al. 2013)

Solid and gaseous products of HTC treatment will be shortly described in this section, whereas the aqueous products of HTC are going to be addressed in section 4.

3.5.1 Solid Products

The solid product of HTC or hydrochar is similar to lignite or sub-bituminous coal in its elemental characteristics. Regarding its chemical composition, hydrochar contains more carbon per mass unit than the original raw biomass. While, its oxygen and hydrogen contents are lower, these characteristics result from the dehydration and decarboxylation reactions. When HTC process is performed at higher temperatures and pressures, the mass of hydrochar decreases, as seen in Figure 22. However, the H/C and O/C ratios decrease, which means that the energy density and subsequently the heating values of the hydrochar increase, accordingly with the Van Krevelen diagram shown Figure 23.

Figure 24 Shows typical H/C and O/C ratios for various biomasses and their respective hydrochar after HTC treatment which illustrates the change in calorific values and the similarities of hydrochar with natural coal, in terms of their calorific value.

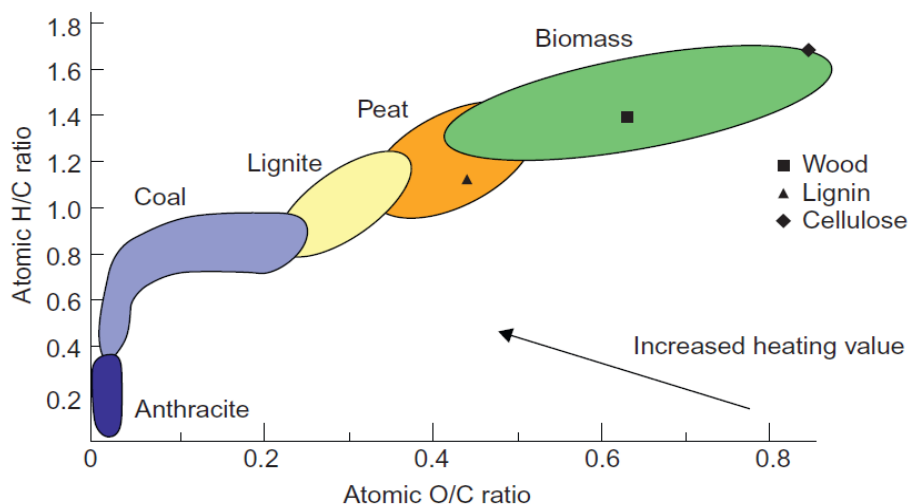


Figure 23 Van Krevelen Diagram for Different Solid Fuels (Basu 2013)

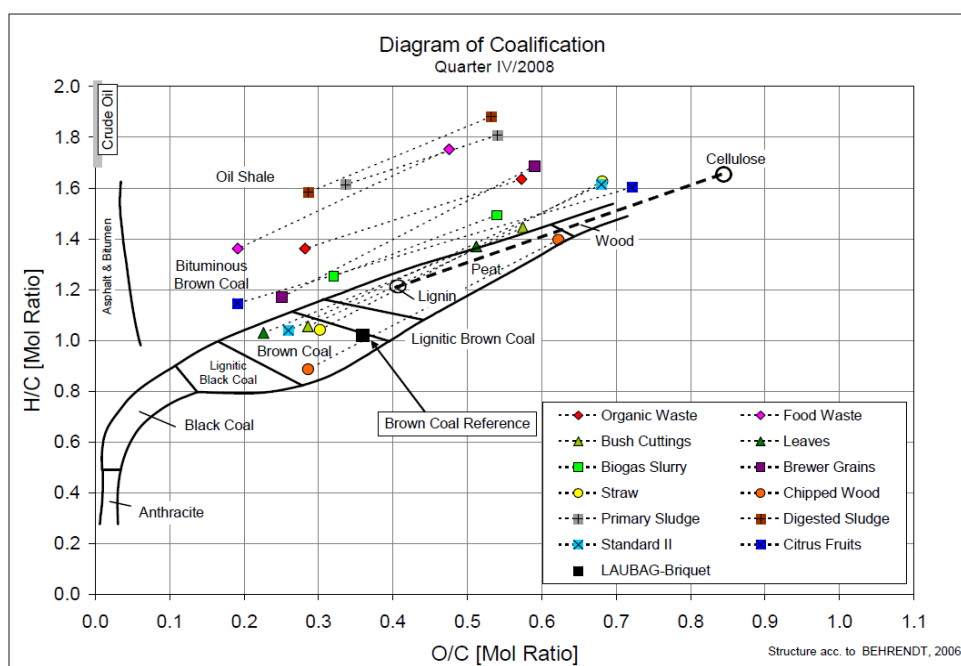


Figure 24 Coalification Diagram (Child 2014)

The structural characteristics of hydrochar have caused especial interest given the range of possible industrial applications, such as water purification, CO₂ capture, medical applications and renewable energy. Nevertheless, the primary purpose of the commercial

implementation of HTC technology is the use of hydrochar as a bio-coal for heat and power applications (Titirici, Funke et al. 2015).

As mentioned before, one of the major challenges of biomass combustion is the low ash melting temperature. Hydrochar has been observed to have similar ash melting temperature to lignite. Moreover, many of the minerals that conform ash are dissolved in the HTC liquors during the treatment (Titirici, Funke et al. 2015). Therefore, the production of particulate materials during the combustion of hydro-char is lower.

3.5.2 Gaseous Products

As shown in Figure 22 the gas yield of HTC is very low in comparison with liquid and solid products, also it can be noted that the gas yields vary in accordance to the process parameters, gaseous yield increases as temperatures increases. The gaseous phase consists mostly of CO₂ which can accounts for over 90%, the remaining part consists in small quantities of CO, H₂ and low-molecular-weight hydrocarbons like CH₄ (Sermyagina 2016). The CO₂ is formed by decarboxylation reactions during the treatment. This reaction is sensitive to temperature, which explains the increasing in the gaseous yield when temperature rises, when this happens, larger amounts of CH₄ and H₂ are observed as well as smaller CO yield.

4 HTC LIQUORS

4.1 Overview

The term HTC Liquors (HTCL) denotes the liquids remaining after filtration of the hydrochar slurry obtained from the reactor at the end of an HTC process. In literature, these liquids are designated as HTC process water, HTC liquid, aqueous phase, spent liquor (SL) (Kabadayi Catalkopru, Kantarli et al. 2017, Dea Marchetti 2013) or aqueous co-products (ACP) (Broch, Jena et al. 2013). HTCL are usually regarded as by-product or co-product of HTC treatments and some authors define it as a drawback or challenge inherent to HTC process due to the organic compounds, chemical and thermal energy that remain in them after HTC treatment and products separation; the thermal energy in the form of sensible heat can be up to one third of the chemical energy stored in the raw biomass, given the high specific heat capacity of water. As established before, the organic compounds are usually referred in a simplified way as TOC (Titirici, Funke et al. 2015)

Figure 25 shows a laboratory sample of HTC liquors. As seen, HTCL is a brownish and watery suspension, the color and/or darkness vary in accordance to the parameters of the treatments and the biomass utilized.



Figure 25 Sample of HTC Liquors (Levine 2010)

During HTC processes, water stays in its subcritical state, due to this fact, water performs several functions: it makes up the heat transfer medium, it works as a solvent, as a reactant and it is also a product of HTC. First, water participates in the degradation of carbohydrates during the hydrolysis which reduces the quantities inside the system. However, water is formed along the dehydration reactions and as the temperature increases, the water formation

increases (Child 2014), this means that in overall, the water content at the end of the treatment is generally higher than the original input (Dea Marchetti 2013).

4.2 Physical and Chemical Characteristics

The characteristics of HTC liquors diverge given that they are fully dependent on process parameters (set Temperature, holding time) and the input (raw biomass and water content). However, some common characteristics are observed in the majority of the HTC liquors analysis performed by researchers.

4.2.1 pH

Probably the most notorious and common characteristic is the rather acidic nature of the HTC liquors, this is mainly due to the formation of organic acids during the process. Acids such as lactic acid, formic acid, acetic acid and levulinic acid, within others, result from the degradation of sugars present in the raw biomass or formed by hydrolysis (Dea Marchetti 2013, Broch, Jena et al. 2013, Reza, Rottler et al. 2015).

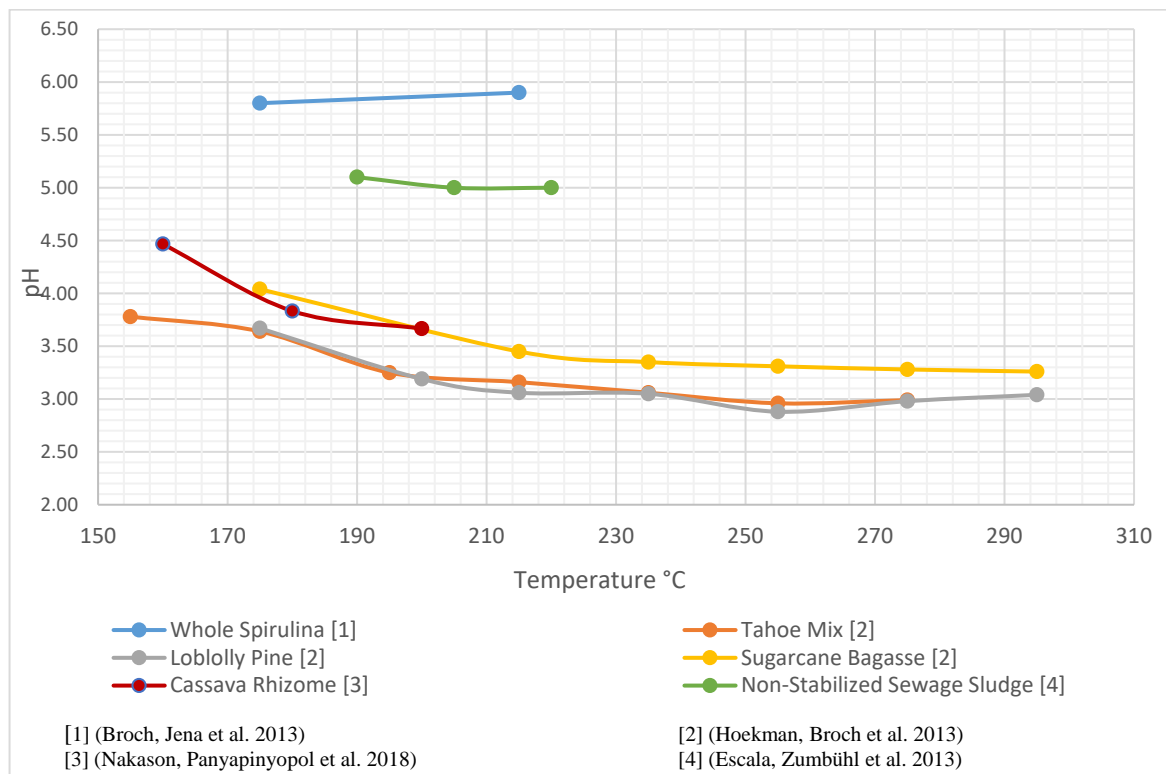


Figure 26 pH Value Variation for Different Biomasses

Figure 26 shows the variation of pH value with respect to the set temperature for diverse biomasses. There is a noticeable tendency of the pH value to decrease as the set temperature increases for HTC treatments of lignocellulosic biomasses, whereas for other biomasses the tendency is less notorious or even opposite, but this last observation is rather inconclusive given the low amount of data.

4.2.2 Electric Conductivity

Another common characteristic of HTC liquors is their relatively high electric conductivity (EC). Table 2 shows some values of EC determined by researchers. According to these results in particular, the EC of HTC liquors is the range between 10 mS/cm – 15 mS/cm. As reference values for comparison, the typical EC of drinking water is between 0.05 mS/cm to 0.5 mS/cm, while the EC of sea water is around 50 mS/cm (Lenntech 2018). The high EC indicates the presence of salts in the HTC liquors (Escala, Zumbühl et al. 2013).

Table 2 Electric Conductivity of HTC Liquors

Source	Biomass	Set Temp °C	Total Time (h)	Holding Time (h)	EC (mS/cm)
(Escala, Zumbühl et al. 2013)	Stabilized Sewage Sludge (Catalyst: Citric acid)	205	7	0.4	13.9
	Stabilized Sewage Sludge	205	7	0.3	14.3
	Non-Stabilized Sewage Sludge	190	5	2.4	11.2
	Non-Stabilized Sewage Sludge	205	5	1.9	10.9
	Non-Stabilized Sewage Sludge	220	5	2.4	12
	Non-Stabilized Sewage Sludge	205	7	4.0	12.2
(Hitzl, Corma et al. 2015) Ingelia	Garden Pruning (mainly)	>200	8 to 16	NM	11.4

4.2.3 TOC and COD

The significant content of total organic carbon (TOC) and the high level of chemical oxygen demand (COD) are also characteristics commonly found in the analysis of HTCL. The TOC concentrations which could reach values close to 20 g/L (Reza, Becker et al. 2014) are the result of dissolved carbon that could not remain bonded to the hydrochar (Dea Marchetti 2013). Figure 27 depicts the behavior of TOC content (as a percentage of dry feedstock) of HTC liquors from the processes of different kinds of Biomass, it can be noticed the overall increasing tendency as temperature increases, with the exception of cassava rhizome.

Nevertheless, the values fluctuate showing peaks for TOC content at intermediate reaction temperatures (230°C - 260°C).

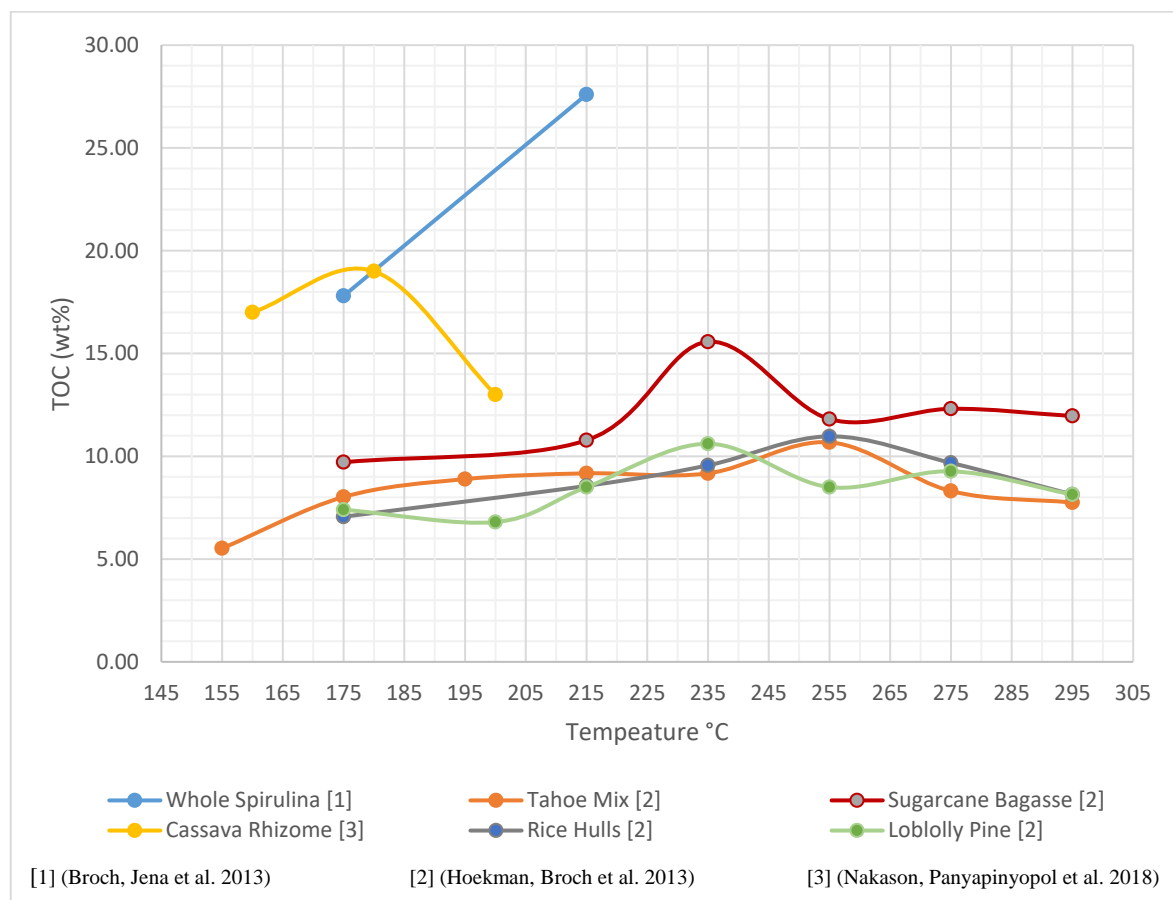


Figure 27 TOC with respect to Set Temperature for Diverse Biomasses

Table 3 TOC Content in HTC Liquors from Treatments at Different Holding Times

Source	Biomass	Set Temp °C	Holding Time (h)	TOC (mg/L)
(Reza, Becker et al. 2014)	Maize Silage	200	0.3	17777
	Maize Silage	200	1	15205
	Maize Silage	200	3	10111
	Maize Silage	200	6	9468
	Maize Silage	250	0.3	11553
	Maize Silage	250	1	9241
	Maize Silage	250	3	9094
	Maize Silage	250	6	7980
	Maize Silage	230	1	16842
(Wirth, Mumme 2013)	Corn Silage	220	6	15660

Table 3 shows the TOC content in mg/L of HTC liquors from treatments performed with different holding times. It is observed that the TOC concentrations decrease as the holding time of the treatment increases, this is probably due to polymerization and condensation that fix organic compounds to the biocrude and consequently to the hydrochar (see Figure 20).

4.2.4 Non-Volatile Residue (NVR)

Figure 28 shows a graph constructed using the NVR concentrations in HTC liquors determined by two different studies in relation to the set temperatures of the treatments. As noticed, the NVR concentrations could be considerably high, in the case of whole spirulina the NVR found in the liquors is 60 wt% of the dry feedstock for treatments at 215°C. The NVR content of liquors from the treatment of lignocellulosic biomasses is lower and varies in the range between 5 wt% and 25 wt% being higher for herbaceous biomasses. In addition, the behavior of NVR content in respect to the treatment temperature is not linear, it fluctuates showing minimum values at intermediate temperatures and relatively high values at low and high temperatures. The fluctuations are uniform for all the lignocellulosic biomasses.

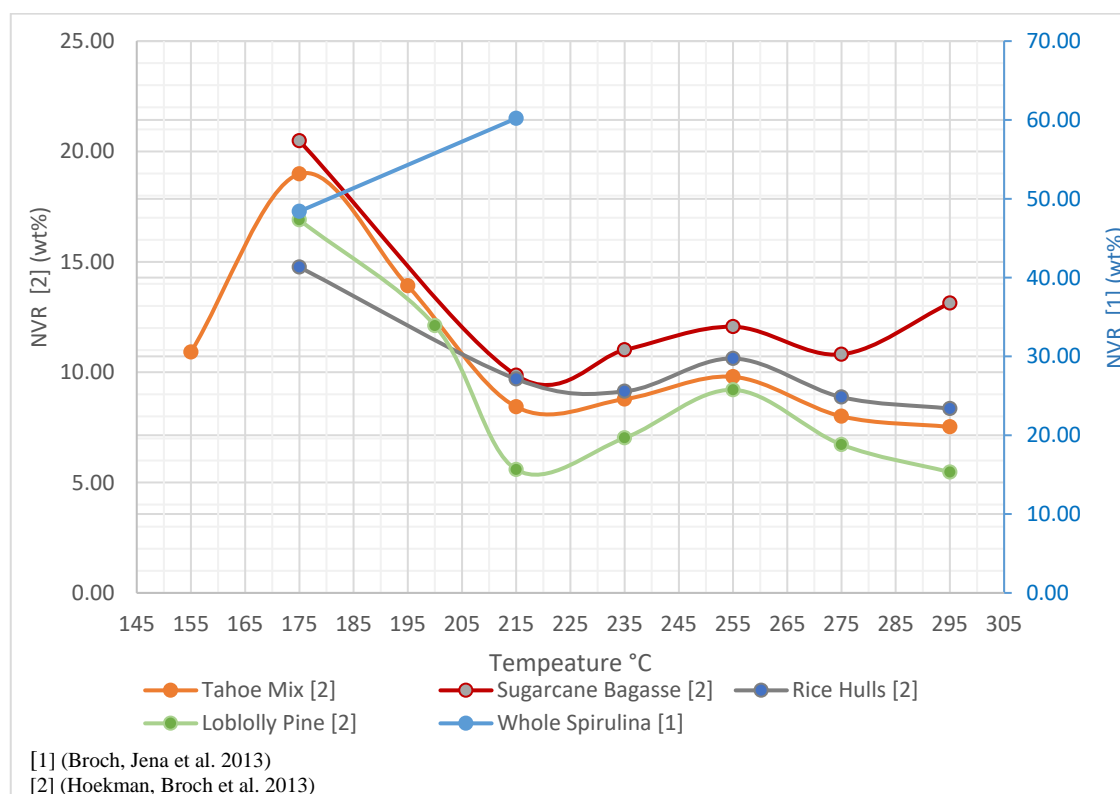


Figure 28 NVR concentration on HTL liquors from different Biomasses

4.3 Chemical Composition

The chemical composition of HTC liquors is also closely linked to treatment parameters and the type of raw biomass fed in the process. Nevertheless, the results of the analysis of HTC liquors found in the literature concur in finding high concentrations of organic and inorganic compounds that can be classified into categories as: sugars, organic acids, HMF and furfurals, phenols and other compounds.

4.3.1 Sugars

The formation of monosaccharides such as xylose, glucose, sucrose, mannose, arabinose and fructose, within others, are the result of the hydrolysis and dissolution of the cellulose, hemicellulose and starch present in the feedstock biomass. Usually, these reactions occur at rather low temperatures, thus, it is expected to find significant amounts of sugars in HTC liquors proceeding from processes conducted at low set temperatures (175°C - 235°C). But also, a part of the cellulose reacts at higher temperatures (230°C - 260°C) (Hoekman, Broch et al. 2013, Yan, Hastings et al. 2010, Reza, Becker et al. 2014). This behavior is generally observed in the results of analysis of HTC liquors available in the literature. Nevertheless, the ratios of sugar formation at different temperatures vary according to the feedstock.

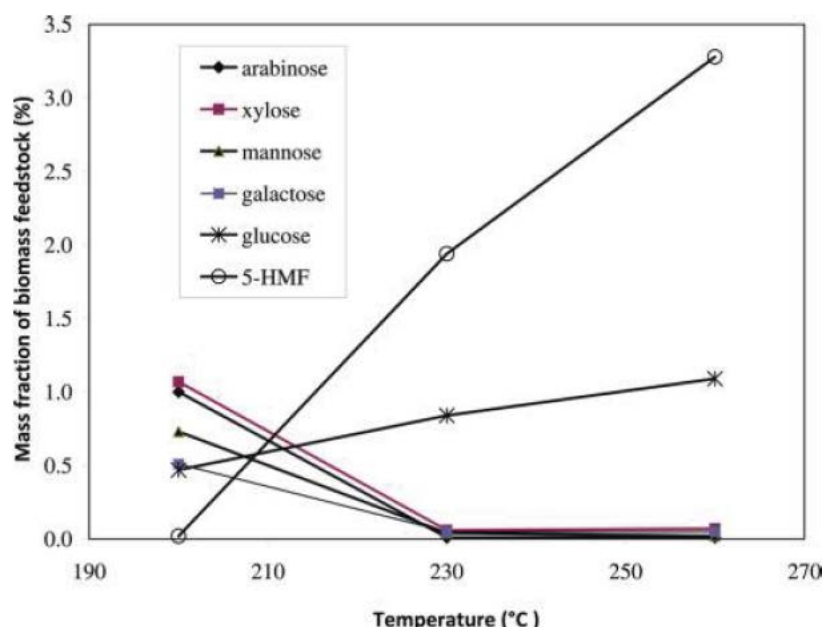


Figure 29 Precipitates of HTC Liquors at different temperatures (Yan, Hastings et al. 2010)

In order to illustrate the correlation between sugars formation and process temperature, Yan, Hastings et al. (2010) measured and graphed the content of the most representative sugars including 5-HMF (5-hydroxymethyl furfural) present in HTC liquors from the treatment of Loblolly Pine at temperatures between 200°C and 260°C, the results are shown in Figure 29. The percentages are based on the dry mass weight of the feedstock. As seen, the content of sugars decreases drastically as the set temperature increases.

With the purpose of understanding the behavior of sugars formation in the HTC liquors from treatments of different feedstock biomasses, results from Hoekman, Broch et al. (2013) were organized and graphed in Figure 30, the quantities are expressed in percentage of dry feedstock. It is important to mention that in this particular study; sugar alcohols are included in this category. As observed, the sugar formation is higher for woody biomasses than for herbaceous biomasses in the range from 175 °C to 235 °C, but the sugar formation for woody biomass occurs at slightly higher temperatures. Also, the tendency with respect to the temperature coincide with ranges of temperatures where hydrolysis occurs, as explained above.

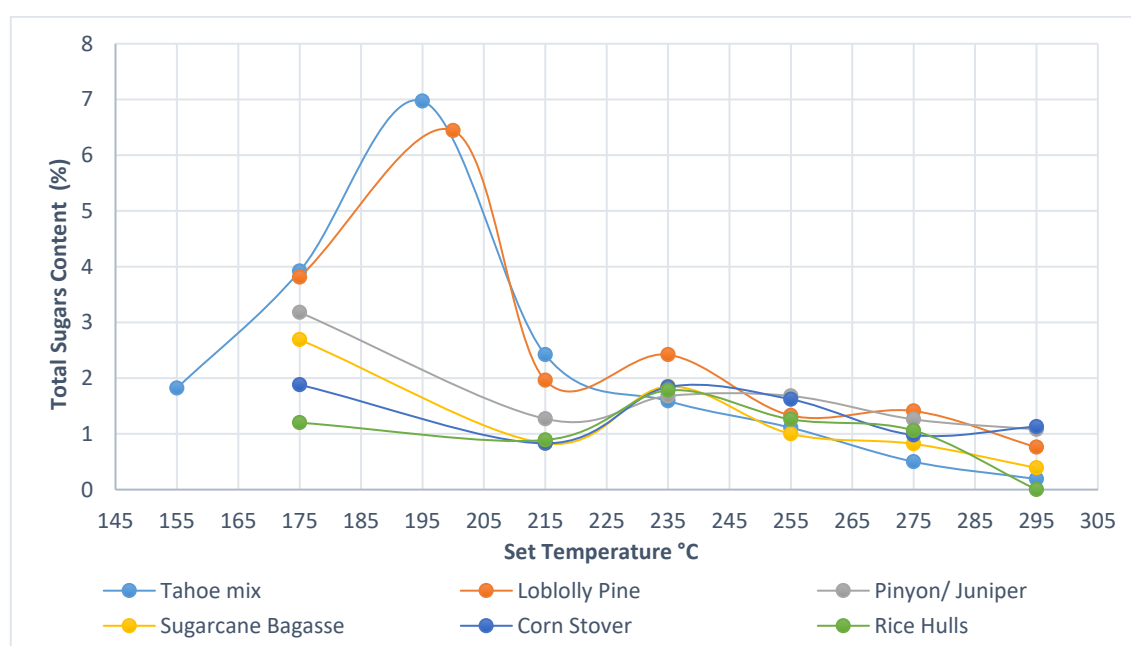


Figure 30 Content of Sugars in HTCL from processes of herbaceous and woody biomasses at different set temperatures. Based on data from (Hoekman, Broch et al. 2013)

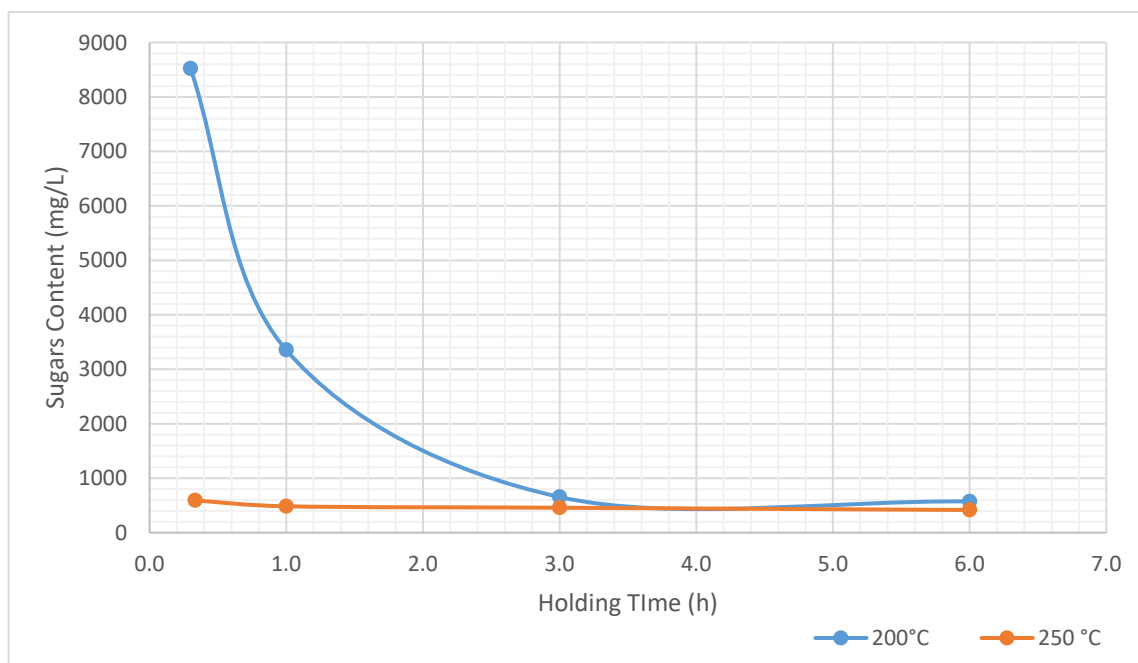


Figure 31 Sugars Content in HTC liquors for Different Holding Times. Based on data from (Reza, Becker et al. 2014)

The concentration of sugars in HTC liquors also changes according to the reaction times. (Reza, Becker et al. 2014) measured the concentration of sugars (glucose, xylose, sucrose) in HTC liquors resulting from the treatments of maize silage at 200°C and 250°C at 4 different holding times. The results are shown in Figure 31. As noticed, high amounts of sugars are produced at mild temperatures (around 200°C), but they degrade quickly into other compounds.

4.3.2 Organic Acids

As stated in sub-section 4.2.1, HTC liquors commonly show high content of organic acids. These compounds result from the degradation of sugars in subcritical water (Reza, Andert et al. 2014, Reza, Becker et al. 2014), and also from degradation of 5-HMF and furfurals at temperatures higher than 275°C (Hoekman, Broch et al. 2013). These phenomena partly explain the abrupt decrease in the overall sugars content in HTC liquors at temperatures >260°C and between 2 and 3 hours of reaction times (See Figure 19 and Figure 20).

The organic acids found in HTC liquors include, maleic, malonic, methane sulfonic (MSA), levulinic, glutaric and oxalic acids. However, generally, the acids found in more substantial concentrations are acetic, formic and lactic acids.

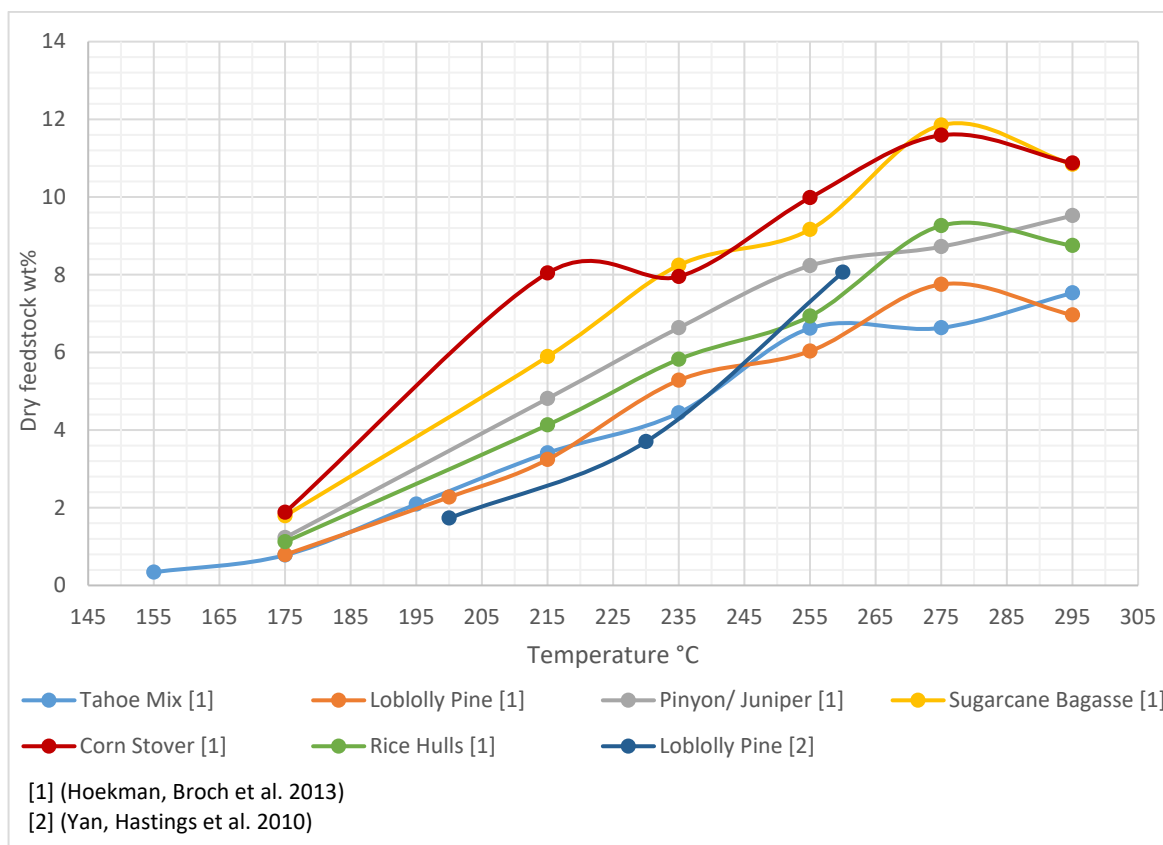


Figure 32 Acids Content in HTC Liquors from treatment of Diverse Biomasses

Figure 32 depicts the overall organic acids content in HTC liquors from the treatment of several kinds of biomass. The graph illustrates the behavior of organic acids formation during the HTC process. The acids content in the liquors increases as the temperature increases, this trend is common for all the biomasses analyzed. But also, it is noticeable that the liquors originated from treatment of herbaceous biomasses have a higher overall organic acids content than woody biomasses (Hoekman, Broch et al. 2013, Yan, Hastings et al. 2010).

Similarly to what it occurs with sugars content, organic acids content also decreases as the process holding time increases. In order to illustrate this behavior, Figure 33 was generated using data from (Reza, Becker et al. 2014), which corresponds to the analysis of HTCL originated by the treatments of Maize silage at with different holding times. The decreasing tendency occurs due to the further degradation (decarboxylation) of organic acids, forming H₂O and CO₂ (Reza, Becker et al. 2014, Hoekman, Broch et al. 2013).

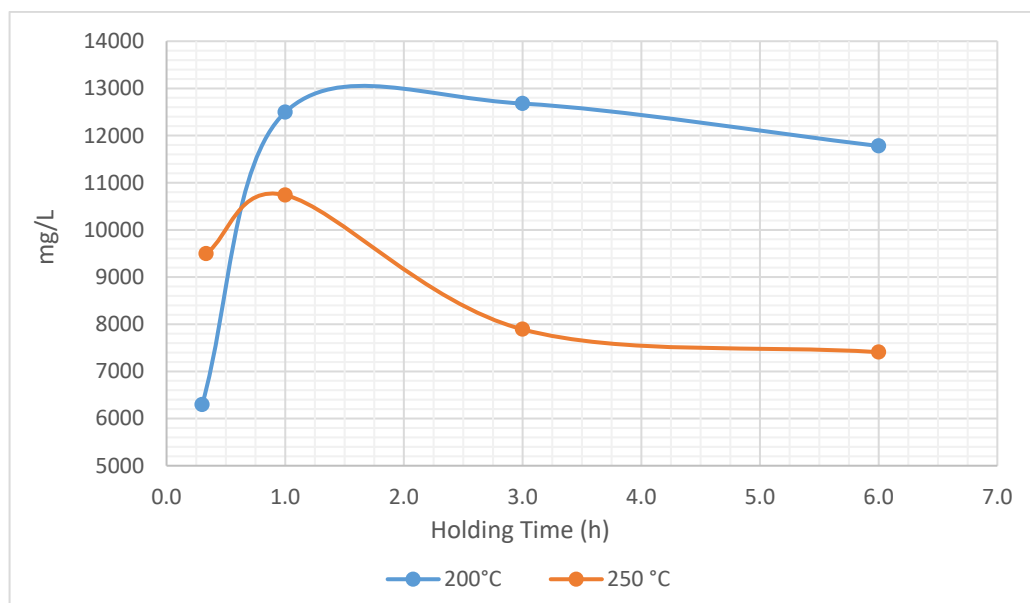


Figure 33 Content of Organic Acids in HTC Liquors Vs Process Holding Time. Based on data from (Reza, Becker et al. 2014)

4.3.3 HMF and Furfurals

HFM and furfurals result from the dehydration of hydrolysis products, more precisely hexoses, the most common compounds in this group are 5-HMF and 2-furfural. These compounds could be considered transitional products within the HTC process, since they form at intermediate temperatures and subsequently, they either continue dehydration and decarboxylation into H_2O and CO_2 or they degrade into organic acids, so their concentration decreases rapidly at higher temperatures (Reza, Becker et al. 2014, Hoekman, Broch et al. 2013, Reza, Andert et al. 2014).

The contents of 5-HFM and furfurals as function of the set temperature are shown in Figure 34 and Figure 35 respectively. Content of 5-HMF peaked close to 4.5 wt% of dry feedstock, in the range between 210°C and 240°C in the case of HTC treatment of woody biomasses. For herbaceous biomasses, the maximum content of 5-HFM was 2 wt% at slightly higher temperatures 230°C -260°C. Contents of furfurals have a similar behavior, the maximum values are found at same ranges of temperatures. However, HTC liquors from herbaceous biomasses show the highest furfurals content, as opposite to woody biomasses.

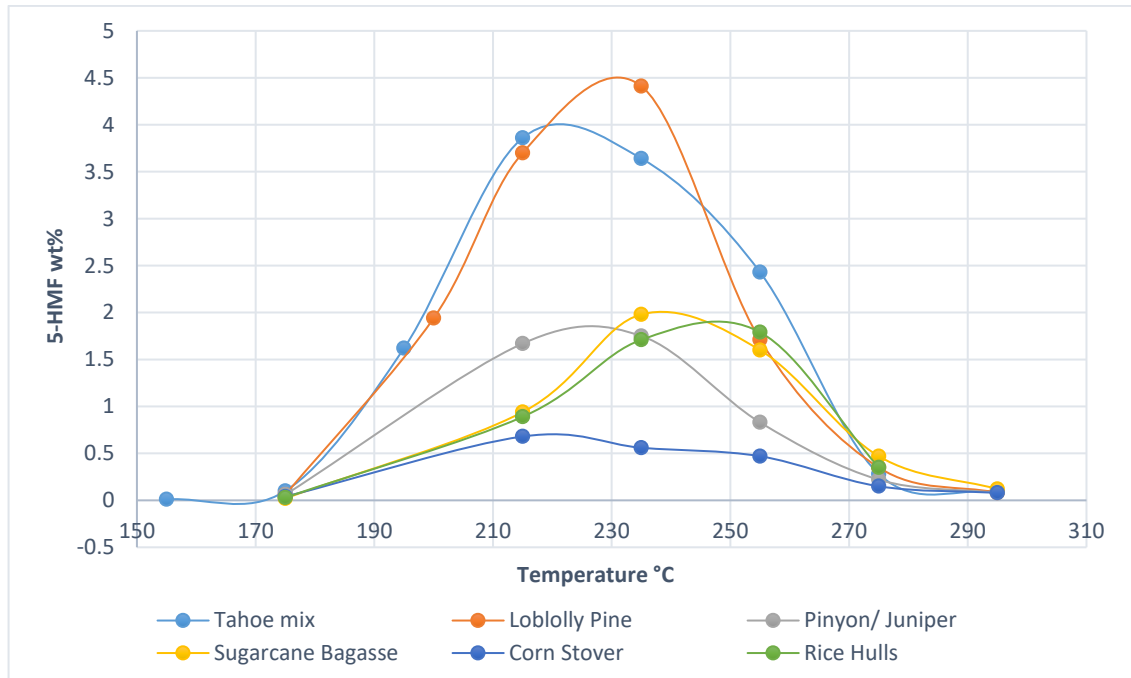


Figure 34 Content of 5-HMF in HTC Liquors from Diverse Biomasses. Based on data from (Hoekman, Broch et al. 2013)

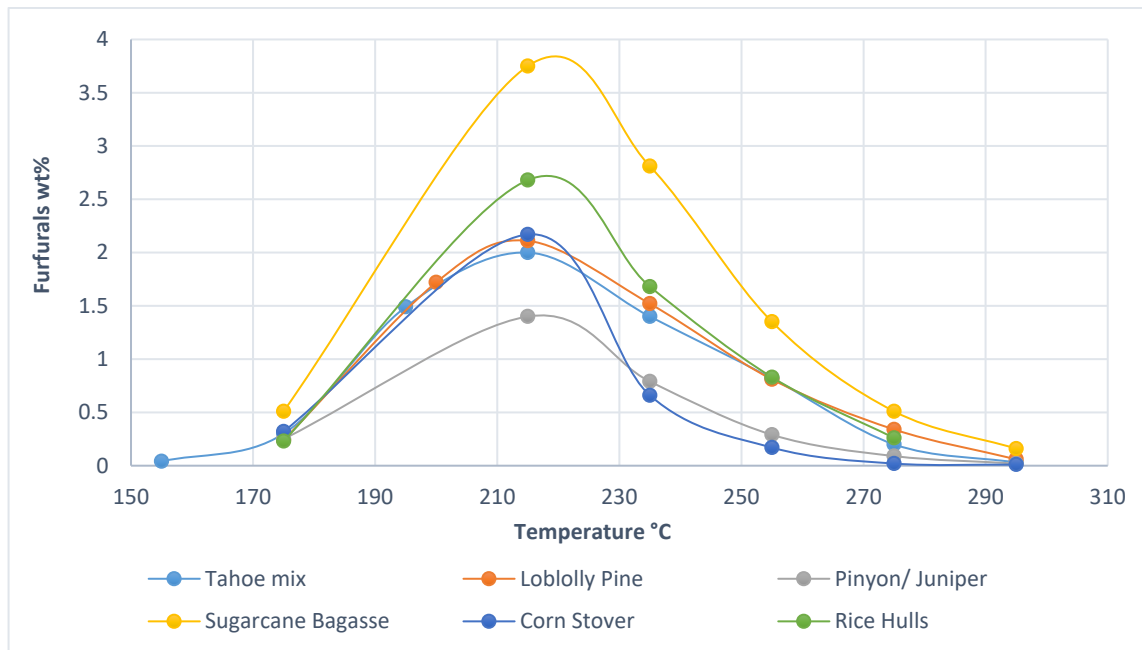


Figure 35 Content of Furfurals in HTC Liquors from Diverse Biomasses

Figure 36 shows the content of HMF and furfurals content in HTC with respect to the treatment holding time for treatments at 200°C and 250°C (Reza, Becker et al. 2014). As seen, the concentration of HMF and furfurals decreases rapidly. In addition, the reduction

rate is proportional to the set temperature. In the case of treatment at 260°C, the concentrations of HMF and Furfurals drop to zero after 3 hours.

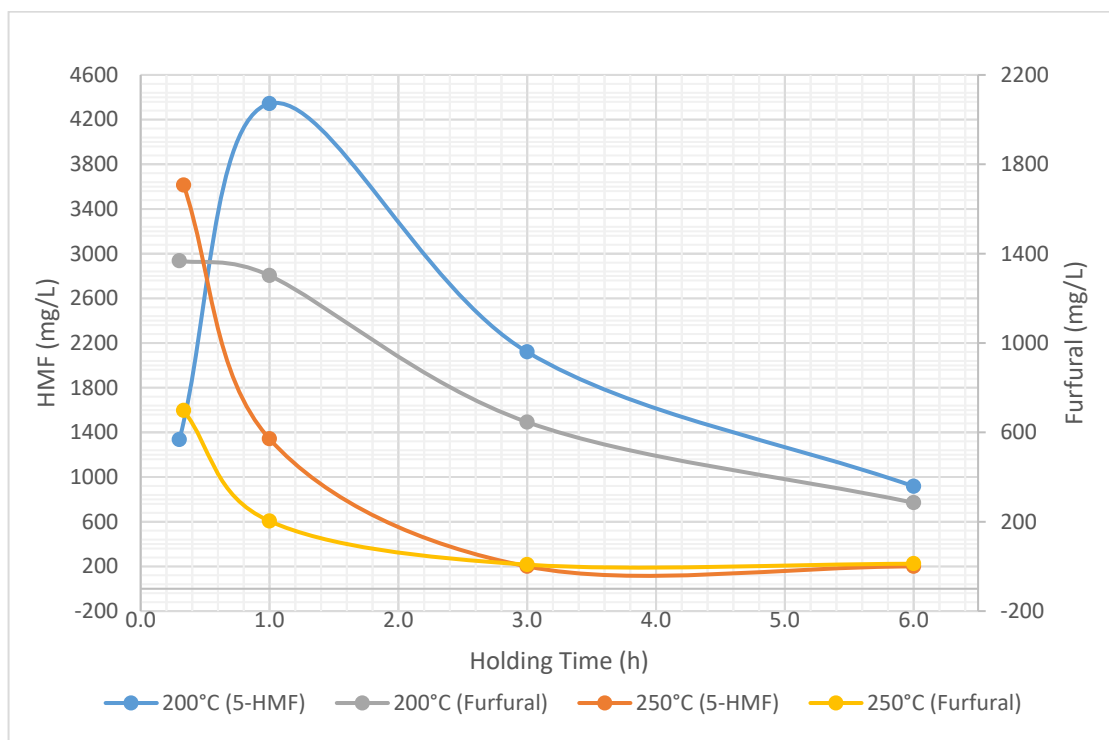


Figure 36 Content of HMF and Furfurals in HTC Liquors from Maize Silage. Based on data from (Reza, Becker et al. 2014)

4.3.4 Phenols

As mentioned in section 3.4, generally most of the lignin present in lignocellulosic feedstocks remains unreactive during the HTC process and stays attached to the solid part. However, small parts of lignin undergo depolymerization and repolymerization in acid media at high temperatures, usually above 260°C. The reactions of lignin produce phenols and phenolic derivatives (Xiao, Shi et al. 2012, Reza, Andert et al. 2014). Table 4 collects data from different studies. It can be noticed that the concentration of phenols in HTC liquors from treatment of sewage sludge is significantly higher than the concentration in liquors obtained from treatment of lignocellulosic biomass. This is due to the presence of phenols in the sewage sludge prior treatment. For example the dry matter analysis of the non-stabilized sludge established that there was a loss of 28 wt% of Phenols between the feedstock and the produced hydrochar. Therefore, this amount of phenols content was transferred to the HTC liquors (Escala, Zumbühl et al. 2013).

Table 4 Phenol contents in HTC Liquors

Source	Biomass	Set Temp °C	Total Time (h)	Holding Time (h)	Phenol (mg/L)
(Escala, Zumbühl et al. 2013)	Stabilized Sewage Sludge (Catalyst: Citric acid)	205	7	0.4	666
	Stabilized Sewage Sludge	205	7	0.3	633
	Non-Stabilized Sewage Sludge	190	5	2.4	361
	Non-Stabilized Sewage Sludge	205	5	1.9	292
	Non-Stabilized Sewage Sludge	220	5	2.4	384
	Non-Stabilized Sewage Sludge	205	7	4.0	384
(Reza, Becker et al. 2014)	Maize Silage	200	NM	0.3	23
	Maize Silage	200	NM	1	45
	Maize Silage	200	NM	3	48
	Maize Silage	200	NM	6	67
	Maize Silage	250	NM	0.3	109
	Maize Silage	250	NM	1	139
	Maize Silage	250	NM	3	109
	Maize Silage	250	NM	6	91
	Maize Silage	230	NM	1	172
(Wirth, Mumme 2013)	Corn Silage	220	NM	6	290

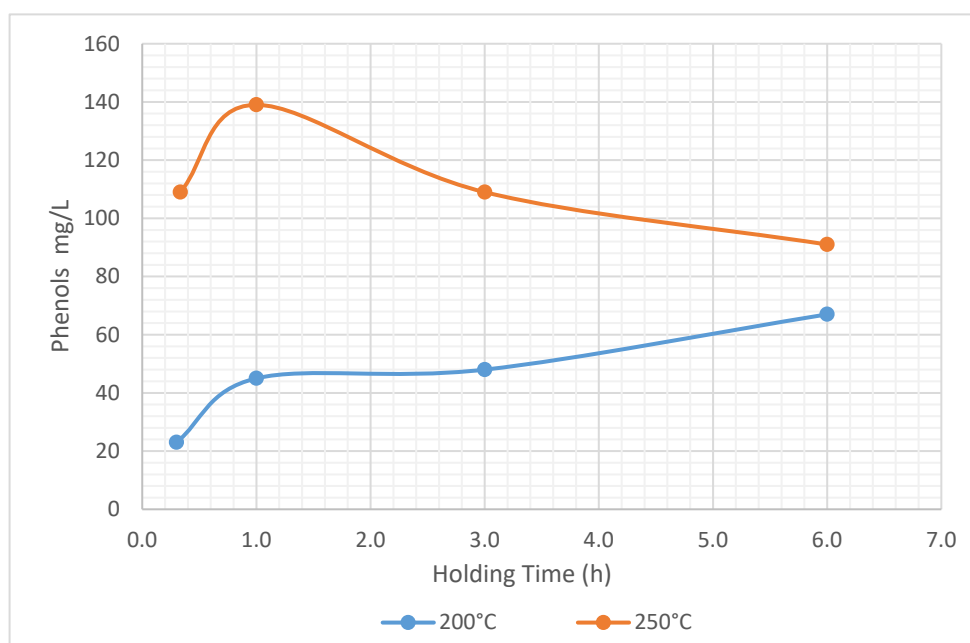


Figure 37 Content of Phenols in HTCL from Treatments at Different Holding Times. Based on data from (Reza, Becker et al. 2014)

The variation of phenols content in HTC liquors from maize silage in respect to process holding times are shown in Figure 37. As depicted, the trends are opposite after one hour of holding time. The content of phenols decreases in time at set temperature of 250°C, whereas for HTC process at 200°C, the phenols content in liquors increases with time. This is probably due to the polymerization and condensation that fix the intermediate products to the biocrude and subsequently to the solid phase (see Figure 19 and Figure 20) (Reza, Andert et al. 2014, Hoekman, Broch et al. 2013).

4.3.5 Nutrients and Inorganic Compounds

As established in section 3.4, typically the inorganic components present in the feedstock biomass remain inert during HTC processes conducted at temperatures below 260°C. During these treatments, the degradation of polymeric components may transfer inorganics compounds from the solid to the liquid phase, which is the main reason for the reduction of ash content in the hydrochar compared to the feedstock (Reza, Andert et al. 2014, Kruse, Funke et al. 2013).

Some researchers have focused their analysis of HTC liquors in the determination of content of nutrients and inorganic compounds in order to explore their attributes as fertilizers. Table 5 encompasses results from different studies showing the most significant nutrients and inorganic compounds found in HTC liquors from different feedstocks. As seen, the most relevant element found in the liquors is Nitrogen. As known, total nitrogen (TN) includes total Kjeldahl nitrogen (TKN), nitrate, nitrite. TN concentrations are higher in HTC liquors from non-lignocellulosic biomasses.

In addition to the elements shown in Table 5, other elements can be found in abundant concentrations in HTC liquors, for example the HTC liquors from the treatment of *Nannocloropsis oculata* (microalgae) showed a sodium (Na) concentration of 8966 mg/L, along with very small concentrations of other metals such as Magnesium (Mg), Manganese (Mn), Iron (Fe), Boron (B), Nickel (Ni) and Chromium (Cr) (Titirici, Funke et al. 2015). Whereas samples of HTC liquors from garden pruning showed an average Na concentration of 571 mg/L and a calcium (Ca) average concentration of 2326 mg/L along with small concentrations of Mg, Fe and B (Hitzl, Corma et al. 2015).

Table 5 Most significant Nutrients Contents in HTC Liquors

Source	Biomass	Set Temp °C	Holding Time (h)	TN (mg/L)	TP (mg/L)	K (mg/L)
(Escala, Zumbühl et al. 2013)	Stabilized Sewage Sludge (Catalyst: Citric acid)	205	0.4	2590	14.3	NM
	Stabilized Sewage Sludge	205	0.3	2710	17.8	NM
	Non-Stabilized Sewage Sludge	190	2.4	3183	159.6	NM
	Non-Stabilized Sewage Sludge	205	1.9	2263	72.7	NM
	Non-Stabilized Sewage Sludge	220	2.4	4720	158.9	NM
	Non-Stabilized Sewage Sludge	205	4.0	4673	85.8	NM
(Schneider, Escala et al. 2011)	Bamboo	220	6	100	52	1642
	Whey	205	6	511	226	1387
	Digestate	205	6	2342	6.4	6213
	Sewage Sludge	205	6	1230	10	446
(Wirth, Mumme 2013)	Corn Silage	220	6	915	197.4	NM
(Hitzl, Corma et al. 2015) Ingelia	Garden Pruning (mainly)	>200	8 to 16	490	18	1306
(Du, Hu et al. 2012)	Nannocloropsis oculata (microalgae)	200	0.67	9650	343	775.5

The analysis of the content of nutrients in liquors and their pH value in comparison to organic fertilizers is going to be addressed in section 6.4 in order to estimate the value of HTC liquors as soil enhancer.

5 ANALYZES OF HTC LIQUORS SAMPLES

5.1 Description

Noteworthy, this study was performed as part of an ongoing research which objectives were focused primary in the analysis of the hydrochar resulting from the HTC process of different tropical biomasses. Therefore, the HTC liquors analyzed for the purposes of this thesis were obtained as side products of experimental HTC treatments performed. Therefore, the parameters of the HTC treatments were previously established according to the goals of this ongoing research.

5.2 Materials

The samples of HTC liquors were obtained after the hydrothermal carbonization of four different biomasses endemic or commonly found in Latin America: Coffee tree, Coffee parchment (both from *Coffea Arábica*), Eucalyptus Grandis wood and Giant Bamboo. Figure 38 Shows the biomass samples prior HTC treatment.



Figure 38 Biomasses Samples before HTC treatment (Silakova 2018)

5.3 Methodology

This section will describe all the procedures followed during the HTC treatment and the analysis of the HTC liquors samples, including generalities of the HTC treatment itself.

5.3.1 HTC treatments

The experimental HTC treatments were performed according to parameters specified in Table 6, using in were performed in the closed, stainless steel batch reactor shown in Figure 39, which has a maximum operation temperature of 300°C and a maximum pressure of 40 bar set by the pressure relief valve.

Table 6 Parameters of HTC experimental treatments. Modified from (Silakova 2018)

	Coffee Bean Parchment	Coffee Wood	Eucalyptus Wood	Bamboo
Water to Biomass Ratio	8	8	8	8
Residence Time[h]	3	3	3	3
Solid Mass [g]	50,92	50,86	51,36	51,07
Solid Mass dry[g]	50,0	50,0	50,0	50,0
Liquid Mass [g]	399,08	399,14	398,61	398,93
Temperatures [°C]	180	180	180	180
	200	200	200	200
	220	220	220	220
	240	--	240	--

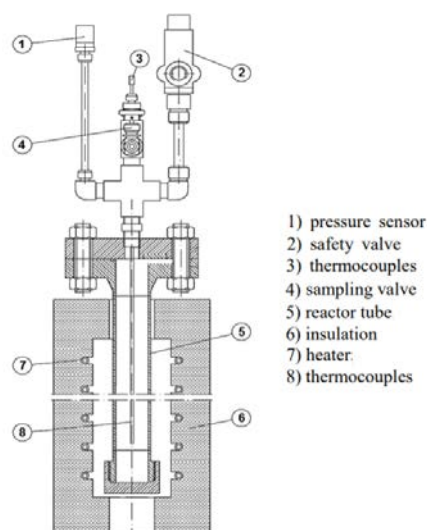


Figure 39 Experimental Unit (Sermyagina 2016)

5.3.2 Obtention of HTC Liquors

At the end of each HTC treatment, the hydrochar slurry formed by the carbonized biomass and liquid products was collected and separated through vacuum filtration by using a Büchner funnel with a Whatman glass microfiber filter paper grade GF/A (pore size: 1.6 μm) on a Büchner flask. The HTC liquors were retrieved from the Büchner flask and kept in closed plastic transparent containers. Samples of approximately 50-100 ml/each were taken from every treatment of all biomasses at the temperatures shown in Table 6, in total 14 samples were taken for analysis. All the samples were kept at room temperature exposed to normal light conditions; the storing time was not the same for all the samples.

To start the analyses the HTC liquors were once again directed through vacuum filtration using a Büchner funnel with a Whatman glass microfiber filters, Grade GF/F with pore size of 0.7 μm , the particles of bigger than this remained in the filter and were not analyzed, the analysis centered in the dissolved matter. This secondary filtration was performed in order to keep the integrity of the laboratory analysis equipment. Figure 40 shows the some of the samples of HTC liquors immediately after secondary filtration.



Figure 40 Liquor Samples after Secondary Filtration

5.3.3 Gravimetric Determination NVR

After secondary filtration, small quantities (approx. 4 ml) were taken from each one of the HTC liquors samples and placed in previously tared and completely clean crucibles. Then, all the crucibles containing the small samples of HTC liquors were weighted by using a high-precision weighting scale, values of the weight were registered.



Figure 41 Some of the HTC Liquors Samples Before Placing them in the oven

Once all the samples were weighted, the crucibles were placed into the oven and kept at the temperature of 105 ± 2 °C for 20 to 24 hours in order to fully eliminate water (Hoekman, Broch et al. 2013) (Figure 41 Shows some samples before drying). Then, the crucibles were weighted one more time and the values were registered. The value of NVR is given by Equation (3). The mass of the liquors sample before drying the yields of liquid and NVR concentration are given by Equations (4), (5) and (6) respectively.

$$\begin{aligned}
 & \mathbf{NVR [g]} \rightarrow m_{nvr} [g] = m_{T_dry} [g] - m_{cru} [g] \\
 & m_{T_dry} \rightarrow \text{Total mass of the crucible and its content after drying} \\
 & m_{cru} \rightarrow \text{tared mass of the crucible}
 \end{aligned} \tag{3}$$

$$\begin{aligned}
 & \mathbf{HTC Liquor mass [g]} \rightarrow m_{liquid} [g] = m_{T_liquid} [g] - m_{cru} [g] \\
 & m_{T_dry} \rightarrow \text{Total mass of the crucible and its content before drying process} \\
 & m_{cru} \rightarrow \text{tared mass of the crucible}
 \end{aligned} \tag{4}$$

$$\mathbf{Yield to Liquid [\%]} \rightarrow LY[\%] = \frac{m_{nvr} [g]}{m_{liquid} [g]} * 100 \tag{5}$$

$$\begin{aligned}
 & \mathbf{NVR Concentration \left[\frac{mg}{L} \right]} \rightarrow \mathbf{NVR \left[\frac{mg}{L} \right]} = \frac{m_{nvr} [mg]}{(m_{liquid} [mg] - m_{nvr} [mg]) / 10^6 [mg/L]} \\
 & m_{r_Biom} \rightarrow \text{Mass of the dry Biomass before treatment}
 \end{aligned} \tag{6}$$

5.3.4 Chemical Analysis

The chemical analysis consists of two parts, firstly pH analysis followed by TOC analysis. The pH analysis was performed by using a digital pH meter after secondary filtration, at room temperature. At least 3 readings were taken per sample, then the average values were registered. The TOC analysis determined also the total carbon and the inorganic carbon (IC). These analyses were performed by using a Shimadzu TOC-Lcph/cpn analyzer unit, with a dilution function in the range 10-100 mg/L, according to recommended procedure for TOC determination of surface and underground water (Shimadzu 2018).

5.4 Results and Discussion

5.4.1 NVR Analysis

Table 7 summarizes the results obtained from the gravimetric analysis by applying equations (3), (4), (5) and (6).

Table 7 Results of the NVR Gravimetric Analyses

Temp. °C	Parameter	Coffee wood	Parchment	Bamboo	Eucalyptus
180	Mass of the crucible[g]	13.5025	13.9697	7.1861	5.8555
	HTC Liquor mass[mg]	3331.2	3531.4	4653.2	4191.5
	NVR [mg]	40.5	108.9	103.1	60.9
	Yield to Liquid [%]	1.22	3.08	2.22	1.45
	NVR (mg/L)	12300	31800	22700	14800
200	Mass of the crucible[g]	13.3527	14.1821	7.4122	8.1374
	HTC Liquor mass[mg]	3881.3	3910.35	3976.2	3957
	NVR [mg]	45.1	103.8	76.6	47.9
	Yield to Liquid [%]	1.16	2.65	1.93	1.21
	NVR (mg/L)	11800	27300	19600	12200
220	Mass of the crucible[g]	13.4546	11.7397	7.4327	7.4491
	HTC Liquor mass[mg]	4345.3	3862.65	4433.7	4107.5
	NVR [mg]	51.4	102.8	72.5	40.2
	Yield to Liquid [%]	1.18	2.66	1.64	0.98
	NVR (mg/L)	12000	27300	16600	9900
240	Mass of the crucible[g]		9.9572		7.2915
	HTC Liquor mass[mg]		3803		4166.1
	NVR [mg]		90.2		106.2
	Yield to Liquid [%]		2.37		2.55
	NVR (mg/L)		24300		26200

The yield-to-liquid is used as a reference value for comparison purposes, this quantity is a relation between the mass of the non-volatile residues and the original mass of liquors of the particular sample. Figure 42 depicts the behavior of the NVR concentration in respect to the set temperature of the HTC treatment. It can be noted that as a general tendency, the NVR in the HTC liquors decreases as the temperature increases. However, in section 4.2.4 it was seen how the NVR concentrations hover within relatively low values at intermediate temperatures and rise at higher temperatures, unfortunately samples of liquors from HTC treatment at 240°C of coffee wood and bamboo were not available for analysis, so the evaluation of their behavior to find similarities with literature is not conclusive. On the other hand, the NVR concentration in HTC liquors from Eucalyptus shows a behavior very similar to the results depicted in Figure 28, nevertheless, the steep increment in NVR concentration between 220°C and 240°C differs from the observed in the mentioned figure. The NVR concentrations in HTC liquors from lignocellulosic biomass are lower than in non-lignocellulosic feedstock, this was also observed in section 4.2.4.

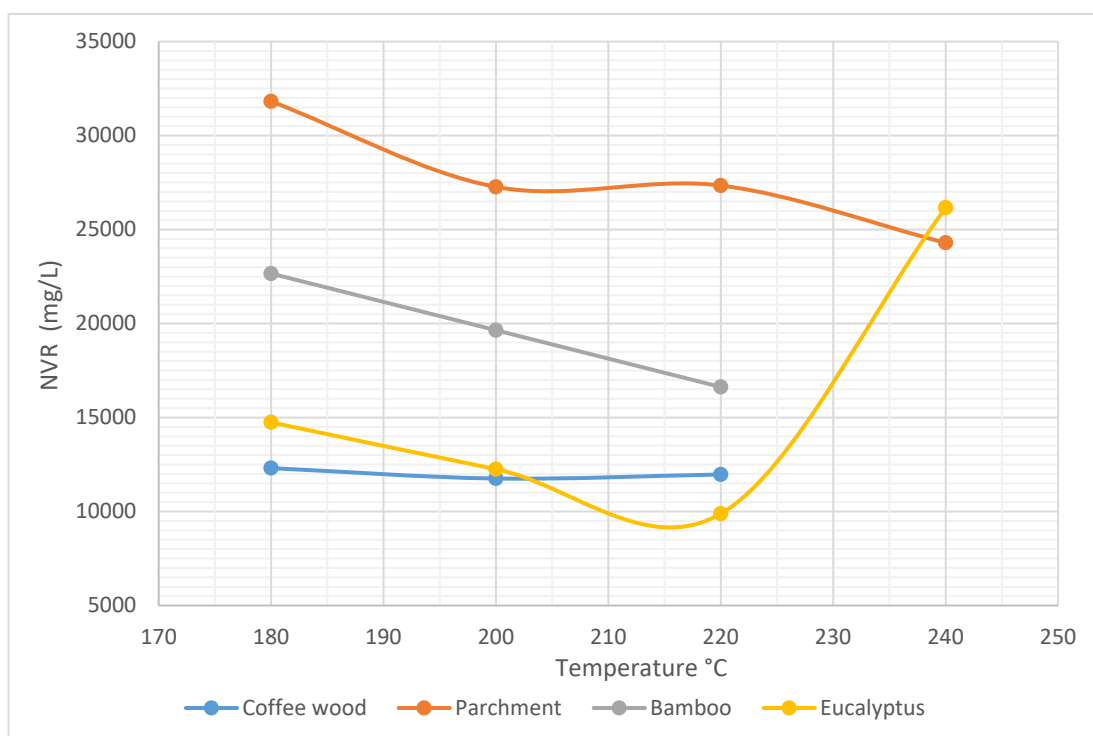


Figure 42 NVR concentration Vs Treatment Temperature

5.4.2 pH Analyses

Table 8 show the results obtained from pH measurements. The high acidity of the HTC liquors was expected given the established in section 4.2.1. The pH values in the range between 2.5 and 4.5 agree with the findings of other studies. Also, HTC liquors from the treatment on lignocellulosic biomasses show lower pH values, which was also expected.

Table 8 Results of pH Measurements

Temperature °C	pH			
	Coffee wood	Parchment	Bamboo	Eucalyptus
180	3.49	4.11	3.24	3.11
200	3.52	4.18	3.25	2.965
220	3.56	4.26	3.18	2.97
240		4.44		2.97

In general the pH values of the HTC liquors samples are rather steady along the range of treatments temperatures. Samples of liquors from Coffee Wood and parchment have an increasing trend, which is stronger in liquors from Parchment. Samples from treatments of Bamboo and Eucalyptus have slow decreasing tendencies.

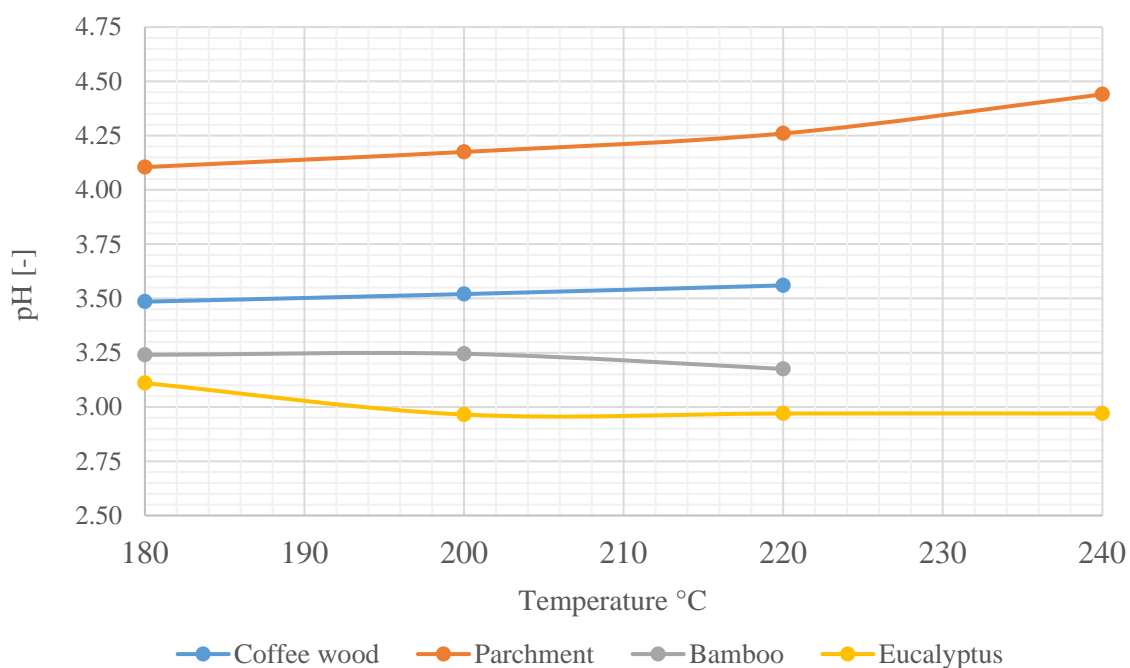


Figure 43 behavior of pH Results in Respect to HCT temperature.

5.4.3 TOC Analyses

Table 9 Summarizes the results obtained from TOC analyses unit for the HTC liquors samples. In general, the TOC concentration in all the samples where significantly high considering the results presented in Table 3, section 4.2.3. The maximum TOC concentration was found in the liquors from HTC treatment of coffee wood at 240°C, reaching 31 g/L, while in Table 3 the maximum concentration was nearly 18 g/L, for liquors from treatment of Maize silage at 200°C with residence time of 0.3 h.

Table 9 Results of TOC Analyses

Biomass	Temperature °C	TOC (mg/L)	TC (mg/L)	IC (mg/L)
Coffee wood	180	18370	18390	15.44
	200	20830	20850	20.66
	240	31050	31060	14.76
Coffee Bean Parchment	180	24800	24820	17.37
	200	24800	24820	15.52
	220	25520	25540	17.53
	240	22510	22530	16.43
Bamboo	180	27150	27160	16.94
	200	24960	24980	16.67
	220	21930	21950	17.01
Eucalyptus	180	20000	20030	15.14
	200	20530	20540	15.25
	220	17780	17800	19.61

Figure 44 depicts the behavior of the TOC concentration. The tendencies to fluctuate within short TOC concentrations ranges are similar to the ones shown in Figure 27 at same temperature intervals. However, also in this case, since no liquid samples of HTC treatment conducted at high temperatures available for analyzed, it is not possible to perform a proper comparative analyzes with results found in the existing literature.

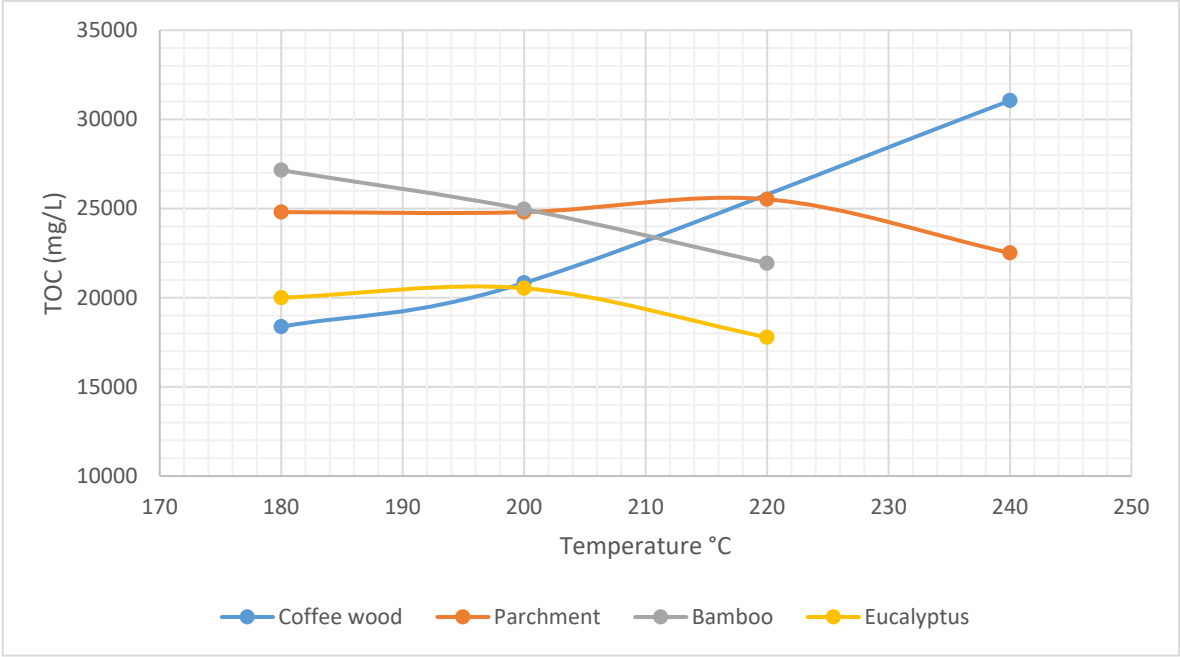


Figure 44 TOC Concentrations in HTC Liquors from treatments at different temperatures

6 HANDLING AND TREATMENT OPTIONS FOR HTC LIQUORS

Section 4 defined the typical characteristics and chemical composition of HTC liquors. Due to some of the attributes that were described, it is compulsory to establish proper treatment options for the HTC liquors, with the aim of ensuring the environmental viability of the HTC processes (Kabadayi Catalkopru, Kantarli et al. 2017). These treatment processes generate additional costs that could affect the profitability of HTC plants and subsequently the implementation and expansion of the technology.

However, as established previously, HTC liquors contain significant amounts of organic and inorganic compounds transferred from the solid products that may result useful for a wide variety of applications. In addition, the thermal and chemical energy could be exploited and used to improve the overall energetic efficiency of HTC plants.

This section will briefly explore different treatment pathways that offer opportunities to overcome the difficulties inherent to HTC liquors ensuring the sustainability of the technology.

6.1 Water Treatment

It is important to mention that HTC liquors do not contain pathogens given the treatment conditions. The organic and inorganic compounds present in HTC liquors can be removed from the water through water treatment in a regular sewage plant (Titirici, Funke et al. 2015), then the cleaned water can either be incorporated to a watershed or used for irrigation. An alternative solution is presented by Ingelia S.L at their HTC pilot plant, where TOC is removed from the liquors by using reverse osmosis, producing between 80 and 200 Kg of clean water per each ton of biomass processed (Ingelia 2018). Nevertheless, either of these solutions causes higher costs and energy consumption that need to be considered when analyzing the viability an HTC plant.

6.2 Liquors Recirculation

A common solution implemented in the existing large-scale HTC plants is the recirculation of the liquors. This method has multiple advantages, in first place the acids contained in the liquors decrease their pH, helping to initiate the degradation of raw feedstock. The

recirculation also improves the solid yield and the carbon content of the solid products reducing the content of organic acid and furfural derivatives in the end liquors. Finally, the recirculation of hot liquors helps the preheating of the incoming feedstock. However, the amount of the liquors that are recirculated is limited by the water content of the feedstock (Kruse, Funke et al. 2013, Reza, Rottler et al. 2015); if the biomass contains enough water to meet the requirements of the process, it would not be necessary to add more water to the feedstock, it is important to remember that one of the main benefits of HTC is that there is no need of dewatering the feedstock. Therefore, recirculation is not always a feasible solution. Moreover, according to process information obtained from Ingelia S.L, the temperatures of the HTC liquors is just above 40°C immediately after the separation from the solid phase in the press filter (Hitzl 2018), which means that in large scale plants, not always the HTC liquors contain exploitable thermal energy.

Kabadayi Catalkopru, Kantarli et al. (2017) conducted experiments executing HTC treatments of grape pomace, orange pomace and poultry litter. In total four runs were performed, the first one mixing the biomass with deionized water and the three following runs using liquors from the previous one for the mixture. This study concluded that part of the content of organic and inorganic compounds present in the liquors were transferred to the hydrochar without changing its heating value, but improving its combustion characteristics, for example the ignition temperature of the hydrochar was lowered.

In the case of the HTC liquors studied (see section 5), liquors recirculation could be a feasible primary treatment, both, in laboratory experiments and also in case of treatments in large scale. In view of that none of the mentioned biomasses have a considerable water content (see Table 6). Therefore, the biomass has to be mixed with water in a solid-water ratio of 1:8. This means that if recirculation is implemented, not only the water consumption would be lowered drastically, but also the characteristics of the hydrochar might be improved, as shown in previous researches. However, the liquors can be recirculated only a limited amount of cycles, then they have to be directed to a secondary treatment.

The quantity of times than the liquors can be recirculated depends on feedstock and process parameters. Nevertheless, in the study mentioned, the liquors were reused 3 times.

6.3 Materials Recovery

The concentration of different compounds in the HTC liquors depends entirely on treatments parameters. However, the HTC process parameters are determined aiming to the optimization of the characteristics of the hydrochar. Improving the yields of compounds found in the liquors is not a criterion for the selection of the treatment parameters.

Nevertheless, when HTC process is scaled up, the amounts of valuable substances produced within the liquors could be considerable, hence, their retrieval from HTC liquors could make treatment of the liquors profitable. Some applications for the substances found generally in highest concentrations are summarized in Table 10.

Table 10 Some Applications of materials found in HTC liquors

COMPOUND	APPLICATIONS
Organic Acids	<ul style="list-style-type: none"> Additive for animal aliment: Fermented Silage from grass, maize and/or legumes produced to feed animals. Organic acids such as formic acid, are used to lower the pH of the silage feedstock after harvest o improve the quality of the product (Cherrington, Hinton et al. 1991).
	<ul style="list-style-type: none"> Agent for decontamination of meat: acetic and lactic acids could be employed to reduce bacteria formation in animal carcasses (Cherrington, Hinton et al. 1991).
	<ul style="list-style-type: none"> Food preservatives: Organic acids are used to conserve human food. An example of this is acetic acid in the form of vinegar (Cherrington, Hinton et al. 1991).
HMF and Furfurals	<ul style="list-style-type: none"> Bio based Solvent: The oxidation of HMF into furandicarboxylic acid (FDA) in water which is an inexpensive and environmentally friendly solvent. (Rosatella, Simeonov et al. 2011)
	<ul style="list-style-type: none"> Bio-fuel or additive for fuels: through hydrogenolysis or of 2,5-bis(hydroxymethyl)furan. (Rosatella, Simeonov et al. 2011)
	<ul style="list-style-type: none"> Polyurethane foams using 2,5-bis(hydroxymethyl)furan. (Rosatella, Simeonov et al. 2011)
	<ul style="list-style-type: none"> 5-HMFt is a building block useful in numerous applications such as polymers, resins, adhesives, dietary foods.(AVA Biochem 2018)

In terms of the hazards involved with the products most abundant in the HTC liquors. In the case of organic acids, there are not important hazards involved, other than the hazard inherent

to substances with high acidity, which can affect flora and fauna in watersheds and essential microbial population.

On the other hand, despite HMF are present in human food and their average intake could be between 30 and 150 mg per person per day, studies in animals have demonstrated that HMF might be toxic when consumed in dosages above 75 mg per Kg. Moreover, effects such as DNA damage and colon cancer could have some relation with 5-HMF, but some studies have been contradicted (Rosatella, Simeonov et al. 2011)

To analyze the feasibility of material recovery of the products, it is important to consider that the removal of Organic Acids and HMF from aqueous solutions requires distillation in multiple steps, which is energy intensive (Lopez, Hestekin 2013). Therefore, this treatment pathway needs to be studied extensively.

6.4 Soil enhancement

Table 11 allows to compare the composition of HTC liquors summarized in Table 5 and the composition of some organic fertilizers. It is observed that in general, the nutrients content of the HTCL especially from lignocellulosic biomass are significantly lower. HTC liquors from microalgae show the highest TN content within the liquors, with a content of 0.965%, which is twice as high as the TN content of compost from grass and hardwood. In the case of TP, all the HTC liquors present poor contents in comparison to organic fertilizers. Regarding Potassium, digestate shows a considerable content if compared to compost from wood, food waste and grass, However, it is lower than vermicompost, mushrooms compost and farmyard manure.

The pH value is another property that must be considered. Organic fertilizers have rather neutral pH values, which are similar to HTC liquors from stabilized sewage sludge. Liquors from lignocellulosic biomass are acidic as explained in section 4.2.1. whereas liquors from digestate show a basic pH value.

Table 11 Contents of nutrients of HTC liquors and Organic Fertilizers

Source	Biomass	TN	TP	K	pH
		% wet weight basis			
(Escala, Zumbühl et al. 2013)	Stabilized Sewage Sludge (Catalyst: Citric acid)	0.259	0.0014	NM	7.0
	Stabilized Sewage Sludge	0.271	0.002	NM	6.9
	Non-Stabilized Sewage Sludge	0.318	0.016	NM	5.1
	Non-Stabilized Sewage Sludge	0.226	0.007	NM	5.0
	Non-Stabilized Sewage Sludge	0.472	0.016	NM	5.0
	Non-Stabilized Sewage Sludge	0.467	0.009	NM	5.0
(Schneider, Escala et al. 2011)	Bamboo	0.010	0.005	0.164	3.4
	Whey	0.051	0.023	0.139	3.9
	Digestate	0.234	0.001	0.621	9.3
	Sewage Sludge	0.123	0.001	0.045	5.0
(Wirth, Mumme 2013)	Corn Silage	0.092	0.020	NM	3.9
(Hitzl, Corma et al. 2015) Ingelia	Garden Pruning (mainly)	0.049	0.002	0.131	6.1
(Du, Hu et al. 2012)	Nannocloropsis oculata (microalgae)	0.965	0.034	0.078	NM
(Mladenov 2018)	Compost (food and park-wood waste)	1.230	0.092	0.530	7.3
	Compost (Grass and coniferous residues)	1.160	0.052	0.160	5.2
	Compost (Grass and hardwood residues)	0.450	0.057	0.120	5.8
(Cabilovski, Manojlović et al. 2014)	Vermicompost	1.502	2.279	0.951	7.6
	Mushroom compost	1.324	1.822	1.453	6.9
	Farmyard manure	1.220	1.449	2.005	7.7

Some studies have been conducted to evaluate the properties of HTC liquors as nutrients source or soil enhancer. (Du, Hu et al. 2012) for example, studied the grow of Wild type *C vulgaris* algae in diluted HTC liquors from the treatment of *Nannocloropsis oculata* microalgae (see Table 5 and Table 11). The study concluded that the algae showed faster growth in a medium consisting of diluted HTC liquors. According to these conclusions, HTC liquors offers good potential to improve the cost efficiency of algae biorefineries.

Another interesting study, Bargmann, Rillig et al. (2013) planted barley seeds in sand saturated with HTC liquors and amended with hydrochar. 5 different types of HTC liquors were used separately (from Grass, Wood, Straw, Biogas digestate, Horse Manure). This study found that both hydrochar and HTC liquors had a negative affectation on germination of the seeds. This is due to compounds as organic acids and phenols that might have phytotoxic properties.

In spite of the above, Ingelia SL offers within their products, a liquid fertilizer based on HTC liquors from the treatment of garden pruning and food waste, the characteristics of this fertilizer are shown in Table 12.

Table 12 Commercial Liquid Fertilizer Based on HTC liquors. (Ingelia 2018)

Parameter	Unit	Value
Dry Matter	% tot	2 - 4%
Organic Matter	% tot	1.7 - 3%
pH:	–	5.8 - 6.5
Tot N	% dry	3 - 4%
C/N	–	8 - 9
Conductivity	dS / m at 25 °C	12 - 17
Na	% Dry	2 - 4
K	% Dry	4 - 9
Mg	% Dry	1.5 - 2.5
Ca	% Dry	5.7 - 9
Si	% Dry	0.5
Fe	% Dry	0.15
Mn	% Dry	<0.02

Useful data has been collected from previous researchers and from an operating HTC plant, besides the results obtained in the analysis performed at LUT laboratories. Based on the similarities between the types of biomass used in the experiments and the biomasses found in the literature, it could be concluded that soil enhancement is a feasible use from the HTC liquors obtained from the treatment of Bamboo, Eucalyptus and coffee wood. However, it is important to point out that there are no analyses available where the absent of hazardous substances such as heavy metals or alkali metals is proven. Also, the pH value of the liquors might be too low to be used directly, probably pH balancing substances should be added.

6.5 Anaerobic Digestion

Despite HTC process should be optimized aiming to reduce as much as possible the concentration of organic compounds diluted in the liquors, anaerobic digestion could be a feasible treatment solution that would benefit the HTC plants both economically and in terms of their overall efficiency (Titirici, Funke et al. 2015).

Some concerns arise when evaluating the feasibility of AD as treatment pathway for HTC liquors. In the first place, HTC liquors generally contain phenols and other organic compounds that could have inhibitory effects on AD. Also, the acidic nature of the HTC liquors could affect negatively the growth of microorganisms. As described in section 2.5.5, the optimal pH value for AD processes is between 6.5 and 7.5, while the typical pH values shown by HTC liquors are in the range between 3.0 to 4.5, specially for liquors from HTC treatment of lignocellulosic biomass.

Researchers have explored the effectivity and feasibility of AD as treatment method for HTC liquors. Wirth, Mumme (2013) performed mesophilic AD treatment of liquors from the HTC processes of corn silage. The results showed a maximum average methane yield of 0.624 Liters STP (Liters standard temperature and pressure) per gram of TOC during weeks 1 to 5, with a reduction of 54% of the original TOC. In Addition, according to the findings, the pH value inside of the reactor decreased when the liquors were added but increased again reaching almost the original value after 3 days of treatment. There was no evidence of inhibitory effects related to substances present in the HTC liquors (Wirth, Mumme 2013).

Another solution is exposed by De la Rubia, M. A., Villamil et al. (2018). It proposes the co-digestion of HTC liquors from sewage sludge treatment with the organic fraction of municipal solid waste (OFMSW). The methane yields of all the substrates were determined separately and then combined in different mixing rates. The methane yield of HTC liquors alone was 124 mL STP per gram of COD, whereas the methane yield for OFMSW alone was 194 mL STP per gram of COD, the methane yields of the mixtures have all values in between. These results allowed to conclude that there was no synergetic behavior of the substrates chosen, in other words, the addition of HTC liquors do not improve the methane yield of OFMSW; in fact, it does the opposite.

Based on the results obtained by the studies and the parallels between the biomasses used in this study and the ones used in other studies. AD shows the best perspectives as a treatment solution in spite of the fact that the expected methane yields are relatively low. This pathway offers the possibility of obtaining heat that may be employed inside of the HTC plant at the time that it reduces significantly the amount of TOC present in the HTC liquors.

AD can be implemented as treatment for the HTC liquors that have been recirculated the optimal amount of cycles.

7 CONCLUSIONS AND RECOMMENDATIONS

The increasing urgency of world's transition towards a low carbon economy has made Biomass essential as a primary energy source and as feedstock for environmentally friendly products. Hence, bioenergy is expected to expand its share in the energy mix worldwide, which is possible thanks to the constant improvement and development of conversion technologies that overcome the challenges inherent to the exploitation of the energy contained in biomass.

Hydrothermal Carbonization is indeed the most versatile biomass conversion technology. It allows not only the use of a very wide range of feedstocks, but also there are numerous applications for hydrochar apart from heat and power generation. However, HTC is relatively expensive due to the additional energy necessary to separate the hydrochar from the liquid phase, the loss of valuable substances that are incorporated to the HTC liquors during the process and the necessity of treatment of the liquors due to environmental reasons.

Consequently, all the research endeavors aiming to optimize the technology must include the analysis of the HTC liquors as well as separation and treatment processes. Otherwise, the appropriate determination of the economic and/or energetic feasibility of any proposed solution would not be accurate or even misleading.

Various HTC liquors treatment solutions have been explored by researchers, except for water treatment, each solution offers different outcomes that might be advantageous. They need to be analyzed in each and every case given the fact that the composition of HTC liquors changes considerably according to feedstock and treatment parameters.

Liquors recirculation could increase the energy efficiency of HTC plants while improving the quality of the hydrochar. However, the quantity of liquors recirculated is limited by the water content of the feedstock of the treatment. Nevertheless, in the case of the biomasses studied in this thesis, water needs to be added to form the required feedstock mixture for the HTC process. Therefore, for HTC treatment of Coffee wood, Coffee parchment, Eucalyptus Grandis wood and Giant Bamboo, recirculation should be implemented. It is important to consider that the amount of times that the liquors can be recirculated is also limited, so eventually they will have to be led to further treatment.

The use of HTC liquors as soil enhancer presents some challenges. First, the nutrients content is rather low and insufficient when compared to organic fertilizers. Second, the acidic nature of the HTC liquors obtained from the biomasses treated could have adverse effects in soils. However, it is important to consider that HTC liquors as soil enhancer is a solution already implemented by Ingelia SL, an industrial scale HTC plant, their feedstock consists mainly of garden pruning with food waste.

Even though HTC liquors contain substances with value in industries such as food and bio-materials, the separation processes could be highly energy intensive. Therefore this solution has to be deeper analyzed, considering energy and cost variables.

Anaerobic digestion is a valuable solution considering that not only reduces effectively the TOC content in HTC liquors, but also in industrial applications, it can supply biogas that might be employed inside the HTC plant for preheating the input mixture and/or to heat the reactor until reaching reaction temperature. Although the data obtained in the analysis of HTC liquors of this study (section 5) do not allow a fully conclusive finding, the similarities between the feedstock, the treatment parameters and the partial results of this study and previous researches indicate good potential in the AD as a treatment pathway, even despite the relatively low methane that has been observed for AD of HTC liquors.

It has been clearly shown that when HTC technology is scaled up, considerable amounts of valuable organic and inorganic compounds and/or chemical energy could be obtained from HTC liquors. Modifying HTC treatment parameters can increase or decrease the concentration of certain substances in the liquors. So, even though the HTC processes are designed to maximize the quality of the hydrochar rather than to increase the matter or energy yields of HTC liquors; an equilibrium can be reached through experimentation. In this way it might be possible to propose HTC processes where both hydrochar and HTC liquors generate revenue. Or even design HTC plants with high rates of energetic self-sufficiency. In both cases the environmental impacts would be minimized.

The analysis of the HTC liquors performed at the laboratory were not sufficient to study any of the treatment options specifically for the biomass feedstock used. Nevertheless, the results obtained of the parameters analyzed (pH, TOC and NVR) show a fairly level of coincidence with results of previous studies on similar biomasses or even the same biomasses. This allows to predict that the HTC liquors from Coffee Wood, parchment, bamboo and

eucalyptus could follow any of the treatment paths. However is recommended to perform further analysis.

The methodology employed for the analysis of the HTC liquors had some omissions and errors, specifically in the obtention and storage. Regarding the storage, it is important to keep in mind that the HTC liquors contain degradable substances, so they have to be kept in conditions that minimize the degradations before the analyses, these conditions include low storage temperatures and obstruction of light such as amber flasks for contain the liquors. It is also important to reduce as much as possible the time between obtention of the liquors and the performance of the analyses.

As explained in section 5.3.2, the HTC liquors where passed through vacuum filtration twice, the second time using microfiber filters with pore size of 0.7 μm . This filtration might have retained a considerable part of the solids which subsequently could have affected the results. This methodology is similar the one followed by some analysis found in the literature and also to ensure the integrity of the high-cost analysis equipment that was used to determine the TOC concentration. Centrifugation of the samples is recommended in future experiments to obtain the solids.

It is essential to keep in mind that experiments conducted in scientific research are mainly intended to prove proposed solutions that in case of being successful and promising will be adopted by industry and scaled up. In consequence, the methodology followed during experimentation needs to be design considering the feasibility of implementation in industrial applications.

Lastly, if in the future further experiments and analyses are conducted, they should be aimed to the obtention of the content of the substances that according to section 4 are most likely to be found in significant concentrations (Organic Acids, HFM, furfurals and phenols) apart from the parameters that were analyzed in this study (TOC, NVR and pH). Also it is recommendable to determine VS, TKN, COD, C:N ratio.

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