Valorization of sugarcane bagasse via slow pyrolysis and its by-product for the protection of wood

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Everything passes. Nobody gets anything for keeps. And that's how we've got to live.

– Haruki Murakami

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Contents

List of Figures

List of Tables

General Introduction

Residual agricultural biomass possesses great potential in providing renewable sources for producing energy and materials. Sustainable utilization of this biomass can be implemented using the pyrolysis technology with the objective of energy densification (converting biomass into rich carbonaceous biochar) while also utilizing the by-product as protection agents for wood or biomaterials. The simple utilization of biomass may be through direct combustion to provide heat and power generation. However, such a technique results in low efficiency and produces a huge amount of CO_2. In addition to that, biomass should be used immediately due to its susceptibility to biodegradation. The potential of lignocellulosic biomass for energy production can be advanced through biomass conversion by means of pyrolysis. This process transforms the organic materials by using heat in an oxygen-deficient environment, breaks down the biomass components, such as hemicellulose, cellulose, and lignin, into smaller compounds, producing solid (char), liquid, and gas fractions (Mohan et al., 2006). By adjusting pyrolysis process parameters, such as temperature level, heating rate, and residence time, the quantity of the most desired products can be controlled (Carrier et al., 2011).

From several types of pyrolysis, slow pyrolysis, or traditionally refers to as carbonization, have been widely implemented for a long time. In the slow pyrolysis scenario, biomass material is slowly heated to produce char, where the organic vapors would often just be passed as waste (Bridgwater et al., 2007). However, past and recent studies have shown some interest in recovering this type of condensable organic vapors due to its large composition of bio-active chemicals such as acids, phenols, furans, and guaiacols compounds. This liquid fraction has various nomenclature in the literature, such as pyrolysis oil, pyrolysis liquid, bio-oil, liquid smoke, wood vinegar and wood distillates (Bridgwater, 2003), and its properties could differ from one another depending on the pyrolysis parameters and feedstock used. As a matter of fact, in many Asian countries, slow pyrolysis has been long practiced producing both charcoal and liquid products (Mathew and Zakaria, 2015). Traditional farmers in such countries benefit from the liquid product by using it as a plant growth stimulant and bio-pesticides (Tiilikkala et al., 2010).

On the other hand, wood has been massively utilized due to its excellent physical, mechanical, and chemical properties. Nevertheless, some timbers species have limited end-uses due to their susceptibility to threats from biological agents, i.e., fungi and insects. In this case, pyrolysis liquid could be

an interesting option/way for wood protection. Several researchers reported that pyrolysis liquid has anti-fungal and anti-termite activity (Oramahi et al., 2018; Barbero-López et al., 2019). Moreover, it was reported that bio-oil could be considered an alternative to creosote, which is more advantageous since it does not contain polynuclear aromatic hydrocarbons (PAHs) (Temiz et al., 2013a), thus limiting the environmental impact. The use of the pyrolysis liquid products for wood protection in the literature is relatively scant and it has a high variability due to the different types of feedstock and method used. Therefore, in this study, we were focused on valorizing the pyrolysis liquid from slow pyrolysis, which generally served as a secondary product.

In this study, sugarcane bagasse, a fiber residue that remained after sugarcane processing, was used as the pyrolysis feedstock. The biomass is originated from Réunion Island and was chosen as the tropical biomass model. The choice of bagasse is determined by taking into account three points: its availability, its presence as a waste/by-product instead of primary materials, and the potential of its valorization. Moreover, to our knowledge there was no precedent research on pyrolysis liquid obtained from sugarcane bagasse for wood treatment application. Converting sugarcane bagasse into char for energy production could also tackle the seasonality and biodegradability of this biomass. Being a seasonal plant, bagasse needs to be stored if it is to be utilized outside of its peak harvesting time. Also, being a hygroscopic material, bagasse is prone to moisture change during storage and subject to biodegradation (Breccia et al., 1997; Dong et al., 2013). To overcome these problems, the thermochemical conversion of bagasse can be applied by transforming it into carbon-rich char, which can subsequently be stored without any energy depletion. Additionally, up until now, few studies are focused on a biomass co-valorization processes coupling (i) the pyrolysis process to produce energy and gases, and (ii) the keeping and the valorization of condensable chemical compounds issued from this first thermochemical process into valuable chemical compounds, more particularly for their anti-fungal and anti-termite's activities. The main objectives of this work will be to:

1. Determine the optimum condition of the pyrolysis process parameter for co-producing char and pyrolysis liquid.

2. Evaluate the chemical composition and the anti-fungal and anti-termite activities of the selected pyrolysis liquid.

3. Treating the pyrolysis liquid into the wood samples to investigate its potential for wood protection, determine the optimum drying temperature, analyze its leaching properties, and obtain the effective concentration threshold against fungi and termites.

This thesis is divided into four parts. The first part is dedicated to the literature review on biomass valorization via pyrolysis and the potential of pyrolysis liquid for wood protection. The second and third parts cover the findings on the experimental works conducted in this study. The second part presents the work on the slow pyrolysis parameters (temperature, heating rate, and holding time) and their effect on the char properties and the yield of char and pyrolysis liquid, along with the chemical composition of pyrolysis liquid. Meanwhile, the third part provides the results on the anti-fungal and anti-termites of pyrolysis liquid in Petri-dishes bioassays, the development of paper area measurement using k-means clustering for the termites' test, and wood treatment using pyrolysis liquid. Finally, the last part presents the general conclusion on the work and findings, as well as the perspective for future work.

Part I

Literature review

Chapter 1

Biomass Valorization via Pyrolysis

1.1 Overview of lignocellulosic biomass

Biomass includes all living organisms (plant or animal) as well as its organic products and waste. It is estimated that 100 billion tons of biomass were produced every year globally (Sheldon, 2014). Example of biomass include:

- Agricultural products and residues: sugarcane bagasse, straw, and corn stalks.
- Forests: wood, bark, and sawdust.
- Municipal: Municipal Solid Waste (MSW), sewage sludge, and food waste.
- Energy crops: sorghum, poplar, switchgrass, and willow.
- Biological: animal waste and aquatic biomass (algae).

Plant biomass can be defined as any organic matter produced by a biological process that stems from plants. It contains energy that is firstly derived from the sun through photosynthesis. Plants use solar energy to convert carbon dioxide and water into carbohydrates that form the building block of biomass. The energy is stored in the chemical bonds of the structural component of biomass (McKendry, 2002).

The term lignocellulosic biomass refers to plant dry matter, non-edible biomass, which are not used for food or feed, mainly composed of energy crops, forestry, and agricultural waste. Lignocellulosic biomass has great potential for energy and material application. It can be burned to produce heat, converted to generate electricity, or indirectly used to produce biofuels.

In this section, the chemical composition of lignocellulosic biomass, its properties regarding the utilization for energy, and an overview of sugarcane bagasse are presented.

1.1.1 Chemical composition of lignocellulosic biomass

Lignocellulosic biomass is composed of the three main building blocks, namely cellulose, hemicellulose, and lignin. As shown in Fig 1.1, cellulose is packed together with hemicellulose and lignin, constituting the plant cell wall. Cellulose serves as the skeleton, providing mechanical strength for the plant structure. Hemicellulose contributes to strengthening the cell walls by surrounding the cellulose fibers and acts as the cell's cementing matter. Lignin works like an embedding material responsible for the structural rigidity and protects the cell wall from microbial degradation. Cellulose and hemicellulose are macromolecules made from different sugars, whereas lignin is an aromatic polymer synthesized from phenylpropanoid precursors (Kataki et al., 2015).

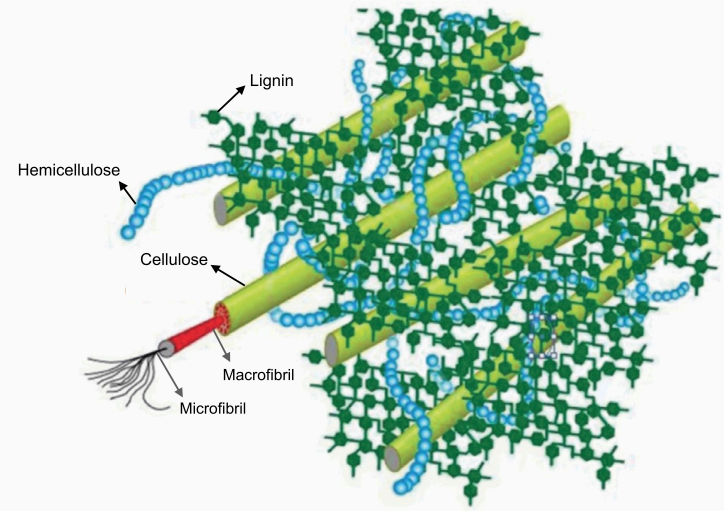

Figure 1.1: Cellulose, hemicellulose, and lignin in plant cell wall (Wang and Luo, 2016)

The contents of cellulose, hemicellulose, and lignin vary depending on the feedstock. Lignin content is typically higher in woody biomass, specifically for coniferous wood (softwood) than deciduous (hardwood) species. Table 1.1 presents the composition of cellulose, hemicellulose, and lignin from selected biomass.

1.1.1.1 Cellulose

Cellulose is the main constituent of plant cell walls, which can reach 40–60% depending on the type of biomass, and almost in the pure form in cotton. The general formula for cellulose is $(C_6H_{10}O_5)_n$, where n is the degree of polymerization (DP). DP is the number of glucose units in a cellulose molecule,

Table 1.1: Proportion of cellulose, hemicellulose, and lignin of selected biomass (Drummond and Drummond, 1996; McKendry, 2002)

Biomass	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)
Softwood	35–40	25–30	27–30
Hardwood	45–50	20–25	20–25
Sugarcane bagasse	40–50	20–30	20–25
Wheat straw	33–40	20–25	15–20
Switchgrass	30–50	10–40	5–20

and its average is at 9,000–10,000 and could be as high as 15,000 (Rowell et al., 2005; Wang et al., 2017). Cellulose is a linear macromolecular polysaccharide with a high molecular weight (10^6 or more) composed of β-D-glucopyranose units linked by (1 $\rightarrow$ 4)-glycosidic bonds (Sjostrom, 1993; Mohan et al., 2006). The polymer is formed from repeating units of cellobiose consisting of two glucose molecules (Fig. 1.2). Each glucose unit has three hydroxyl groups that can interact to form intramolecular and intermolecular hydrogen bonds that provide a crystalline structure of cellulose with unique mechanical strength and chemical stability (Dhyani and Bhaskar, 2018). The crystallinity of cellulose varies widely across biomass. The relative amount of crystalline material (or termed as crystallinity index) in cellulose is 30–60% for biomass fibers. Cellulose also exists in amorphous form, with a loose and disordered hydrogen bonding network and fewer H-bonds. Compared to the cellulose crystalline region, the amorphous region has lower thermal stability (Wang et al., 2017; Leng et al., 2018).

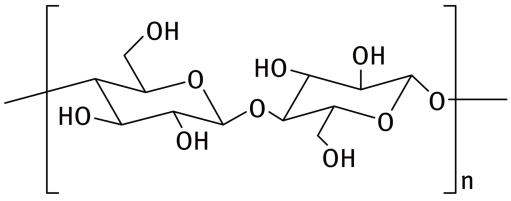

Figure 1.2: Basic monomer structure of cellulose (cellobiose unit) (Wang and Luo, 2016)

1.1.1.2 Hemicellulose

Hemicellulose consists of various monosaccharide units such as glucose, mannose, galactose, arabinose, xylose, 4-*O*-methyl glucuronic acid and galactur-

onic acid residues (Fig. 1.3). It belongs to a group of heteropolysaccharides with an amorphous form and branched structure (Wang et al., 2017). The DP of hemicellulose is far lower than that of cellulose, which is only about 150–200. Hemicellulose is soluble in alkali and easily degraded into monomer components by acids. Hemicellulose in hardwood largely consists of glucuronoxylan, xyloglucan, and glucomannan, while softwood hemicellulose primarily consists of xyloglucan, arabinoglucuronoxylan, and galactoglucomannan. Herbaceous hemicellulose mainly includes glucuronoarabinoxylan and xyloglucan (Wang et al., 2017).

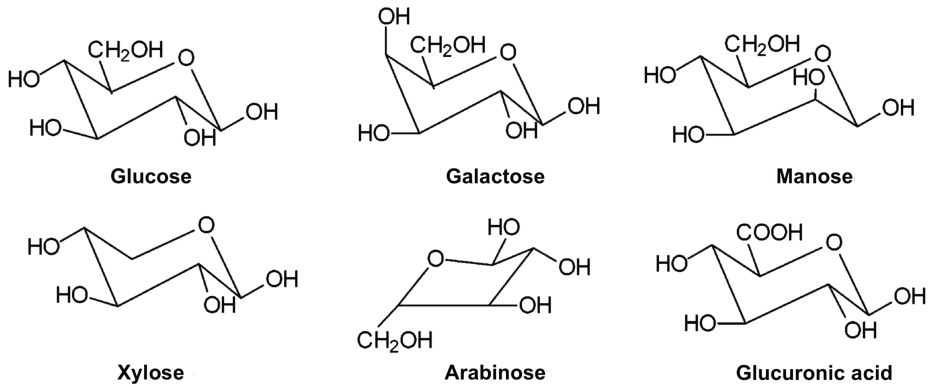

Figure 1.3: Main components of hemicellulose (Mohan et al., 2006)

1.1.1.3 Lignin

In contrast to cellulose and hemicellulose, lignin has a very complex structure, belongs to the non-saccharides macromolecular materials (Wang and Luo, 2016). Lignin is an aromatic, amorphous three-dimensional polymer with phenylpropane units as the predominant building block (Sjostrom, 1993; Rowell et al., 2005). As illustrated in Fig. 1.4, the three basic structures of lignin include *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, which are also known as p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively. The H/G/S units proportion in lignin principally depends on the biomass species. Softwood lignin has a content of guaiacyl unit, hardwood lignin contains a mixture of guaiacyl and syringil units, while the mixture of all three units is typically found in grass lignin (Rowell et al., 2005; Wang et al., 2017). Although lignin has only three basic structural units, there are different functional groups on the benzene ring, which leads to the structural complexity of the lignin (Wang and Luo, 2016).

Lignin has an amorphous structure, leading to many possible linkages between individuals, including ether bonds, carbon-carbon bonds, and ester bonds. Ether bonds predominate between lignin units, accounting for 60–70% of the total linkages, whereas carbon-carbon bonds account for 30–40%. The ester bond content in the lignin structure is low and is primarily found in herbaceous plants (Mohan et al., 2006; Wang et al., 2017).

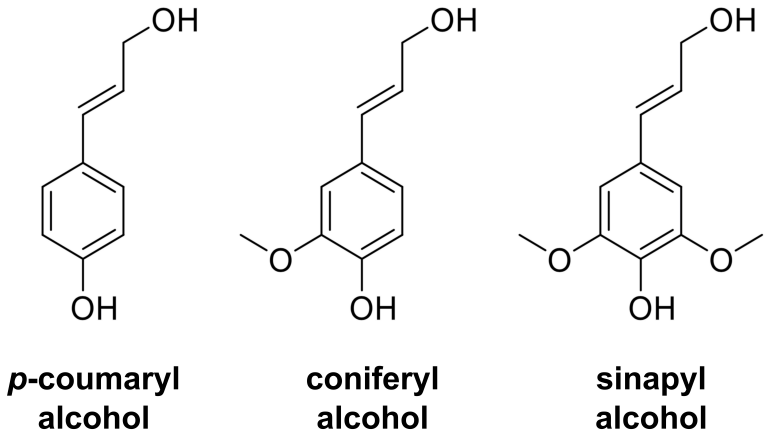

Figure 1.4: Basic units of lignin

1.1.1.4 Extractives and inorganic compounds

Apart from the three major cell wall constituents, biomass also contains low molecular weight substances composed of various organic matter (extractives) and inorganic matter (ash). These compounds are the non-structural components that do not constitute the cell walls.

Extractives are the chemical compounds that can be extracted by non-polar solvents (such as toluene and hexane) or polar solvents (such as water, alcohol, and methylene chloride). These include waxes, fat, tannins, resins, starches, essential oils, simple sugars, gums, saponins, and phenolics. Extractives function as intermediates in metabolisms, as energy reserves, and as defenses against microbial and insect attack (Mohan et al., 2006).

A small amount of inorganic mineral content is also found in lignocellulosic biomass, such as calcium, potassium, magnesium, sodium, silicon, sulfur, and chlorine. Traces of aluminum, titanium, manganese, iron, cobalt, copper, zinc, and other heavy metals may also be present (Wang et al., 2017). Agricultural residues generally contain more inorganics than woody biomass.

1.1.2 Biomass properties

Proximate and ultimate (or elemental) composition are the two common types of analysis used in the thermal conversion. Proximate analysis of biomass gives the amount of (a) moisture; (b) fixed carbon, the non-volatile biomass fraction; (c) volatile matter, the condensable vapor and permanent gas (except water vapor) released from biomass when it is heated; and (d) ash, the inorganic residue remains after combustion. Fig. 1.5 demonstrates the proximate analysis results from typical biomass and coal samples. It indicates that woody biomass and sugarcane bagasse contain higher volatile matter, while rice husk and straw contain higher ash, in comparison with other biomass.

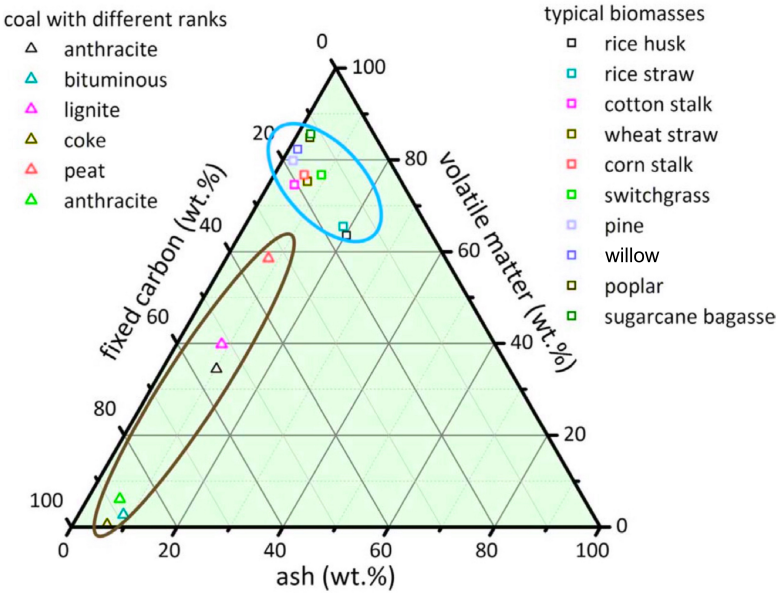

Figure 1.5: Proximate analysis results from typical biomass and coal samples (Cai et al., 2017)

The ultimate analysis aims to determine the contents of carbon, hydrogen, nitrogen, sulfur, and oxygen. Biomass is mainly composed of carbon (C), hydrogen (H), and oxygen (O), with a total content of above 95%. It also contains a smaller amount of nitrogen (N) and sulfur (S). Compared to fossil fuels, biomass is characterized by lower carbon content (thus lower heating value), higher hydrogen and oxygen content, and a much lower nitrogen and sulfur content. Biomass contains more volatile components and is more reactive than coal, which is explained by the O/C and H/C ratios in the Van Krevelen diagram (Fig. 1.6).

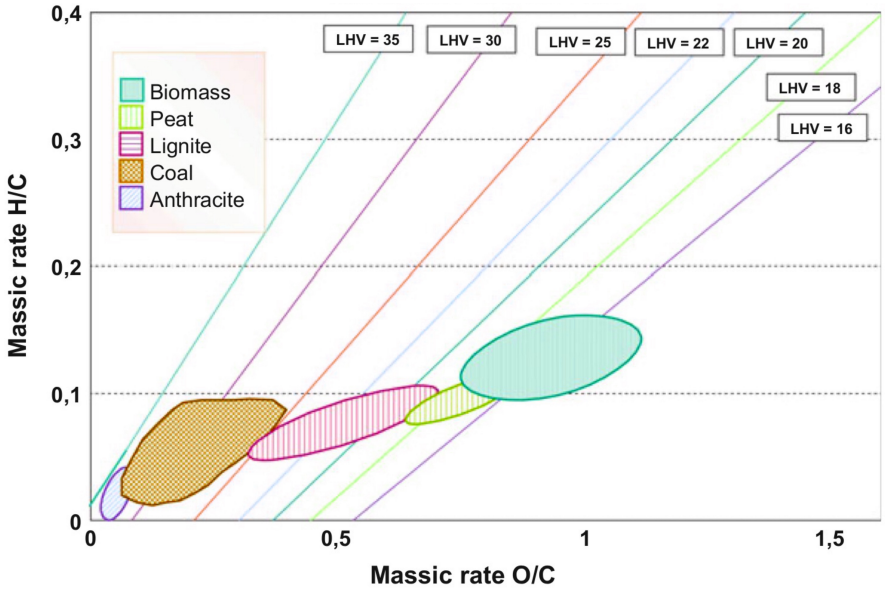

Figure 1.6: Variation ranges of oxygen and carbon in the volatile matter of biomass and the more common fossil fuels with their Lower Heating Value (LHV) (Fantini, 2017)

Several important properties related to the energy conversion processes are discussed below:

a. Moisture content

The moisture content in biomass can be present in two forms: (a) inherent or equilibrium, the moisture that is absorbed with the cell walls (does not depend on the weather condition); and (b) free or external, the moisture which is influenced by the weather condition during harvesting. Moisture drains much of deliverable energy from the conversion process, as the energy used in evaporation can not be recovered (McKendry, 2002; Cai et al., 2017).

b. Calorific value

Calorific value or heating value is the total energy released as heat during combustion and is commonly measured in terms of energy content per unit mass (MJ/kg). Depending on the physical state of the water present in the combustion products, two heating value types can be distinguished: higher heating value (HHV) and lower heating value (LHV). HHV is defined as the total amount of heat, including the latent heat contained in the water vapor. The LHV does not include the latent heat of water vaporization (McKendry, 2002; Cai et al., 2017). Compared to fossil fuel, the biomass heating value is

lower due to the large presence of oxygenated bonds.

c. Proportion of fixed carbon and volatiles

Biomass with a high volatile matter has the highest conversion than biomass with high fixed carbon (Dhyani and Bhaskar, 2018). The importance of fixed carbon and volatile matter is the measure for the ease of ignition and further gasification or oxidation, depending on how biomass will be used as an energy source (McKendry, 2002).

d. Ash and alkali metal content

The biomass ash content can affect both handling and processing cost in the biomass energy conversion. As has been previously mentioned, the primary ingredients of biomass ash include the oxide form of silica aluminum, calcium, magnesium, iron, sodium, titanium, and sodium. The presence of alkali metal such as potassium or halides such as chlorine may play a significant role in serious agglomeration, fouling, and corrosion in boilers or gasifiers (Fantini, 2017). Also, alkali metals and silica's reaction may produce a sticky, mobile liquid phase, leading to blockage of airways in the furnace and boiler plant (McKendry, 2002).

e. Cellulose/lignin ratio

The ratio between cellulose and lignin is important only in biochemical processes due to the higher biodegradability of cellulose than that of lignin. This is significantly related to the feedstock selection for such conversion (see further about the biochemical process in subsection 1.2.1).

1.1.3 Sugarcane bagasse

Sugarcane (*Saccharum* spp.) is a perennial monocotyledonous plant, belongs to the grass family, Poaceae and native to the warm temperate to tropical regions of India, Southeast Asia, and New Guinea. It is an important agricultural commodity cultivated in many countries. The extraction of juice to produce sugar in sugar mill resulted in the fiber residue called bagasse, which is considered its primary by-product. Generally, one ton of raw sugarcane can produce about 100 kg of sugar, approximately 270 kg of dry bagasse, and about 35 kg of molasses (Garcia-Perez et al., 2002).

Bagasse is obtained after the extraction of sugar juice for the production of sugar and ethanol. Bagasse is a lignocellulosic residue, thus classifying it into the second generation biofuel, meaning that it does not compete with food crop production. Bagasse is a highly heterogeneous material consist of 50 wt% true fiber, 15 wt% fibrovascular bundles, 30 wt% pith, and 5 wt%

wax based on its dry weight. The chemical composition of bagasse varies between 27 and 50% cellulose, 20 and 35% hemicellulose, 10 and 25% lignin, and 1 to 6% ash on a dry weight basis (White et al., 2011). At present, in most of the sugar industry, bagasse is mostly used for generating heat and electricity (José et al., 2015).

Figure 1.7: Bagasse storage facility to generate heat and electricity (To et al., 2018)

By combusting the biomass directly, large quantity of bagasse will not be practical to store because it is susceptible to degradation if stored too long in warm humid conditions. Through thermochemical process, bagasse will extend its uses to high energy density products. Storage, transport volume, and the degradation of energy resource will be greatly reduced by the implementation of pyrolysis as energy densification method (Hugo, 2010).

1.2 Biomass Utilization and Valorization

Biomass is a versatile material that has been used by humankind since dawn time. Even now, biomass is still used as the primary energy sources in many developing countries and contributed 10 % of the world's energy supply (Popp et al., 2020).

Principally, to produce energy, biomass can be exploited in two forms, namely traditional biomass, and modern biomass. The so-called modern biomass is often characterized as the more sustainable biomass utilization method, including electricity generation, heat production, and transportation fuels. On the contrary, traditional biomass is produced in an unsustainable manner and is still the primary use form in most islands and many developing countries (Goldemberg and Coelho, 2004). Biomass for energy can be directly used or converted in different forms such as solid, liquid, or gaseous products. Primary solid biofuels include wood chips, pellets, charcoal, and fuelwood for cooking and heating in many developing regions. Liquid biofuels include bioethanol and biodiesel, usually used for transportation purposes. Meanwhile, gaseous biofuels cover biogas generated by anaerobic digestion of organic wastes and syngas from gasification (Guo et al., 2015).

In this section, the general overview of biomass conversion technology is reviewed. State of the art on the pyrolysis process and its products is also presented.

1.2.1 Conversion of biomass

Biomass valorization can be defined as transforming the biomass and various residues into energy, fuels, and other useful materials, focusing on environmental indicators and sustainability goals (Nzihou, 2010). Lignocellulosic biomass can be converted in the following ways: (a) direct combustion to produce heat or (b) converted into biofuels and valuable hydrocarbons.

1.2.1.1 Direct combustion

Direct combustion is the simplest and most common method of utilizing biomass to generate heat but results in low energy efficiency (15–30 %). This approach also leads to undesirable ash buildup and produces a considerable amount of CO_2 as its by-product. The heat produced must be exploited immediately because storage is not a viable option (Bridgwater, 2003).

Another option to utilize biomass is through conversion using biochemical or thermochemical pathways (Fig 1.8). The comparison between the two

conversion methods is provided in Tab. 1.2.

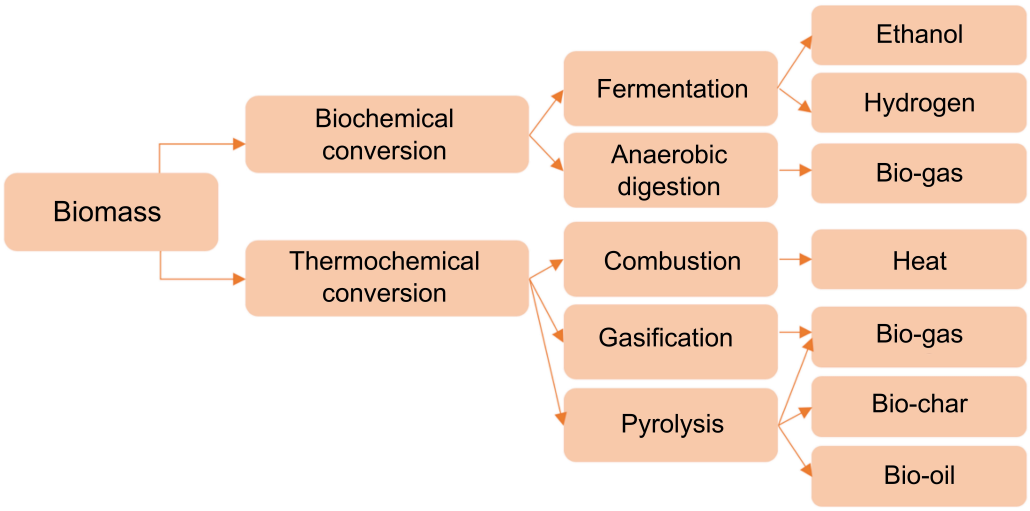

Figure 1.8: Biomass conversion using biochemical and thermochemical routes with some examples of the main products (Ferreira, 2017)

1.2.1.2 Biochemical conversion

Biochemical conversion converts the holocellulose (hemicellulose and cellulose) into simple sugars through a process called hydrolysis (Fig. 1.9). These sugars are intermediate products that can be fermented into various value-added chemicals. The most common biochemical conversions are fermentation and anaerobic digestion.

1.2.1.3 Thermochemical conversion

Thermochemical conversion is the controlled heating or oxidation of biomass as part of several pathways to produce intermediate energy products, which can also be upgraded to valuable products (Tanger et al., 2013). Combustion (complete oxidation), gasification (partial oxidation), and pyrolysis (thermal degradation without oxygen) are examples of thermochemical conversion. Tab. 1.3 presents the types of the thermochemical conversion process.

It is important to differentiate pyrolysis from gasification as the latter decomposes biomass to syngas by carefully controlling the amount of oxygen present (Mohan et al., 2006). Pyrolysis is also the first step in combustion

Table 1.2: Comparison between biochemical and thermochemical conversion of biomass

Biochemical conversion	Thermochemical conversion
• Using enzymes and microorganisms. • Process takes time (in the range of days) to complete. • Convert carbohydrates (hemicellulose and cellulose) into sugar. Produce lignin as a by-product.	• Using heat and catalyst. • Process occur faster (in a few seconds to hours). • Utilize the whole feedstock to produce value-added hydrocarbons (not feedstock specific).

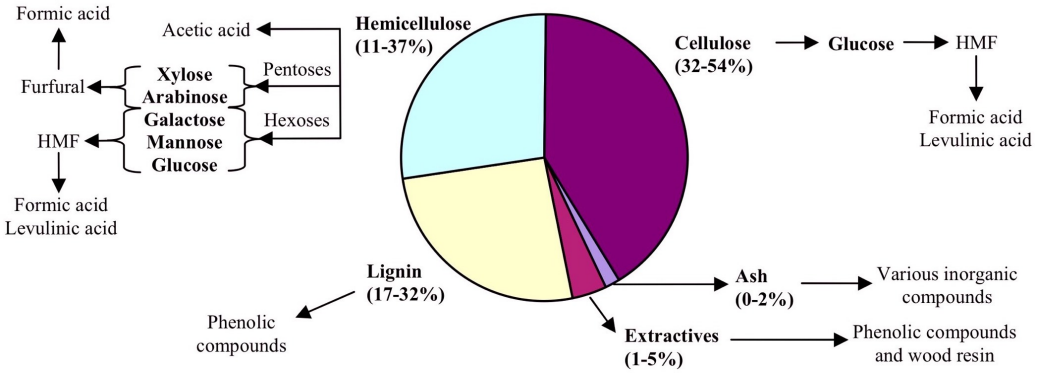

Figure 1.9: Composition of lignocellulosic materials and their potential hydrolysis products with further degradation compounds (HMF = Hydroxymethylfurfural) (Taherzadeh and Karimi, 2007)

Table 1.3: Thermochemical conversion process (Ronsse et al., 2015)

	Torrefaction	Carbonization/ Slow pyrolysis	Fast pyrolysis	Gasification
Temperature	<300 °C	>400 °C	∼500 °C	600–1800 °C
Heating rate	-	<80 °C/min	Up to 1000 °C/min	-
Reaction time	<2 s	Hours∼days	Few seconds	-
Medium	Oxygen-free	Oxygen-free or oxygen-limited	Oxygen-free	Oxygen-limited (air or steam/ oxygen)
Solid yield	80%	35%	12%	10%
Liquid yield	5%	30%	75%	5%
Gas yield	15%	35%	13%	85%

and gasification processes, followed by total or partial oxidation of the primary products. Further, pyrolysis can be categorized into different types depending on the operating parameters and desired products. Pyrolysis is usually classified based on the heating rate (slow or fast). Slow pyrolysis, which may also be similar to conventional pyrolysis (carbonization), occurs at a low heating rate and long vapor residence time, and is intended to produce charcoal or solid product primarily. It also covers torrefaction, a low-temperature pyrolysis process that usually serves as a pretreatment process. Torrefied biomass has a typical higher energy content than the original feedstock and requires less energy to grind. On the other hand, fast pyrolysis occurs at a high heating rate and short vapor residence time (less than 2 seconds). It targeted the liquid, named bio-oil, as the main product, where its yield can reach up to 70 wt% (Bridgwater et al., 2007).

Another conversion technique, such as a thermo-catalytic conversion, can also be considered. The examples include the Fischer–Tropsch synthesis (convert syngas obtained by gasification into liquid transport fuels) and liquefaction (Ferreira, 2017).

1.2.2 Biomass pyrolysis and its mechanisms

Among several types of thermochemical pathways mentioned earlier, pyrolysis has been extensively studied as a promising route to produce fuels and chemicals from biomass. Pyrolysis is a term used to describe a thermal decomposition of organic materials in the absence or a poor oxygen condition so that it is highly unlikely for the complete combustion to occur (Mohan et al., 2006). The word pyrolysis originated from the two Greek words: *pyro*, meaning "fire," and *lysis*, meaning "separating."

Biomass pyrolysis is a very complex mechanism. The complexity stems from variations in the decomposition of biomass components with varying reaction mechanisms and reaction rates. Fig. 1.10 shows the reaction pathway for biomass pyrolysis. It is commonly accepted that biomass pyrolysis follows three steps mechanisms: (i) dehydration, the initial evaporation of free moisture; (ii) primary reaction, which is responsible for the largest biomass degradation, forming the solid char at 200–400 °C; and (iii) secondary reaction (e.g., cracking and repolymerisation of primary volatile compounds), which continues in a solid matrix with a further increase in temperature (>400 °C) (Fisher et al., 2002; Kan et al., 2016). The secondary reactions are only predominant if sufficient vapor residence times are allowed (>1 s), such as in the slow pyrolysis case (Ronsse et al., 2015). Moreover, it is likely that primary char (the solid product from the primary reaction) acts as catalyst for the cracking organic vapors, forming additional char (secondary char), non-condensable gases, and water, thus lowering the bio-oil yield (Bridgwater, 1999). In case of fast pyrolysis, the secondary reaction is prevented to maximize the bio-oil yield by rapid heating of biomass as well as rapid removal and rapid quenching of the condensable vapors (Venderbosch and Prins, 2010).

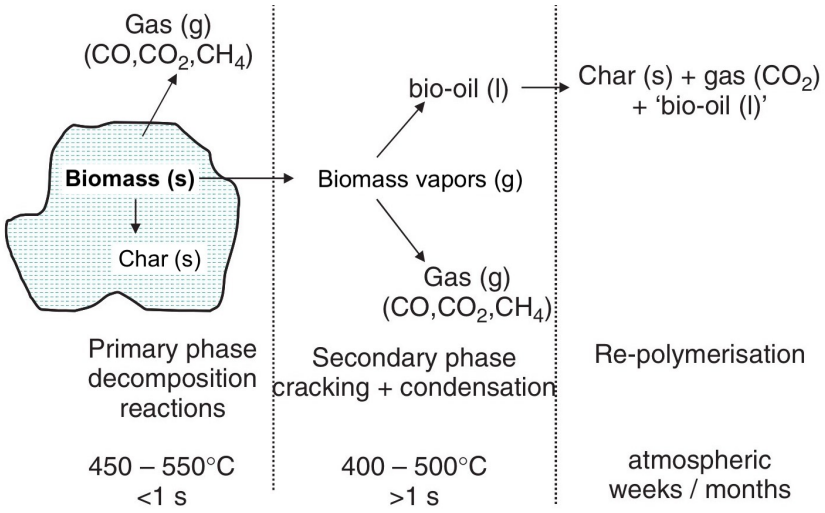

Figure 1.10: Representation of the reaction pathway for biomass pyrolysis (Venderbosch and Prins, 2010)

During pyrolysis, cellulose, hemicellulose, and lignin undergo their own reaction pathways, such as cross-linking, depolymerization, and fragmentation at their temperature, producing solid, liquid, and gaseous products. The decomposition behavior of biomass during pyrolysis is commonly observed

using thermal analysis, including thermogravimetric analysis (TGA) and differential scanning calorimetry. In general, the process begins with moisture evolution followed by the hemicellulose, cellulose, and lignin decomposition.

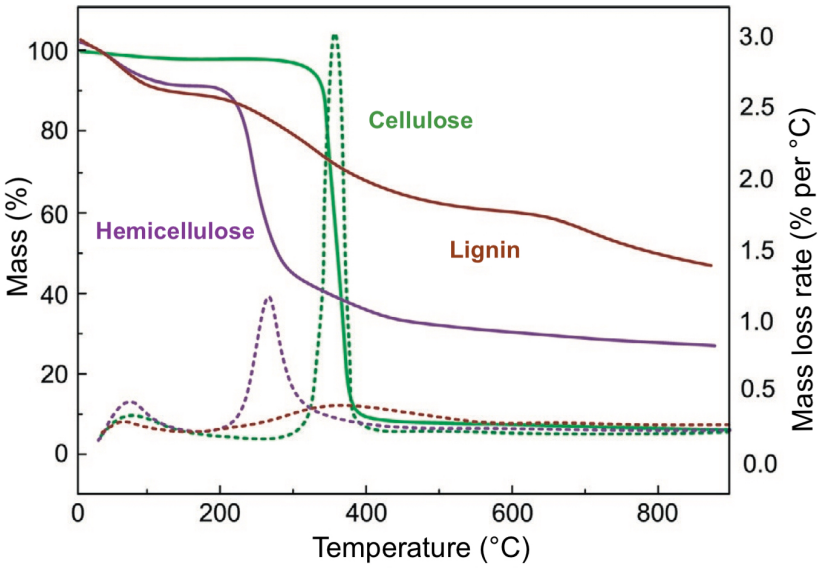

Figure 1.11: TG (full lines) and DTG (dashed line) curves for cellulose, hemicellulose, and lignin at a heating rate of 10 °C/min (Yang et al., 2007; Ronsse et al., 2015)

Fig 1.11 illustrates the typical TGA results where the mass loss and mass-loss rates versus temperature are recorded. At the temperature range between 100 and 160 °C, the free and bound water is removed from the biomass. Afterward, hemicellulose become the first constituent to decompose, at a temperature between 220 °C and 315 °C, with the maximum mass loss rate (0.95 wt%/°C) occur at 268 °C (Yang et al., 2007), and completed around 400 °C (Venderbosch and Prins, 2010). Hemicellulose has low thermal stability due to its amorphous properties and low degree of polymerization. It gives rise to more volatiles, less char, and less tar in contrast to cellulose. Decomposition of hemicellulose primarily results in the release of methanol, acetic acid, and acetone. At around 320 °C, the more stable cellulose starts to decompose (Ronsse et al., 2015). At temperature higher than 400 °C, almost all cellulose was pyrolyzed (Yang et al., 2007) and converted to non-condensable gas and condensable organic vapor, with levoglucosan as the main pyrolysis product. Lignin decompose slowly under a wide temperature range between 160 °C and 900 °C, producing the highest residual char. It also yields phenols and heavy tars (larger molecular fragments) via the cleavage of ether and

carbon-carbon linkages (Mohan et al., 2006; Ronsse et al., 2015).

Several parameters such as biomass type, biomass particle size, temperature, heating rate, vapor residence time, and reaction atmosphere influence the biomass pyrolysis process, yields, and products' properties. As previously stated, the pyrolysis of each biomass constituent has a unique reaction pathway and thermochemical characteristics. Cellulose and hemicellulose contribute mostly to bio-oil yield, while lignin yields a large proportion of char. Smaller biomass size particles promote the intraparticle heat and mass transfer to form uniform temperature during pyrolysis, thus augment the bio-oil yield. The temperature at the range from 400–550 °C maximized the solid and liquid products, then decreased with the increased heating. Higher heating rates promote higher liquid yield, while lower heating rates favor the production of char. The slightly oxidized atmosphere and increased residence time promote gasification and reduce the liquid yield (Kan et al., 2016).

1.2.3 Pyrolysis products: properties and applications

During pyrolysis, exposure to the high-temperature results in the breakdown of biomass chemical constituents (cellulose, hemicellulose, and lignin), producing solid char (biochar), vapor condensate (liquid bio-oil), and non-condensable vapor (syngas) (Fig. 1.12). Below the characteristics and the potential uses of the three pyrolysis products are discussed.

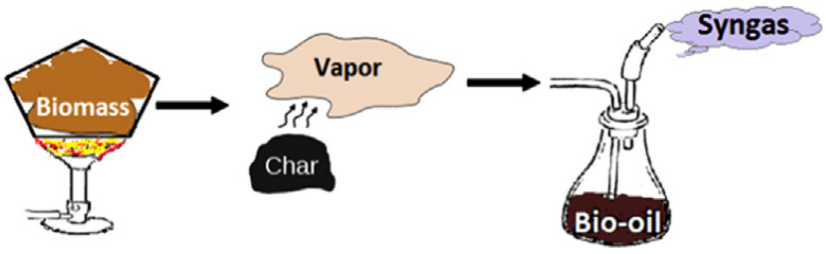

Figure 1.12: Pyrolysis products (Guo et al., 2015)

1.2.3.1 Solid product

A solid product from pyrolysis (char) is a carbonaceous material that is commonly combusted to produce heat, steam, or electricity. The term "charcoal" is typically used when the intended purpose is to use it as a fuel or as a reducing agent in a metallurgical smelting point. The heating value of char ranges from 15 to 30 MJ/kg. The high heating value makes char attractive

to be used for the fuel application. When combusted, ash would remain. The remaining ash found its application in cement production (Pecha and Garcia-Perez, 2020).

Another interest is to use char as a low-cost adsorbent, carbon sequestration, and soil amendment. "Biochar" is a common term used in the literature for the soil application interest. Char has unique surface properties and has an extensive porous structure with comparatively high surface area-to-weight ratios to be used as a potential low-cost adsorbent for CO_2 capture (Creamer et al., 2014). Char has recalcitrant nature, very stable when stored in the soil, and resistant to biological decay; thus, it can store carbon and prevents the rapid release of CO_2 if the biomass would be kept untreated (Woolf et al., 2010). Char is also believed to increase soil productivity through its unique physicochemical properties. The highly porous char lead to the increase of water holding capacity and soil's aeration. Moreover, it provides a favorable habitat for beneficial soil microorganisms, increasing soil microbial activity (Laird et al., 2009; Vanholme et al., 2013). Fig. 1.13 shows how biochar application can enhance soil quality for agricultural purposes.

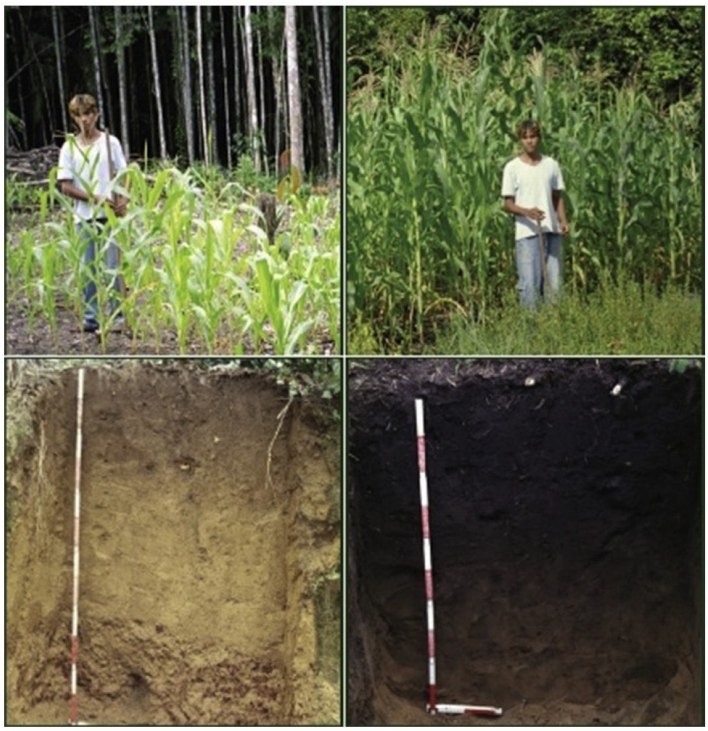

Figure 1.13: Soil amended by biochar called "terra preta" on the right improves the crop yield compare to unamended soil on the left (Pecha and Garcia-Perez, 2020)

1.2.3.2 Liquid product

Liquid fractions from pyrolysis consist of a complex mixture of water and an organic phase containing many chemical compounds, such as acids, alcohols, aldehydes, ketones, ethers, esters, phenols, sugars, alkenes, furans, nitrogen compounds, and miscellaneous oxygenate (Kan et al., 2016). The chemical composition of the pyrolysis product is highly dependent on the variation in the composition of the biomass feedstock. Fig. 1.14 illustrates the chemical compositions and product distribution of pyrolysis liquid. The final water content depends on the initial moisture content of biomass and water formation during pyrolysis, ranging from ∼15 wt% to an upper limit ∼30-50 % (Mohan et al., 2006). This product can be considered a micro-emulsion, forming a stable monophasic mixture. The aqueous solution (notably originated from the holocellulose decomposition) acts as a continuous phase that stabilizes the discontinuous phase of pyrolytic lignin macro-molecules through mechanisms such as hydrogen bonding (Mohan et al., 2006; Bridgwater, 2012). This liquid fraction has various nomenclature in literature, such as pyrolysis oil, bio-oil, liquid smoke, wood distillates, pyroligneous tar, and pyroligneous acid (Bridgwater, 2003).

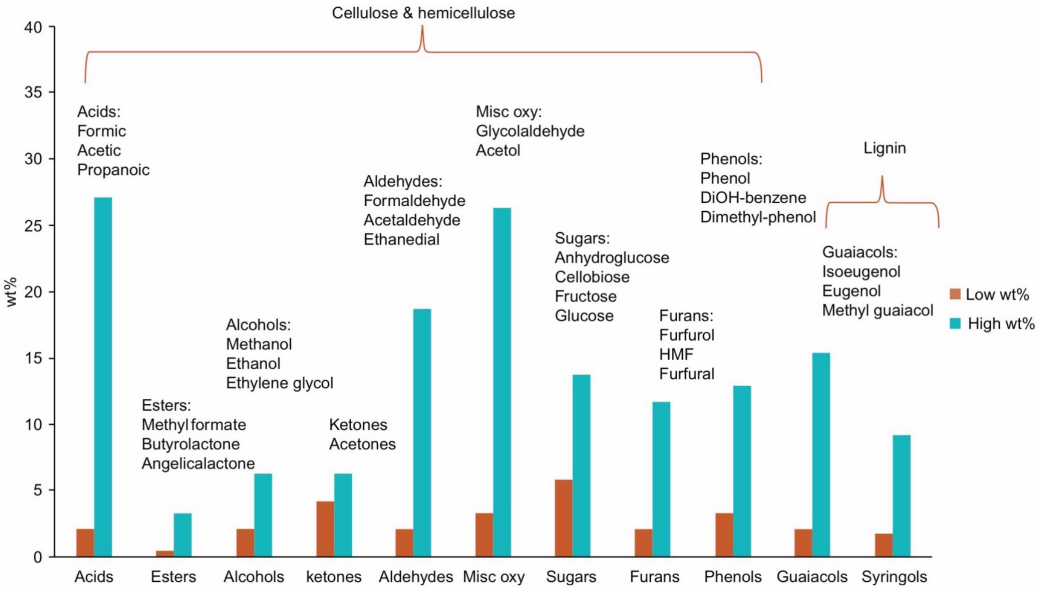

Figure 1.14: Chemical compositions and product distribution of pyrolysis liquid (Huber et al., 2006)

Tab. 1.4 shows typical physical properties of wood pyrolysis bio-oil. The

Table 1.4: Typical properties of wood pyrolysis bio-oil (Bridgwater, 2003)

Physical property	Value
Moisture content	15–30%
pH	2.5
Specific gravity	1.20
Elemental composition	
C	55–58%
H	5.5–7.0%
O	35–40%
N	0–0.2%
Ash	0–0.2%
HHV	16–19 MJ/kg
Viscosity (at 40 °C and 25% water)	40–100 cp
Solids (char)	1%
Vacuum distillation residue	Up to 50%

elemental composition of pyrolysis liquid resembles the biomass, which contains a large oxygen content (45–50%). The higher heating value (HHV) of pyrolysis liquid thus considerably low, ranges between 15–20 MJ/kg, compared to the petroleum oils (42–45 MJ/kg) (Kan et al., 2016). Although the pyrolysis liquid is often called bio-oil or pyrolytic oil, in fact, it has a high polarity and has a hydrophilic nature; thus, it is not miscible with liquid hydrocarbons. Pyrolysis liquid is miscible with polar solvents such as acetone, ethanol, and methanol but cannot be dissolved in water (Mohan et al., 2006). It can tolerate the addition of some water until the phase separation occurs.

Other undesirable properties of pyrolysis liquid are low pH (2–3), which can be corrosive to common structures. Pyrolysis liquid contains a substantial amount of carboxylic acids such as acetic acid and formic acid that contribute to the acidic properties. It is also chemically unstable during storage due to the ongoing chemical reactions to form large molecules such as polymerization, etherification, and esterification, where the instability increases with heating (Mohan et al., 2006; Kan et al., 2016).

Pyrolysis liquid can be used in energy applications such as being combusted in residential or industrial boilers, co-fired with natural gas or coal for power generation, blended with either ethanol or gasoline, or converted into fuels and chemicals through hydrocracking/hydroprocessing (Roy and Dias, 2017). Bio-oil upgrading by steam reforming and gasification can produce combustible syngas and hydrogen. Bio-oil can also be used as feedstock to produce chemicals, such as phenols for resin production, flavoring agents (i.e., glycolaldehyde) in food industries, and additives in fertilizing and phar-

maceutical industries (Kan et al., 2016). Another utilization of pyrolysis liquid related to pesticide and wood preservation is discussed particularly in Chapter 2.

1.2.3.3 Gaseous product

Pyrolysis gas mainly contains several combustible gases, including H_2, CO, CH_4, and C_2-hydrocarbons, with a high concentration of incombustible CO_2 (Crombie and Mašek, 2014). CO and CO_2 are the main products of pyrolysis that originated from the decomposition and reforming of carbonyl (C=O) and carboxyl (COO) groups and are preferably produced at low temperatures. H_2 is generated from the secondary decomposition and reforming of the aromatic C=C and C–H groups at high temperatures. Meanwhile, the light hydrocarbons (CH_4) are mainly due to the decomposition of weakly bonded methoxyl and methylene, and the secondary decomposition of the oxygenated compounds (Qu et al., 2011; Kan et al., 2016).

The heating value of pyrolysis gas is relatively low (6.4–9.8 MJ/kg) (Varma and Mondal, 2017). It can be regarded as a low-energy-density product (6 MJ/kg), compared to liquid and solid products (Crombie and Mašek, 2014). Instead of using it for heat production and power generation, pyrolysis gas is potentially used to sustain the pyrolysis system, such as for heating the unit or to dry the feedstock (Becidan et al., 2007).

1.3 Conclusion

In this chapter, the importance and potential of biomass valorization through pyrolysis have been presented. The biomass conversion, especially from agricultural waste, offers benefits in producing value-added products. As mentioned, pyrolysis liquid serves a wide variety of applications, including its potential for wood protection. In the next chapter, the literature review will focus on the pyrolysis liquid potential for wood protection. An introduction to wood as a material and its relationship to natural durability, biological degradation, and various protection methods are discussed. Several past studies dealing with pyrolysis liquid for wood protection are also reviewed.

Chapter 2

Pyrolysis Liquid for Wood Protection

2.1 Wood Protection

For millennia, wood has been used by humankind, which played a vital role in civilization's history and the world's economy. It is becoming the primary source of numerous applications, from its utilization as fuel for cooking and heating to raw material for constructions, engineered products, furniture, paper, and chemical sources. Moreover, wood is the only building material that can be regrown. Sustainably, by converting wood into products, wood continues to store carbon, and by replanting the trees, carbon dioxide was removed from the atmosphere by the natural process of the carbon cycle during photosynthesis.

Nonetheless, wood can be degraded by weathering (abiotic factor) and biological degradation (biotic factor). Wood is also hygroscopic due to the hydroxyl group's presence, which means that it attracts or releases water from the surrounding environment until it reaches equilibrium. This hygroscopic character can render wood with poor dimensional stability. Also, in a condition where the moisture content is suitable, fungi can grow and decay the wood. All of these undesirable properties limit the utilization of wood in terms of its durability or quality. Thus, various wood preservation or wood protection methods have been developed to extend the wood's service life.

This section discusses the importance of wood protection related to its biological degradation and protection methods.

2.1.1 Wood as a material and its natural durability

Wood is a type of lignocellulosic biomass composed of cellulose, hemicellulose, and lignin as its major structural component. It also contains mineral matters (ash) and extractive. Based on its dry weight, wood consists mainly of sugar-based polymers (carbohydrates, 65–75%) combined with lignin (18–35%). In total, dry wood has an elemental composition of about 50% carbon, 6% hydrogen, 44% oxygen, and trace amounts of inorganics. Generally, the conif-

erous species (softwoods) have a higher cellulose content (40–45%), higher lignin (26–34%), and lower pentosan (7–14%) content than deciduous species (hardwoods) (cellulose 38–49%, lignin 23–30%, and pentosans 19–26%). Depending on the species, extractive contents may vary from about 0.5 – 20% by weight, which some are responsible for the color, smell and can provide natural durability to the wood. In general, softwoods have a higher extractives content than hardwoods (Rowell et al., 2005).

As shown in Fig. 2.1, the three-dimensional section of a tree trunk shows well-defined concentric subdivisions, which consists of periderm, bark, vascular cambium, sapwood, heartwood, and the pith. All of the tissue in the cambium layer to the center of the tree is xylem or wood. Wood is typically differentiated into sapwood and heartwood. Sapwood is the lighter, younger region of wood closer to the cambium, in which the parenchyma cells are still alive and metabolically active. Heartwood is older xylem located in the interior of sapwood which is darker, denser, and more resistant than sapwood (Wiedenhoeft and Miller, 2005; Li, 2011).

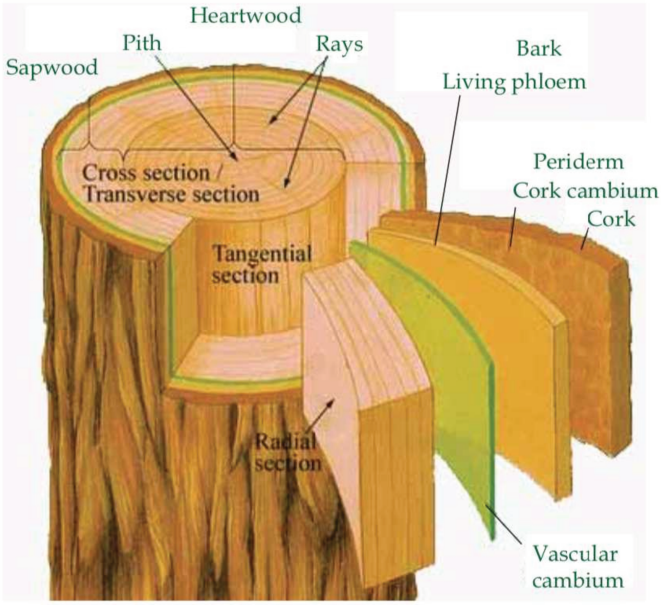

Figure 2.1: The three dimensional section of a tree trunk (Li, 2011)

Natural durability or natural resistance of wood is the ability of timber species to resist biological degradation. Such definition is assigned to a timber species' heartwood, except for those with no differentiation between heartwood and sapwood (Wong et al., 2005). The natural durability of sapwood is generally low, but the heartwood of some species can be very resistant to

biological attack, mainly due to the extractives (Taylor et al., 2002). Biological resistance can be given to a certain extend by lignin content (Miedes et al., 2014). Wood containing a high amount of silica (Si) can also be more resistant, especially to insect (Ghosh et al., 2012). European standard EN 350 (2016) provides the durability class corresponding to the natural resistance of wood species. Today, the reduced availability of naturally durable wood species increases reliance on the use of fast-grown non-durable wood, thus requiring protection treatment to lengthen their service life.

2.1.2 Biological degradation of wood

As biological material, wood is susceptible to various deteriorating organisms when exposed to various environments. At the same time, however, wood decomposition by biological organisms is essential for the ecosystem as it is part of nature's carbon cycle. Fungi (particularly basidiomycetes and soft rots), insects, and marine borers are the type of organisms that can cause severe damage to wood.

2.1.2.1 Fungi

Tab. 2.1 provides the summary of the main types of fungi that can colonize and degrade wood, with some images of attacked wood illustrated in Fig. 2.2.

The fungi that degrade wood and causing decay can be classified into brown-rot, white-rot, and soft-rot. Decay fungi need food (hemicellulose, cellulose, and lignin), oxygen, moisture (above the fiber saturation point; about 30 % moisture content), and suitable temperature (10 °C to 35 °C; optimum 24 °C to 32 °C) to grow (Ibach, 2005). These fungi degrade the wood cell wall's structural polymer by secreting enzymes that can break down the wood lignocellulosic constituents into simple molecules that can be metabolized and absorbed by their hyphae's membrane. In principle, carbohydrates of cellulose and hemicellulose are more easily degraded, while lignin is more resistant to most microorganisms because of the structure of the phenylpropane units and the strong bonds between the units. The hydrophobic nature of lignin prevents the diffusion of enzyme degradation inside the large three-dimensional molecules. Lignin is effectively degraded by the type of white-rot fungus, while it serves as a barrier against wood decay for other microorganisms (Schmidt, 2006).

Table 2.1: Main types of fungi that can colonize and degrade wood (Blanchette, 2000; Ibach, 2005; Broda, 2020; Goodell et al., 2020)

Type of Fungi	Characteristics	Effect on wood
- Decay Fungi:		
Brown-rot (Basidiomycota)	Degrade mainly softwood; metabolize polysaccharides (cellulose and hemicellulose), and demethylation of lignin; degradation is made both by enzymatic systems and by non-enzymatic systems.	Shrinkage and cracking of wood into cubical pieces; rapid loss of mechanical properties; brown coloration due to the presence of remaining lignin.
White-rot (Basidiomycota)	Degrade mainly hardwood but also softwood; able to effectively attack lignin enzymatically so that they can then break down carbohydrates.	Wood becomes soft, spongy, and has a whitish color with a fiber-like appearance; strength properties decrease with the decay progress
Soft-rot (Ascomycota, fungi imperfecti)	Degrade preferentially cellulose and hemicelluloses, less extensively lignin; attack wood found in very humid environments	Cavity formation in the wood cell wall (type I) and general erosion of the wood cell wall layers (type II); discoloration and soft consistency; significant mechanical reduction at early stages of degradation
- Stain Fungi:		
Mold (Zygomycota or Ascomycetes)	Inhabit the wood surface; feed on simple sugars and starches, but do not metabolize wood structural component	Discoloration of the wood surface; degrade the appearance of finished wood
Blue Stain (Ascomycota and Deuteromycota)	Able to penetrate the sapwood and sometimes living trees; preferentially attacks conifers; feed on simple sugars and starch in the parenchyma cells	Dark coloration on the surface of the wood; degradation of pit membranes which lead to increased water permeability

Brown-rots depolymerize cellulose rapidly during the initial stages of wood colonization. They cause dramatic strength loss in early decay stages, often before decay characteristics are visually evident. White-rots can degrade all cell wood constituents. Compared to brown-rot, the strength losses occur more slowly and not significant until the late decay stages. They typically erode the cell from the cell lumen outward by breaking down successive layers of cell walls. Hence, the wood becomes progressively thinner with greater weight loss at the later decay stage, which can up to 97%. Soft-rots cause progressive degradation from the wood surface inward. As decay progresses, extensive carbohydrate loss occurs with increasing lignin concen-

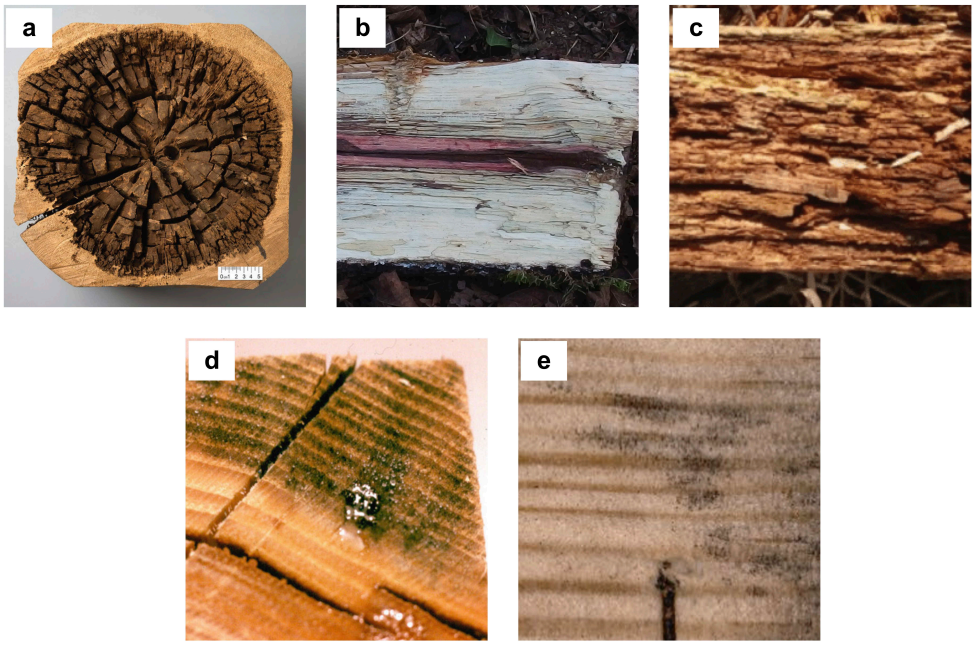

Figure 2.2: Attack of fungi on wood: a) brown-rot (Goodell, 2020); b) white-rot (Auró 2016); c) soft-rot (Mariano et al., 2020); d) blue stain (Goodell, 2020); and e) mold (Imken et al., 2020)

trations in the residual wood. Extremely poor strength characteristics are observed when soft-rotted wood is visually apparent due to the significant cellulose degradation and cavity formation in the wood (Blanchette, 2000; Shmulsky and Jones, 2011; Goodell et al., 2020).

Other types of fungi such as mold and blue stain can also attack wood, causing only damage to the wood surface and affecting wood's aesthetic value due to wood discoloration. However, they do not significantly cause structural damage to wood. Simple drying to less than 20 % moisture content is often sufficient to protect the wood from these types of fungi.

2.1.2.2 Insects

The most important wood-destroying insects are beetles (order *Coleoptera*) and termites (order *Isoptera*). Beetles only degrade wood during their larval stage and mainly degrade sapwood or all wood when there is no difference between sapwood and heartwood, such as beech (*Fagus sylvatica*). They mainly degrade the starch, even if some beetles can degrade cellulose to a small extent (Martin, 1983).

Termites are probably the type of insects that cause the most damage to wooden structures. It is estimated that the global economic impact of this pest is counted for more than 40 billion annually, in which the subterranean termites contribute 80 % of the damage (Rust and Su, 2012). Based on their living environment, three main categories of termites can be distinguished: (i) subterranean termites, which live undergrounds; (ii) dry termites, which can live in the dry wood and do not need to be near the soil; and (iii) damp wood termites, which live in very moist wood and do not need soil to survive (Govorushko, 2019). All termites are eusocial insects, and they have three stages of metamorphosis (egg, nymph, and adult). Termites live in a colony made up of reproductives (kings, queens, and alates), soldiers, and workers. Each termite in the colony does a specific job that benefits the colony as a whole. The primary reproductives, a king and queen, were initially developed from winged forms (alates) that have left their parent colony and shed their wings to mate and build new colonies of their own. Nymphs can become alates, young winged reproductives with a black pigmentation. Depending on the climatic conditions, these alates will leave the nest in swarmers. Once they have fallen back to the ground and pair, they will establish a new colony by becoming king and queen (Vargo, 2019). The soldiers (adults) are responsible for defending the colony, and particularly the queen and the king. They represent about 10% of the colony. The workers (adults) are responsible for the formation of galleries in the wood, and therefore for its degradation. They make up about 90% of the colony, which their tasks are to care for the young, repair the nest, build foraging tunnels, locate food, and digest cellulose to feed the whole termites (Bignell et al., 2010; Miller, 2010).

2.1.2.3 Marine borers

Marine borers can cause extensive damage to wood submerged in salt or brackish water. Crustaceans (gribbles) and mollusks (shipworms) are the most important. Gribbles or *Limnoria* spp are 3–5 mm long, and they settle on wood, forming superficial burrows less than 12 mm, but the borers continually bore in deeper with water erosion. The molluscan borers belong in the family *Teredinidae* and the genera *Teredo* or *Bankia*. The best-known genus is Teredo (shipworms). The young larvae can swim and eventually settle on wood where they boreholes about 0.5 mm in diameter (Richardson, 2002; Ibach, 2005).

2.1.3 Principle of wood protection

The service life of wood products can be considerably extended by proper treatment or species selection. Wood products users must understand the conditions under which deterioration occurs and the appropriate preventive measures to be taken (Shmulsky and Jones, 2011). European standard EN 335 (2013) defines the five use classes for different service situations on the solid wood and wood-based products, which correspond to more or less significant exposure to biological degradation agents (Tab. 2.2).

One of the important aspects of using wood while limiting its degradation is based on the idea of disrupting the principal physiological needs for microorganisms' growth and development. For instance, to avoid fungal decay, the wood must be kept dry, and this is most easily achieved by protecting it from rain (using rain barrier) and excess humidity (using vapor barrier) (Richardson, 2002). Serious decay can also come from the wrong choice of wood: natural durability is not adequate to resist the biological risk. Avoidance of moisture is thus a key principle for wood protection by design (Mahnert and Hundhausen, 2018). In case of avoiding termites attack, for example, the best way to protect the wood can be achieved by preventing the termites from gaining hidden access to a building, such as making the foundation made from concrete with cement mortar (Clausen, 2010).

However, in some conditions where the deterioration is inevitable and in order to comply with the desire service life of wooden commodities, protection treatments should always be used (Ibach, 2005). The classical concept of wood preservation is to eliminate suitable nutrition by treating wood with biocide (active ingredients) that are toxic to wood-degrading organisms, thus preventing biological attacks. There are four basic requirements to ensure the level of protection from particular preservatives in the treatment process, including the toxicity (the effectiveness of chemical against biological organisms), permanence (the resistance of the preservative to leaching, volatilization, and breakdown), retention, and depth of penetration into the wood (Ibach, 2005).

It is also possible to use methods other than the application of toxic chemicals (for example, aiming not only to increase its durability but also to improve wood properties). Protecting wood from moisture variations (reducing the tendency of wood to take on moisture) and keeping the wood dimensionally stable can be achieved by applying water repellents and dimensional stabilizers. Such treatment can be categorized under two principles: whether it causes changes in the cell wall (refers to wood modification) or not (Rowell and Banks, 1985; Sailer and Van Etten, 2004). In the end, all of these treatments will ultimately depend on the final usage of wood products.

Table 2.2: Summary of use classes and relevant attacking biological agents for wood and wood-based products according to standard EN 335 (2013)

Use class	General use situation[a]	Occurrence of biological agents [b]				
		Disfiguring fungi	Wood-destroying fungi	Beetles	Termites	Marine borers
1	Interior, dry	-	-	U	L	-
2	Interior, or under cover, not exposed to the weather. Possibility of water condensation	U	U	U	L	-
3	Exterior, above ground, exposed to the weather. When sub-divided: 3.1 limited wetting conditions 3.2 prolonged wetting conditions	U	U	U	L	-
4	Exterior in ground contact and/or fresh water	U	U	U	L	-
5	Permanently or regularly submerged in salt water	U[c]	U[c]	U[c]	L[c]	U

U = ubiquitous in Europe and EU territories
L = locally present in Europe and EU territories

[a] Border line and extreme cases of use of wood and wood-based products exist. This can cause the assignment of a use class that differs from that defined in this standard.

[b] It may not be necessary to protect against all biological agents listed as they may not be present or economically significant in all service conditions in all geographic regions, or may not be able to attack some wood-based products due to the specific constitution of the product.

[c] The above water portion of certain components can be exposed to all of the above biological agents.

2.1.4 History and development of wood preservation

The history of preserving wood can be traced to ancient Egypt and Roman times, where they use natural products from the extracted durable timbers or plants such as oil, resin, and tars. The Chinese used metallic salts as preservatives for the wood building materials by immersing them in seawater or salt lakes' water (Thompson, 1991; Richardson, 2002). In the 1700s to 1800s, various chemical formulations have been tested, including mercuric chloride, copper sulfate, and zinc chloride; however, they remain leached out in the water, limiting the use for the exterior applications (Thompson, 1991; Freeman et al., 2003). Major significant advances in industrial timber preservation were developed during the 19th century by using coal-tar creosote. The first-generation oil-borne preservatives, creosote, patented in 1836 by Franz Moll, is a by-product of coke production. During the industrial revolution, notably in the European countries, large volumes of sleepers and poles were treated by creosote through a pressure impregnation known as Bethell process (full-cell process), patented by John Bethell in 1838. In the early 19th century, creosote was made from beech wood tar, and distillation of coal tar began later (Freeman et al., 2003).

Other major first-generation preservatives systems also include oil-borne pentachlorophenol and the water-borne arsenicals, predominantly chromated copper arsenate (CCA). Pentachlorophenol, formed by chlorine's reaction on phenol, was developed in the 1930s and widely used in industrial applications as an oil-borne preservative. On the other hand, the first-generation metallics CCA involved classical poison arsenic that kills wood-eating insects and copper, which are toxic to fungi. Chromium was added in the formulation as a chemical fixing agent, binding the two toxic metals through chemical complexes to the wood cell walls. CCA was broadly used for residential use from the 1970s to the early 2000s since it left timber with no surface residue or oily smell. However, in the 1990s, public perception of the toxicity risk for human health and its environmental impact on bioaccumulation and disposal concern led to the ban of toxic chemicals (Schultz et al., 2007).

The second-generation wood preservatives are water-borne copper-rich systems that contain amine- or ammonia-complexed alkaline copper(II) and an organic cobiocide. Various products based on organic or inorganic formulation such as alkaline copper quat (ACQ), copper azole (CA), and copper-HDO were the CCA substitutes for residential applications. However, the leaching of copper and its adverse effect on the aquatic ecosystem remains an issue. Micron-sized copper(II) as copper carbonate, dispersed in water (microdispersed or micronized copper systems), were then developed (Schultz et al., 2008).

Another type of non-metallic water-borne preservative is borates (boron-based compounds), which have a long history as wood preservatives. The most common borate preservatives are boric acid, sodium octaborate, sodium tetraborate, sodium pentaborate, and disodium octaborate tetrahydrate (DOT or borax). They are colorless, odorless, not corrosive to metal fasteners, and have low mammalian toxicity. Because borates have insecticidal and fungicidal properties, they are efficient preservatives even when used alone (Richardson, 2002); however, they remain water-soluble in wood and readily leach out in soil/rainwater (Schultz et al., 2007). While fixing boron may increase its leaching resistance, it may lock the boron, which leads to the loss of biological efficacy. Thus, the key to expanding borate use is to improve their permanence in wood while retaining sufficient mobility to maintain its biological activity (Obanda et al., 2008).

The third-generation biocides, which totally organic material derived from agrochemicals, include triazoles (e.g., tebuconazole or propiconazole), which are active against Basidiomycete fungi and exhibit leach resistance and good stability once formulated in wood, and the synthetic pyrethroids (e.g., permethrin) or the highly active neonicotinoids (e.g., imidacloprid or thiamethoxam) which exhibit good efficacy against insects (Schultz et al., 2007).

2.1.5 Trends in wood protection

Environmental, health, and safety concerns related to the use of active substances in conventional wood preservation have led to governmental regulation. For more than a decade, formulations such as creosote, pentachlorophenol (PCP), and copper chromium arsenate (CCA) have been severely restricted or banned due to their adverse effects on the environment and human health. At the European level, regulations such as the REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) Directive (EC 1907/2006) also significantly contribute to reducing the environmental risks of current treatment products. Over the past two decades, the trend on wood protection has gradually shifted from traditional "wood preservation" to "wood protection," which is a more general concept based not only on the inherent characteristics of the material itself but also on its interaction with the environment, such as design, maintenance, exposure and risk of moisture (Kutnik et al., 2014).

Various efforts to develop alternative protection methods have also been made. One of them is the use of natural products (Singh and Singh, 2012). Another approach is improving the wood properties and durability through non-biocidal application, such as thermal and chemical modification of wood

(Gérardin, 2016).

2.1.5.1 The use of natural products

The development of environmentally friendly wood protection, especially those from natural materials, has been undertaken to find sustainable substitutes for hazardous substances in wood protection applications (Singh and Singh, 2012; González-Laredo et al., 2015). This includes several different approaches, such as using naturally occurring hydrophobic agents (e.g., waxes, plant oils, and resins) for moisture control or the utilization of natural compounds with biocidal properties and fixing them into wood (Broda, 2020). Several natural compounds derived from plants and animals have been shown to be effective against wood-destroying organisms, such as plant extract (Tascioglu et al., 2013), essential oils (Kartal et al., 2006; Pánek et al., 2014), tannin (Hu et al., 2017; Tomak and Gonultas, 2018), chitosan (Hussain et al., 2012), and propolis (Woźniak et al., 2020).

The use of natural products for wood protection is not free of limitations. Retention of organic biocides in impregnated wood tissues and their susceptibility to biodegradation are two major problems. The application of many of these compounds is also hampered by the leachability of treated wood when exposed to water. Potential methods for overcoming their shortcomings and increasing their bioactivity already exist, such as co-impregnation with different polymers, cross-linking, metal chelating, or antioxidants (Singh and Singh, 2012). Co-impregnation with water repellents (such as resin acid) can be an effective way of keeping the biocide leached out from treated wood (Panov and Terziev, 2009).

Another question remains regarding their toxicity towards human and environment since many studies on natural products for wood protection mainly focus on efficacy and often did not provide the ecotoxicity test. Indeed, as stated by De Vetter et al. (2008), it is not easy to find a way of treating wood with sufficient efficacy while at the same time also provide an excellent ecotoxicological profile of the leachates. While adequate protection against wood degrading organisms should be achieved, the ecotoxicity evaluation of the wood leachates should be followed until both durability and ecotoxicity are within satisfactory limits.

2.1.5.2 Wood modification

The wood modification method can use chemical (chemical modification) or heat (thermal modification) to change the wood structure. Various wood modification methods have been well studied, such as acetylation, furfury-

lation, and heat treatment. In the acetylation process, the reagent such as acetic anhydride reacts with wood polymers. The process results in the substitution of the wood hydroxyl groups by acetyl groups through esterification (Mantanis, 2017). The reaction of wood with acetic anhydride can be carried out with or without catalyst within temperature between 100 and 130 °C followed by a vacuum step to remove unreacted volatile reagent or acetic acid (by-product) (Obataya and Minato, 2008). The acetylation process improved physical, mechanical, and biological material properties. Furfurylation treatment is the process based on in situ polymerization of furfuryl alcohol, a compound derived from furfural, which is obtained from the hydrolyzed biomass. The properties of the modified wood depend on the retention of grafted/polymerized poly-FA. Once polymerized, the toxicity of furfuryl alcohol is significantly reduced (Gérardin, 2016). At high retention (high modification levels), some wood properties such as dimensional stability, hardness, MOR, MOE, resistance to decay, and insect attacks were improved (Lande et al., 2004).

Heat treatment or thermal wood modification is typically performed at temperatures between 180 °C and 260 °C (Hill, 2007). Various process conditions can differ, such as the presence of a shielding gas (nitrogen, oxygen, water steam) or the use of oil (rapeseed oil, linseed oil, or sunflower oil) as treating media (Lee et al., 2018). Several chemical reactions occur during the treatment, considerably modifying the wood structure and improving the wood properties. The partial degradation of the hemicellulose components and cellulose and lignin, to some extent, causes a decrease in wood hygroscopicity, converting the hydrophilic nature of wood to become hydrophobic. Heat treatment improves the dimensional stability, lowers the equilibrium moisture content, and increase resistance against wood-decaying fungi (except in contact with soil). However, it has little effect on termites and caused degradation of mechanical properties (Esteves and Pereira, 2009).

Both chemical and thermal modification of wood have worldwide industrial application, such as Plato and Thermowood for heat treatment; and Accoya and Kebony for chemical modification. Moreover, until today, chemical modification research is very active, such as wood modification with succinic acid (L'Hostis et al., 2020), citric acid (Mubarok et al., 2020), and lactic acid (Grosse et al., 2019).

2.1.6 Conclusion

Despite its various qualities, some wood species have limited end-use due to their susceptibility to biological attack. Several studies have been carried out on different protection methods aiming to improve the wood's service life. In

this section, the various type of biological agents that attack wood and the importance of wood protection have been discussed. As we are interested in investigating the potential of pyrolysis liquid for wood protection, the following section covers the literature review of previous work related to the topic.

2.2 Potential of Pyrolysis Liquid

The utilization of pyrolysis liquid is already of interest in many areas such as biocide, insecticide, fungicide, plant growth stimulator, and source of valuable chemicals (Tiilikkala et al., 2010; Mathew and Zakaria, 2015; Pimenta et al., 2018). A high concentration of acetic acid and furfural make pyrolysis liquid a potent natural pesticide. Due to its large composition of bioactive chemicals, such as organic acids, phenols, ketones, aldehydes, furans, and guaiacols, pyrolysis liquid was presumed to protect the wood against fungi and termite (Temiz et al., 2013a).

In this section, the potential of pyrolysis liquid related to its utilization as biocides and its application for wood treatment is presented. A brief history on the utilization of pyrolysis liquid both from slow and fast pyrolysis is also discussed.

2.2.1 History and utilization of pyrolysis liquid

Pyrolysis has been practiced by the Egyptians, Greeks, and Romans for producing charcoal from carbonization of wood, and collected the condensable volatiles for embalming purposes and for filling joints in wooden ships (Tiilikkala et al., 2010). Other than slow pyrolysis or carbonization, destructive distillation and dry distillation are similar terms used to describe this thermal process.

In the past, pyrolysis is also known as a technology for "distilling wood." In 1850, wood distillation was widely practiced on a commercial scale by heating wood in a closed retort (Pecha and Garcia-Perez, 2020). The condensed vapor was collected to give tar and aqueous layer (pyroligneous acid). Firstly, this liquor needs to be settled to separate the tar (soluble tar or settled tar) from the aqueous layer (Fig. 2.3). The settled tar phase can be distilled to produce pitch and other volatiles. Pitch is considered more solid than tar and was used for waterproofing and adhesives purposes if the biomass was softwood. On the other hand, the hardwood pitch was used as fuel because it had a lower value (Diebold, 1997). Pyroligneous acid was obtained by decanted the liquor from tar sedimentation and is the primary source for acetic acid, methanol, and acetone. During that period, wood was the only source for those chemicals (Tiilikkala et al., 2010).

From the 1920s to the 1950s, the wood distillation market was replaced by the petroleum industry (Pecha and Garcia-Perez, 2020). Currently, chemical production from wood distillation is rarely economically attractive in the Western Hemisphere. Wood carbonization is still practiced worldwide for heating, cooking, and industrial purposes, while chemicals are occasionally

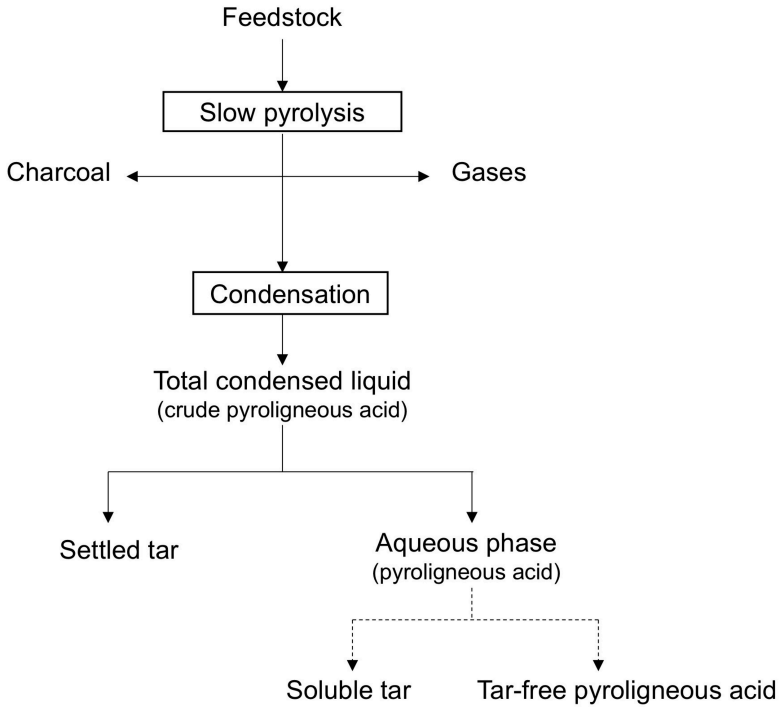

Figure 2.3: The condesable vapors of slow pyrolysis process

produced as a by-product (Tiilikkala et al., 2010).

2.2.1.1 Carbonization and traditional use of pyroligneous acid

It is known that the traditional farmers in some Asian countries have benefited from the pyroligneous acid as a by-product of the charcoal-making process (Fig. 2.4). In fact, pyroligneous acid has been used notably for agriculture purposes since the 1930s. Pyroligneous acid was used as alternatives to chemicals for improving crop yields (e.g., as a fertilizer and plant growth stimulant) and controlling pests (bio-pesticide). Currently, pyroligneous acid is also commercially available, such as in China, Japan, Thailand, Indonesia, and Malaysia.

In traditional charcoal production, woody biomass has been generally preferred feedstock. Therefore, pyroligneous acid often refers to wood vinegar. Wood vinegar is produced when smoke from charcoal production is cooled by the outside air as it passes through the chimney or flue pipe. The temperature of smoke ranges between 80 and 180 °C. A long hollow green bamboo pole is usually used to collect the condensable smoke by connecting it to the flue pipe (elevated to 40°). The bamboo pipe is only attached

Figure 2.4: Traditional charcoal making process (left) and its by-product from the condensation of smoke (right) (Kishimoto and Tsuyoshi, 2015)

when the smoke turns yellowish and acrid. A very thick and white smoke before that should be avoided due to the high moisture content. The bamboo is wrapped with damp cloths to help to give the cooling effect. One to two holes were made underneath the bamboo, 30 cm from the connection with the flue pipe. These holes will be the exit for the raw wood vinegar that can be collected using containers tied up underneath the bamboo holes (Burnette, 2010). When the droplets turn black, which indicates that tar has formed, the process is stopped. At this stage, the decomposition of char becomes very active, resulting in a stickier tar, and the smoke emitted during high temperature can also contain substances that are harmful to humans. The temperature of carbonization is usually kept under 425 °C to avoid these hazardous compounds (PAHs) (Kishimoto and Tsuyoshi, 2015).

Raw wood vinegar can be purified by a simple standing method by sealing it inside a tight container and let sit until 3-6 months in the ambient temperature. The three layers will be formed, with wood vinegar in the middle layer having a yellow to reddish-brown. The wood vinegar will separate itself from the sedimented tar which forms at the bottom. On top of wood vinegar, a light oily liquid is formed and will have a skim of wood tar. Wood vinegar is usually diluted in water in ratios between 1:50 (1 liter wood vinegar and 50 liters water) to 1:800 before use (Burnette, 2010).

2.2.1.2 Development of fast pyrolysis as a method to produce bio-oil

Until 1960, slow pyrolysis was the only technologically available method. At that period, fundamentals research on biomass pyrolysis reactions was studied, and researchers found that more liquid can be recovered when heating the feedstock very fast using small particles. Such technology refers to the fast pyrolysis method. Following the oil crisis in the 1970s, researchers develop reactors and conversion methods of chemical products from bio-oil until the 1990s. Until now, the research on pyrolysis focuses on the development of bio-oil upgrading (for the production of renewable fuels and chemicals) and the production of carbonaceous products (Pecha and Garcia-Perez, 2020).

2.2.2 Biological activity of pyrolysis liquid against fungi and termites

Tab. 2.3 and Tab. 2.4 summarize the biological activity of various pyrolysis liquid against rot-fungi and termites in laboratory bioassays. Most of the work found in the literature was using liquid from slow pyrolysis of various biomass.

Among many type of wood-decaying fungi, pyrolysis liquid has been showed to have activity against white-rot (*Trametes versicolor*, *Rigidoporopsis amylospora* and *Pleurotus ostreatus*) and brown-rot (*Coniophora puteana*, *Rhodonia placenta, Gloeophyllum trabeum*, *Fomitopsis palustris*, *Lentinus lepideus*, and *Tyromyces palustris*). Termites such as *Coptotermes formosanus* and *Reticulitermes speratus* have also tested in previous experiments using liquid product from pyrolysis. Based on the literature review, the active concentration for termites is higher than that of fungi.

The anti-fungal and anti-termite properties of pyrolysis liquid depend significantly on its composition, which is influenced by the raw material and processing conditions. For example, Barbero-López et al. (2019) tested different distillates using a range of pyrolysis temperature. They found that the liquid products from slow pyrolysis show higher fungal activity than torrefaction-produced liquid. Torrefaction, a low-temperature pyrolysis process (between 225 °C and 300 °C), usually produces a liquid with lower organic compounds, mainly organic acid and water.

Theapparat et al. (2015) used several type of biomass such as *Eucalyptus camaldulensis*, *Leucaena leucocephala*, *Azadirachta indica*, *Hevea brasiliensis* (rubberwood) and *Dendrocalamus asper* (bamboo) to produce pyroligneous acid from carbonization along with two commercial products. Before use, the samples were stored at room temperature in a closed container for at least

6 months to separate the heavy tar. They found that the liquid product from the pyrolysis of bamboo and rubberwood exhibited higher antifungal activity, due to the higher total phenolic concentrations, notably higher for 2-methoxy-4-propylphenol and 2-methylphenol.

Oramahi et al. (2018) found pyrolysis liquid from oil palm trunk produced at 350 °C showed higher anti-fungal and anti-termites activity than those of liquid produced at 400 and 450 °C due to the higher acid and phenolic compound. Oramahi and Yoshimura (2013) also highlighted the termiticidal activity and repellent effect of wood vinegar produced from *Vitex pubescens* to both *R. speratus* and *C. formosanus* workers.

Kartal et al. (2011) reported that tar oil recovered from the slow pyrolysis of macadamia nutshell was effective in inhibiting the growth of different rot fungi and sapstain fungus (*Ophiostoma piliferum*). At dilution 1:5000 (tar oil:growth medium), total inhibition was observed for white-rot *P. ostreatus* and *T. versicolor*. Higher concentration is required to completely inhibit the brown-rot fungi *T. palustris* and *L. lepideus* (1:500).

The biological activity of pyrolysis liquid against fungi and termites is often associated with the synergistic action of various compounds, instead of one molecule individually. The number of organic components of the pyrolysis liquid usually can be detected by GC-MS. However, single analytical method is inaccessible to thoroughly characterize the chemical species, so it requires the combination of more than one analytical methods (Garcia-Perez et al., 2007). GC-MS is usually employed for the identification of volatile compound, whereas the non-volatile compounds can be detected by HPLC and HPLC/electrospray MS. Other analytical methods include Fourier transform infrared (FTIR) spectroscopy for identifying the functional groups, gel permeation spectroscopy (GPC) for the molecular weight distributions, and nuclear magnetic resonance (NMR) for the types of hydrogens or carbons in specific structural groups, bonds, and area integrations (Mohan et al., 2006).

Phenolic derivatives and organic acids (mainly acetic acid) is reported behind the fungicidal and insecticidal properties of pyrolysis liquid. The phenolic compounds such as 2-methoxy-4-methylphenol, 2,6-dimethoxyphenol (syringol), 2-methoxyphenol (guaiacol), 4-ethyl-2-methoxyphenol were frequently found as major constituents in pyrolytic fractions with antifungal effects. However, for the insecticidal activity, few studies have made the chemical analysis of active fractions, thus little is known about the interaction between the bio-oil constituents and the effects their effect on the insecticidal activity (Mattos et al., 2019).

Table 2.3: Biological activity of various slow pyrolysis liquid against wood-decaying fungi.

Biomass	Temperature (°C)	Main chemical constituents	Target organisms and active concentrations (v/v)	Reference
Bark of *P. abies* and *B. pendula*, and fibre hemp (*C. sativa*)	275 and 350	Propionic acid; furfural; ethanol, acetic acid; methanol; formic acid; hydroxymethylfurfural.	*C. puteana* (1%), *R. placenta* (1%), *G. trabeum* (1%).	Barbero-López et al. (2019)
Oil palm trunk	350, 400, and 450	Acetic acid; phenol; propanoic acid; 1-Hydroxy-2-propanone; 3-Hydroxy-2-butanone.	*T. versicolor* (1.5%), *F. palustris* (>1.5 %).	Oramahi et al. (2018)
L. leucocephala, *A. indica*, *E. camaldulensis*, *D. asper*, *H. brasiliensis*.	400	Acetic acid; methanol; 2-methylphenol; syringol; 4-propyl-2-methoxyphenol; 4-methyl-2-methoxyphenol; 4-ethyl-2-methoxyphenol.	*T. versicolor*, *R. amylospora* (6.25-12.50 mg/ml), *G. trabeum* (3.13-12.50 mg/ml).	Theapparat et al. (2015)
V. pubescens	350, 400, and 450	Acids and phenols.	*T. versicolor* (1.5%), *F. palustris* (>2 %).	Oramahi and Yoshimura (2013)
Macadamia nutshell	-	Phenol; O-Cresol; aromatic hydrocarbons; hydrocarbons. 2,4 dimethylphenol; PAHs compounds.	*T. versicolor* (0.02%), *P. ostreatus* (0.01%), *L. lepideus* (0.20%), *T. palustris* (0.20%).	Kartal et al. (2011)
Pistachio shell	500	2,6-Dimethoxy phenol; 2-Hydroxy phenol; 2-Methoxy phenol; 2-Methoxy-4-methyl-phenol.	*T. versicolor* (50 mg/ml).	Okutucu et al. (2011)

Table 2.4: Biological activity of various slow pyrolysis liquid against termites

Biomass	Temperature (°C)	Main chemical constituents	Target organisms and active concentrations (v/v)	Reference
Oil palm trunk	350, 400, and 450	Acetic acid; phenol; propanoic acid; 1-Hydroxy-2-propanone; 3-Hydroxy-2-butanone.	*C. formosanus* (10%).	Oramahi et al. (2018)
V. pubescens	350, 400, and 450	Acids and phenols (detail chemical species are not identified).	*C. formosanus* (10%), *R. speratus* (5%).	Oramahi and Yoshimura (2013)
Coconut shell	350-400	-	*Odontotermes* sp. (1:50).	Wititsiri (2011)
Chips of *C. japonica*, *P. menziesii*, *Q. serrata*, and *P. densiflora*.	-	Acetic acid; propanoic acid; phenol; 2,6-dimethylphenols, 2-methoxy-4-ethyl-phenol.	*R. speratus* (0.1 mg/mL).	Yatagai et al. (2002)

2.2.3 Pyrolysis liquid treatments for wood protection

The potential of pyrolysis liquid for wood protection has been studied by previous researchers using various type of biomass and pyrolysis process (Tab. 2.5). Methods are varied regarding the liquid recovery (e.g., through fractination, liquid-liquid extraction, or using the whole liquid as obtained from the pyrolysis process). Before applying it to wood, some concentration can be performed using dilution in solvent such as ethanol or methanol.

Table 2.5: Example of various study of bio-oil from slow and fast pyrolysis process for wood treatment

Type of Pyrolysis	Biomass	Reference
Slow Pyrolysis	Giant cane	Temiz et al. (2013a)
Slow Pyrolysis	Macadamia nut shell	Kartal et al. (2011)
Slow Pyrolysis	Scots pine	Temiz et al. (2010)
Slow Pyrolysis	Oil palm trunk	Lee et al. (2010)
Fast Pyrolysis	Eucalypt wood	Lourençon et al. (2016)
Fast Pyrolysis	Yellow poplar sawdust	Kim et al. (2012)
Fast Pyrolysis	Oak and pine (wood and bark)	Mohan et al. (2008)
Fast Pyrolysis	Southern pine	Cooper et al. (2008)

2.2.3.1 Pyrolysis liquid from slow pyrolysis

Temiz et al. (2010) pyrolyzed scots pine (*Pinus sylvestris* L.) wood at 550 and 600 °C, and fractionated the liquid obtained into two parts (heavy and light fraction), using a glass separation funnel based on the color differences, while the liquid obtained at 450 °C was homogeneous with no visible fractions. They reported that the mass loss of treated samples against brown rot *R. placenta* was 7–10%, where no significant differences observed between the light and heavy fractions samples. The retentions of the impregnated samples varied between 306 to 823 kg/m^3.

Kartal et al. (2011) utilize the term of tar oil to describe the dark brown oily liquid from slow pyrolysis of macadamia nutshell. They found that the tar oil (retention of 460 kg/m^3) protected wood well against the fungi and termites even after leaching. Their results showed that the mass losses in leached specimens were less than those observed in unleached specimens.

Theapparat et al. (2015) tested the antifungal effect of several pyroligneous acid from the carbonization of different wood and bamboo on the soil block experiments. They found all pyroligneous acid were moderately resistant or non-resistant to white-rot, brown-rot, and sapstain fungi with retention of 17.62 to 35.88 kg/m^3. They also stated that the antifungal activities

of all samples tested were higher against brown rot fungus (*G. trabeum*) than the two white rot fungi (*T. versicolor* and *R. amylospora*).

2.2.3.2 Pyrolysis liquid from fast prolysis

Mohan et al. (2008) fractionated different types of bio-oil from wood and bark of pine and oak that were generated at different pyrolysis temperatures and residence times to obtain lignin-rich fractions which consist mainly of phenols and neutrals. They reported that the lignin-rich fractions showed greater fungal activity than whole bio-oils for a impregnation solution at 10% concentration level (effective concentration for whole bio-oil was 25%), however the activity is lost after leaching. For the whole bio-oil, the results showed that the toxic fungicide threshold was between 96 and 192 kg/m^3.

Kim et al. (2012) used the pyrolysis liquid from the fast pyrolysis (500 °C and residence time of 1.9 s) of yellow poplar (*Liriodendron tulipifera*) sawdust. They found that pyrolysis liquid at 100% (retention = 214 kg/m^3 and 117 kg/m^3) or 75% (retention = 149 kg/m^3 and 27 kg/m^3) concentrations showed good decay resistance against wood-rot fungi *T.palustris* and *T.versicolor*. They also observed the agglomeration of product in the internal part of the wood which can be associated with the antifungal effect.

Lourençon et al. (2016) studied the bio-oil derived from fast pyrolysis of residual eucalypt wood fines at a concentration 10%, 50% and 100% against white-rot *T. versicolor* and brown-rot *G. trabeum*. Before application to wood, the bio-oil was heated at 80 °C to decrease its viscosity. They reported the bio-oil impregnated pinewood with high loading (57.44% and 81.30%) caused the complete mortality of the whole fungal colony in the first days of test. The authors also proposed the potential of bio-oil as an efficient hydrophobic agent as it is proved to decrease the water absorption and wettability of the treated pine wood. When wood is impregnated with bio-oil, it agglomerates and coats the surface of the wood's vascular microstructure, thus blocking the water flow inside the wood.

2.2.3.3 Combination with other compounds

Previous studies have been highlighted the limitation of pyrolysis liquid due its leachability. However, only few study conducted the analyses the chemical composition from the leachate products. Temiz et al. (2010) reported that a significant amount of phenolic compounds were leached, however detailed chemical analysis was not performed. Temiz et al. (2013b) employed epoxidized linseed oil (ELO) as potential hardener to decrease the bio-oil leaching and increase the wood's hydrophobicity. Their results suggested that ELO

treatment significantly decreased the water uptake which confirmed by the water absorption test. However, the second impregnation with ELO slightly increased the mass loss caused by decay fungi. Nonetheles, the decay resistance of treated wood samples with 20% of bio-oil against brown (*C. puteana*) and white rot fungi (*T. versicolor*) was very effective (less than 3% mass loss with retention of 50–100 kg/m^3).

Some studies also reported that bio-oils may be very effective as additives to biocide formulations or co-impregnation with pentachlorophenol, creosote, organic biocides and boron compounds for synergistically enhanced activity (Cooper et al., 2008; Mohan et al., 2006). Cooper et al. (2008) combined bio-oil with three different biocides (disodium octaborate tetrahydrate, tebuconazole and copper sulfate). Their results suggested that treating solutions combining 25% of bio-oil with tebuconazole or copper sulfate fungicides may have potential as wood preservatives.

2.3 Conclusion

In this chapter, particularly in section 2.2, it has been presented that pyrolysis liquid from different types of biomass can be used for wood protection due to its bioactive chemicals that have activity against various types of biological agents such as fungi and termites. However, those liquid products produced from either slow and fast pyrolysis can vary in terms of their effectiveness and chemical composition depending on the processing temperature and feedstock used.

Sugarcane bagasse is a raw material available in many southern countries and provides its potential for energetic valorization. As presented, in many developing countries, slow pyrolysis is practiced to get interesting char, and pyrolysis liquid as its by-product to be used for different purposes. In the next chapter, we will demonstrate our research findings on the valorization of sugarcane bagasse through slow pyrolysis for co-producing char and pyrolysis liquid. In the end, the use and efficacy of pyrolysis liquid to treat non-durable wood is investigated to evaluate the possibility and potential of this product for wood protection treatment.

Part II

Energetic valorization of sugarcane bagasse via slow pyrolysis

Chapter 3

Introduction

This part presents the experimental study on the slow pyrolysis of sugarcane bagasse. As previously mentioned, the potential of lignocellulosic biomass for energy production can be advanced through biomass conversion by means of pyrolysis. Slow pyrolysis, which occurs at a low heating rate and long vapor residence time, yields a good quality of char (Bridgwater, 2003). This technique is attractive in converting the unstable biomass, which contains higher volatile matter, such as sugarcane bagasse, to a stable energy-rich product. Also, an interesting balance of char and liquid production can be obtained using this process.

Since slow pyrolysis favors the production of char as the main target, we employed several parameters based on the previous studies. Past studies have reported that slow pyrolysis of sugarcane bagasse is optimum to produce the highest char yield at a heating rate range of 2 °C/min to 16 °C/min and at a temperature above 240 °C, where significant differences of mass loss occurred at a temperature between 300 °C to 500 °C (Katyal et al., 2003; Carrier et al., 2011). In addition, the optimal pyrolysis temperature for the maximum yield of solid and liquid products has been reported in the range of 400 °C–550 °C (Kan et al., 2016). From those results, we could establish the slow pyrolysis experiments at a lower heating rate (1 °C/min and 10 °C/min) and intermediate temperature (400 °C and 500 °C).

The objective of this work is to evaluate the potential of sugarcane bagasse valorization via slow pyrolysis to co-produce char and pyrolysis liquid. The char resulting from different pyrolysis settings was assessed according to its yield and thermal properties, including the proximate, ultimate, and calorific analysis for evaluating its potential as an energy source. The liquid product was recovered by condensing the pyrolysis vapor and was subsequently used as a candidate for wood protection agents. The chemical composition of pyrolysis liquids selected from the process was also investigated.

Chapter 4

Materials and Methods

4.1 Slow pyrolysis of sugarcane bagasse

4.1.1 Biomass preparation

Sugarcane bagasse (*Saccharum* spp.) was obtained from three consecutive annual harvests from la Réunion Island (French overseas territory) (Fig. 4.1). The bagasse has a moisture content of 8.48 % and was provided as a grounded form with a particle size of <2 mm. Prior to the pyrolysis process, the samples were oven-dried at 105 °C for two hours to remove its moisture content (<1 %). Samples of 100 g were used for each pyrolysis experiment.

Figure 4.1: Sugarcane bagasse

4.1.2 Reactor set-up and parameters

A bench-scale fixed bed reactor equipped with a set of condensation system was used for the slow pyrolysis experiments (Fig. 4.2). This device was placed in a muffle furnace oven, which generates heat to the reactor. The reactor vessel has a cylinder form with a diameter of 24 cm and a height of 20 cm. The reactor cap has a 59.5 cm long connecting pipe, which allows smoke to exit the oven towards the condensation system. The condenser was circulated with the ice-cooled liquid, a mixture of water and ethylene glycol

contained in the cooling bath. The condenser's temperature was held at the temperature of −15 °C at the beginning of the pyrolysis experiments.

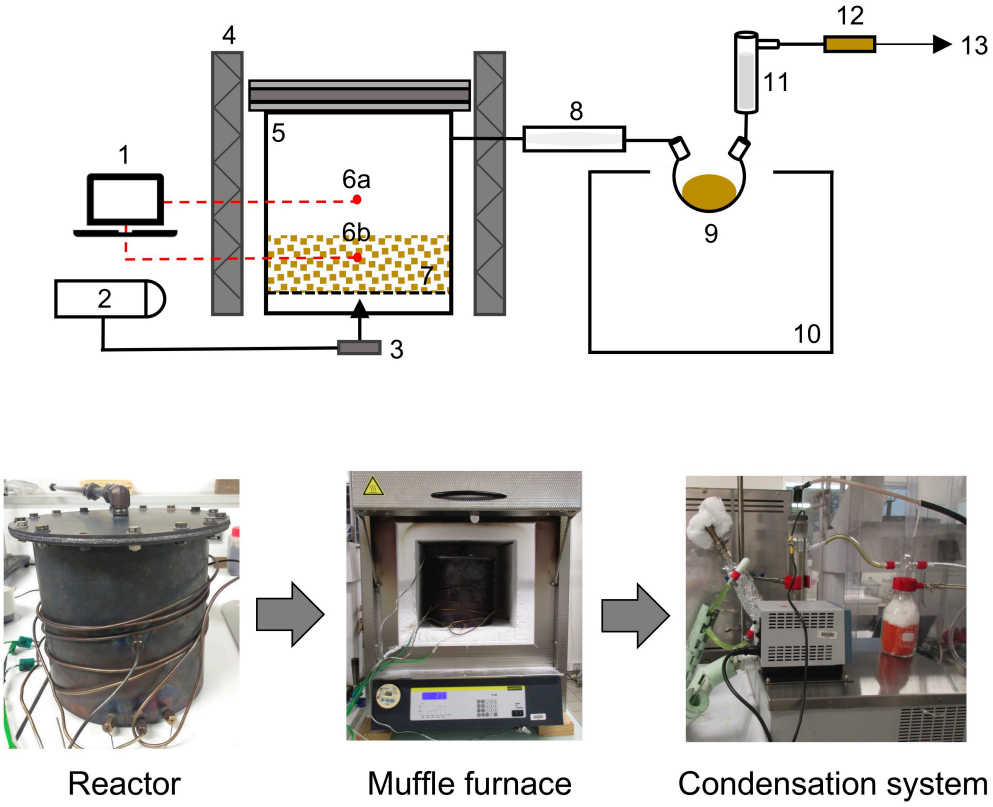

Figure 4.2: Experimental set-up of the pyrolysis reactor: (1) temperature control, (2) nitrogen gas supply, (3) flow control, (4) muffle furnace, (5) pyrolysis reactor, (6a and 6b) thermocouples, (7) bagasse/char, (8) condenser, (9) condensed liquid, (10) cooling bath, (11) electrostatic precipitator, (12) light product, and (13) gas vent

The experiments were carried out at a temperature of 400 °C and 500 °C, a heating rate of 1 °C/min and 10 °C/min, and holding time of 30 min and 60 min, resulting in eight pyrolysis treatments in total. In order to ensure the expected pyrolysis parameters, two thermocouples were set up inside the reactor to monitor and record the evolution of temperature as a function of time using the *Data Control* software. One thermocouple is placed in direct contact with the biomass, while another was located in the middle of the reactor (see Fig. 4.2). The constant flow of inert gas (N_2) was applied at

a rate of 1 L/min. The nitrogen flow removed the organic vapors and gas products from the reactor. Further, the pyrolysis vapors were cooled down in a single-stage consisting of a double tube condenser, which is maintained at a temperature between 0 and 5 °C and an electrostatic precipitator. A bottle filled with silica gel was set up at the end of the condenser system, and the mass of the light-end compounds trapped here was used for mass balance purposes only. The pyrolysis liquid (Fig. 4.3) was then collected from the round flask and then stored in a refrigerator at 5 °C before further use.

Figure 4.3: Pyrolysis liquid of sugarcane bagasse

The percent yield of char (CY) and pyrolysis liquid (LY) was calculated based on the ratio between the final products' weight to biomass's initial weight (Eq. 4.1 and Eq. 4.2). The gas yield can be calculated as difference; however it was not recovered and analyzed in this study. Each pyrolysis experiment was repeated three times.

$$CY(\%) = \frac{m_{\text{char}}}{m_{\text{initial}_{\text{biomass}}}} \times 100 \tag{4.1}$$

$$LY(\%) = \frac{m_{\text{liquid}}}{m_{\text{initial}_{\text{biomass}}}} \times 100 \tag{4.2}$$

4.2 Characterization of biomass and char

4.2.1 Proximate analysis of biomass and char

The proximate analysis was conducted to evaluate the moisture, volatile matter, fixed carbon, and ash content of bagasse and char.

The moisture content of bagasse (ISO 18134-3, 2015) and char (EN1860-2, 2005) was determined by heating the samples in a drying oven at 105 °C for 2 h or until reaching a constant weight. For the ash content, the samples of bagasse and char was heated in a muffle furnace to 550 °C and 710 °C, respectively. Briefly, the samples of bagasse or char were put in the uncovered crucible. For bagasse, the sample was first heated from the ambient temperature to 250 °C for 60 min, then ramped up from 250 °C to 550 °C for 60 min, and maintained at that temperature until constant weight (or at minimum 2 h) (ISO 18122, 2015). For char, the sample was first heated from the ambient temperature to 250 °C for 30 min, then ramped up from 250 °C to 550 °C for another 30 min, and finally ramped up again until (710 ± 10) °C for 30 min and held until constant weight (or at minimum 2 h) (EN1860-2, 2005). The volatile matter was released from the sample by heating the bagasse (ISO 18123, 2015) or char (EN1860-2, 2005) in the covered crucibles inside a muffle furnace to 900 °C for 7 min. Lastly, the fixed carbon was determined by difference.

4.2.2 Elemental analysis of biomass and char

The elemental analysis was carried out to determine the content of carbon (C), hydrogen (H), and nitrogen (N) of bagasse and char by using an elemental analyzer VariMACROcube according to ASTM D5373 (2016) and ISO 16948 (2015). Meanwhile, the oxygen content (O) was obtained by difference. Samples of approximately 100 mg of bagasse and 30 mg of char were used within each run. Phenylalanine (Sigma-Aldrich) was used as a standard reference. The O/C and H/C atomic ratios were then determined from the obtained weight percent and atomic weights of the corresponding elements.

4.2.3 Higher Heating Value (HHV)

The gross calorific value or the higher heating value (HHV) of bagasse and char was experimentally measured using a bomb calorimetric PARR 6200

(ISO 18125, 2017) and determined on its anhydrous basis (Eq. 4.3).

$$HHV(\mathrm{J/g}) = 4.1855 \times \frac{E_{\mathrm{cal}} \times T \times Q_{\mathrm{fuse}} \times Q_{\mathrm{N}}}{m} \times \frac{100}{100 - MC} \tag{4.3}$$

where 4.1855 is the conversion factor (from Cal to J), m is the mass of the sample (g), E_{cal} is the average value of the effective heat capacity of the calorimeter as determined during calibration tests, T is the corrected temperature increase, Q_{fuse} is the energy input from the combustion of the firing wire (Cal), Q_N is the energy input from the formation of nitric acid (from water in the liquid state, nitrogen, and oxygen in the gaseous state) (Cal), and MC is the moisture content of the sample (%).

4.2.4 Ash Recovery (AR)

The ash recovery quantifies the amount of ash stored within the solid biochar phase after slow pyrolysis. The ash recovery (AR) was calculated following the study conducted by Ghysels et al. (2019) and determined from the ash content of bagasse ($\mathrm{Ash_{bag}}$), the ash content of char ($\mathrm{Ash_{char}}$), and the char yield (CY) (Eq. 4.4).

$$AR(\%) = \frac{Ash_{\mathrm{char}}}{Ash_{\mathrm{bagasse}}} \times CY \tag{4.4}$$

4.2.5 Energy Yield (EY) and Energy Density (EY)

The energy yield and energy density were determined according to the study conducted by Yang et al. (2017). The energy yield (EY) was expressed as the ratio of the heating value of char ($\mathrm{HHV_{char}}$) and bagasse ($\mathrm{HHV_{bagasse}}$) multiplied by the char yield (CY) (Eq. 4.5). For energy density (ED), the value was determined as the ratio of energy yield and char yield (Eq. 4.6).

$$EY = \frac{HHV_{\mathrm{char}}}{HHV_{\mathrm{bagasse}}} \times CY \tag{4.5}$$

$$ED = \frac{EY}{CY} \tag{4.6}$$

4.3 Characterization of pyrolysis liquid

4.3.1 Water content and pH of pyrolysis liquid

The water content of pyrolysis liquid was determined using a Karl Fisher volumetric titration (Mettler Toledo, Karl Fisher V20) following the standard test method of ASTM E203-08 (2008). The pH of pyrolysis liquid was also measured using a pH meter (Portames® 911pH). Only pyrolysis liquid produced at a temperature of 400 °C and 500 °C, a heating rate of 10 °C/min, and a holding time of 60 min were analyzed.

4.3.2 FTIR analysis of pyrolysis liquid

Fourier transform infrared spectroscopy (FTIR) spectra of the pyrolysis liquid were recorded using a Perkin Elmer Frontier spectrometer equipped with an Attenuated Total Reflection (ATR) illustrated in Fig. 4.4. FTIR spectra were obtained at a nominal resolution of 4 cm^{-1} for 4 scans in the range of 4000–650 cm^{-1}. The spectra were treated using RStudio using the package of MALDIquantForeign (Gibb and Strimmer, 2012; R Core Team, 2019).

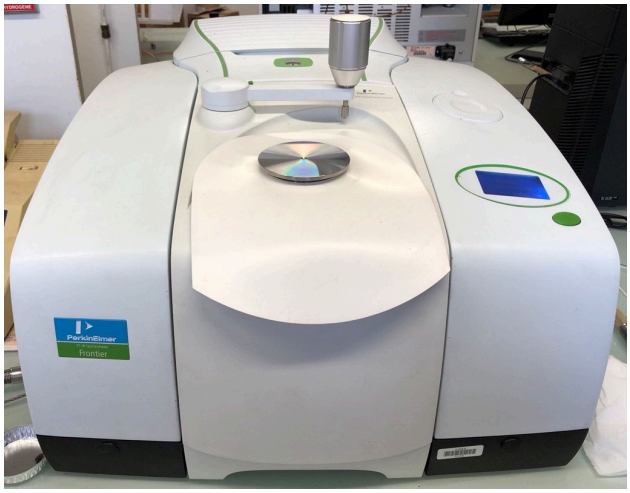

Figure 4.4: FTIR device

4.3.3 GC-MS analysis

Gas chromatography-mass spectrometry (GC–MS) analysis of pyrolysis liquid was performed using an Agilent 6890N gas chromatograph and Agilent

5975 mass spectrometer, all materials and chemicals being provided by Agilent. A 1 ml of pyrolysis liquid sample was dissolved in 10 ml of analytical grade acetone and filtered with a nylon microfilter of 0.45 mm. Afterward, 1 ml of sample volume was transferred into a glass vial followed by the introduction of internal standards (acetic-acid-d4, toluene-d8, phenol-d6, and phenanthrene-d10). The gas chromatograph was equipped with an electronically controlled split/splitless injection port and a capillary column DB-1701. The injection (1 µl) was performed at 250 °C in the split mode (split = 1/10). Helium was used as carrier gas at constant flow (1.9 ml/min). GC oven temperature was programmed to hold at 45 °C for 4 min, then heated to 120 °C at a rate of 3 °C/min, and finally increased to 270 °C at a rate of 20 °C/min. The internal standard used for the quantification was acetic-acid-d4 and toluene-d8. For the splitless mode, the injection was performed at 250 °C. The oven temperature program was as follows: the initial temperature was set at 45 °C for 4 min, then increased to 250 °C at a rate of 3 °C/min, increased again to 270 °C at a rate of 20 °C/min and held there for 60 min. Phenol-d6 and phenanthrene-d10 internal standards were used for the quantification of the compounds. The mass spectrometer was fixed at 70 eV ionization energy (ion source temperature = 230 °C). Detail apparatus specification can be found in study by Lê Thành et al. (2015). In addition, a dilution to 1/10 (v/v) of a mixture sample in acetone was also performed to obtain the actual concentration of some calibrated compounds that were higher than the upper limit of the calibration range.

4.4 Data analysis

Multivariate regression analysis was conducted to determine each parameter's correlation and effects on the yield values and char properties. Temperature, heating rate, and holding time were the independent parameters. We then determined the significance of each of those parameters individually using p-value and globally by seeing their R^2 value.

Chapter 5

Results and Discussion

5.1 Characteristics of biomass

Tab. 5.1 summarizes the proximate, ultimate, and calorific analysis of the studied sugarcane bagasse and references from different studies. The proximate analysis provides information related to the burning quality of biomass (Varma and Mondal, 2017). Sugarcane bagasse contains 8.5 % of moisture content, 82.4 % of volatile matter, 13.4 % of fixed carbon, and relatively higher ash (4.2 %) compared to other studies. The ash content of biomass tends to be higher when smaller particles were used (Garcia-Perez et al., 2002; Carrier et al., 2011). Ash content has a detrimental effect as it is an inorganic, incombustible material that can lower the burning rate. The amount of ash content depends on the nature of biomass. As an illustration, rice straw has 14 % of ash content, while wood biomass such as birch wood has the lowest ash content, which is approximately 0.3 % (Yang et al., 2017). Bagasse also contains a very low fuel ratio (fixed carbon/volatile matter) due to the high content of volatile matter. A fuel ratio of 1 or less is considered very low, while, as a comparison, the anthracite has a fuel ratio of 12 (Chae et al., 2020).

The ultimate analysis demonstrates the elemental composition of biomass. Sugarcane bagasse has 47.3 % of carbon, 5.7 % of hydrogen, 0.4 % of nitrogen, and 46.7 % of total oxygen and sulfur. The carbon and hydrogen contents are a good criterion for power generation and contribute most to the calorific value (Pereira et al., 2013). The HHV of sugarcane bagasse was 18.1 MJ/kg. It is one of the most important energy analysis parameters, defined as the released energy per unit mass or volume from the material after the complete combustion. In contrast, the presence of oxygen decreases the fuel's calorific value, while the low content of nitrogen and sulfur is imperative in terms of environmental aspects (Demirbaş and Demirbaş, 2004). The analysis demonstrates that the present biomass is comparable to other sugarcane bagasse reported in different studies and possesses the potential as pyrolysis feedstock.

Table 5.1: Proximate and ultimate analysis of sugarcane bagasse

Characteristics	Bagasse	Ref. 1[a]	Ref. 2[b]	Ref. 3[c]
Proximate analysis (dry wt.%)				
- Moisture	8.5	15.4	6.0	5.4
- Volatile matter (VM)	82.4	-	82.1	80.2
- Ash content	4.2	3.1	1.6	3.1
- Fixed carbon (FC)	13.4	-	16.3	11.3
Fuel ratio (FC/VM)	0.16	-	0.20	0.14
Ultimate analysis (dry wt.%)				
- Carbon (C)	47.3	50.2	49.6	44.8
- Hydrogen (H)	5.7	5.6	6.0	5.8
- Nitrogen (N)	0.4	1.1	0.5	0.2
- Oxygen + Sulphur (O + S)	46.7	40.0	43.8	49.0
Higher Heating Value (HHV; MJ/kg)	18.1	18.5	18.5	18.0

[a] Sugarcane bagasse obtained from South Africa (Carrier et al., 2011).
[b] Sugarcane bagasse obtained from Florida, United States (Garcia-Perez et al., 2002).
[c] Sugarcane bagasse obtained from India (Varma and Mondal, 2017).

5.2 Effect of pyrolysis parameters on the product yields

The evolution of temperature as a function of time was monitored and corresponded well with the expected scheme (Fig. 5.1). The yield of char and pyrolysis liquid are presented in Tab. 5.2, followed by their coefficient of regression given in Tab. 5.3. The temperature was observed as the most important parameter, influencing the char yield (p-value = 5.37×10^{-12}) and liquid yield (p-value = 2.41×10^{-5}). The two heating rates (1 °C/min and 10 °C/min) also showed a significant effect on char yield (p-value = 5.33×10^{-6}) and liquid yield (p-value = 1.8×10^{-5}). Meanwhile, there is no significant difference in the product yields for the holding time of 30 min and 60 min.

Lower temperature promotes a higher char yield; however, it reduces the liquid yield and vice versa. The char yield was decreased from the temperature of 400 °C–500 °C as much as 12.65 % on average. Katyal et al. (2003) stated that below 300 °C, the mass loss or the conversion of bagasse in slow pyrolysis is low and significant conversion occurs between 300 °C and 500 °C.

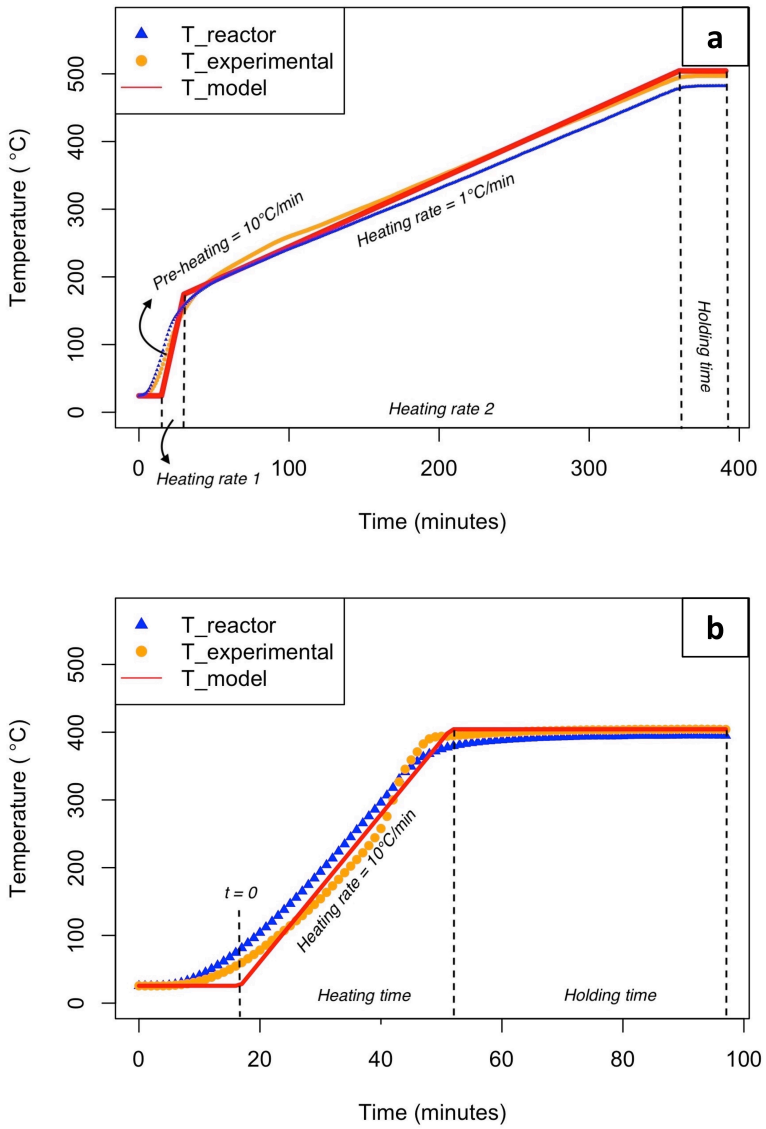

Figure 5.1: Comparison between the expected pyrolysis process (T model) and experiment (T experimental) at temperature of 500 °C and heating rate of 1 °C/min (a) and at temperature of 400 °C and heating rate of 10 °C/min (b)

The high yield of char at low temperature indicates that the biomass has only been partially pyrolysed. Further, they reported that the mass loss after 500 °C is negligible and the decrease of char yield was considered insignificant (3–4 %) when pyrolysed between 500 °C–700 °C. In Tab. 5.2, the energy density of char was found higher (1.53–1.58) at higher pyrolysis temperatures, as the HHV also increases as the temperature increase. From all the conditions tested, the average of char and liquid yield varied between 28.81 %–35.12 %, and 49.67 %–55.46 %, separately. Aboulkas et al. (2017) reported that pyrolysis liquid made from algal waste reaches a maximum yield at the temperature range of 500 °C–550 °C, while it decreases at the temperature of 600 °C. At higher temperatures, the secondary reaction is likely to occur and produce a significant amount of gas.

Results showed that the heating rate of 10 °C/min increased the liquid yield, but decreased the char yield. Katyal et al. (2003) reported that the effect of heating rate on the char yield is more noticeable at temperatures lower than 400 °C. It conveys a negligible effect of the heating rate at a higher temperature when char production is the main target. The reduction of char yield at a higher heating rate has been explained as the result of the secondary cracking of the pyrolysis vapors and secondary decomposition of the char (Carrier et al., 2011). While preferring the high liquid yield, the higher heating rate should be chosen. However, at pyrolysis of 500 °C, Aboulkas et al. (2017) reported no significant impact on the char or liquid yield using a higher heating rate (10 °C/min–50 °C/min). In our study, the highest liquid yield was observed at a temperature of 500 °C and a heating rate of 10 °C/min (55.46 %).

The decomposition of biomass during pyrolysis is associated with cellulose, hemicellulose, and lignin content. Varma and Mondal (2017) reported that sugarcane bagasse comprises 47.6 % of cellulose, 39 % of hemicellulose, and a considerable low content of lignin (11.2 %). According to Morais et al. (2017), who investigated the thermal behavior of sugarcane bagasse, there are at least three critical stages in this process: (1) dehydration, (2) degradation of hemicellulose and cellulose, and (3) lignin decomposition. They investigated the maximum loss rate of hemicellulose was observed at 250 °C, cellulose at 330 °C, and lignin between 190 °C and 500 °C, with the maximum mass loss rate occurs at 430 °C. Hemicellulose and amorphous part of cellulose principally yield the condensable volatiles, whereas cellulose and lignin's degradation produces gases, tar, and char (Katyal et al., 2003).

Table 5.2: Energy analysis of bagasse char and the yield of bagasse char and pyrolysis liquid

Process condition	Char yield (%)	HHV[a](MJ/kg)	EY[b](%)	ED[c]	Liquid yield (%)
400 °C; 1 °C/min; 30 min	35.12 ± 0.96	27.44 ± 0.03	53.12	1.51	49.67 ± 0.28
400 °C; 1 °C/min; 60 min	34.63 ± 0.20	27.41 ± 0.14	52.33	1.51	49.18 ± 1.33
400 °C; 10 °C/min; 30 min	33.26 ± 0.60	27.20 ± 0.05	49.87	1.50	52.91 ± 0.60
400 °C; 10 °C/min; 60 min	33.78 ± 0.60	26.86 ± 0.14	50.01	1.48	51.40 ± 1.12
500 °C; 1 °C/min; 30 min	31.32 ± 0.25	28.52 ± 0.04	49.25	1.57	51.24 ± 0.71
500 °C; 1 °C/min; 60 min	30.42 ± 0.31	28.67 ± 0.09	48.08	1.58	52.61 ± 0.95
500 °C; 10 °C/min; 30 min	28.81 ± 0.19	27.81 ± 0.06	44.17	1.53	54.08 ± 0.50
500 °C; 10 °C/min; 60 min	28.97 ± 0.36	27.85 ± 0.09	44.47	1.54	55.46 ± 0.22

[a] Higher Heating Value
[b] Energy Yield
[c] Energy Density

Table 5.3: Coefficient of regression between pyrolysis parameters and the yield of bagasse char and pyrolysis liquid based on multivariate analysis

Dependent variable	Independent variable	Estimate	std. error	t-value	$Pr\ (>\|t\|)$	R^2
Char Yield	Intercept	52.883	1.182	44.726	3.10×10^{-18}	0.958
	Temperature	-0.044	0.002	-17.874	$5.37 \times 10^{-12*}$	
	Heating rate	-0.186	0.028	-6.676	$5.33 \times 10^{-6*}$	
	Holding time	-0.003	0.008	-0.306	7.63×10^{-1}	
Liquid Yield	Intercept	38.611	2.112	18.280	3.81×10^{-12}	0.821
	Temperature	0.026	0.004	5.861	$2.41 \times 10^{-5*}$	
	Heating rate	0.309	0.050	6.242	$1.18 \times 10^{-5*}$	
	Holding time	0.005	0.015	0.314	7.58×10^{-1}	

* Correlation is significant at confidence level 0.05.

5.3 Effect of pyrolysis parameters on the char properties

The proximate and ultimate analysis of bagasse char from different pyrolysis conditions are presented in Tab. 5.4, followed by their coefficient of regression illustrated in Tab. 5.5. Temperature and heating rate significantly influenced the content of volatile, ash, fixed carbon, elemental carbon, and HHV, while holding time contributes to the volatile matter content only. After being pyrolyzed, bagasse char has a volatile matter of 24.31 %–25.80 % at 400 °C, and 13.01 %–16.43 % at 500 °C. Previous studies confirmed that the volatile matter is affected by the pyrolysis temperature (Katyal et al., 2003; Crombie et al., 2013), as the decrease of volatile matter follows the increase of temperature. The reduction of volatile content between the two temperatures occurs due to the cellulose and lignin decomposition. As the volatile released, fixed carbon and ash content percentage increased. The highest fixed carbon was observed at 68.50 %–73.01 %, while the ash content was found to be higher than 10 %. The ash content in the present study varied from 10.79 %–15.50 %; however, it is still lower than the study conducted by Varma and Mondal (2017), who found it to be 16.25 %. High ash recoveries presented in Tab. 5.4 also showed that ash is retained within the char and attractive for its application as soil amendments (Ghysels et al., 2019).

Higher temperature and lower heating rate also favor the higher carbon content and higher HHV. At 500 °C, lower heating rate resulted in higher carbon content (73.53 %–75.70 %) than those obtained at the higher heating rate (71.95 %–72.90 %). HHV produced from the sugarcane bagasse pyrolysis also increases from 18.14 MJ/kg to 28.67 MJ/kg at the higher temperature and lower heating rate. The char has a higher carbon content and a lower oxygen content compared to its raw material. The O/C and H/C molar ratio of char were lower than sugarcane bagasse due to the loss of H and O during pyrolysis. The O/C and H/C molar ratio of sugarcane bagasse was found as 0.74 and 1.43, respectively.

For energy application, low volatile content, low ash content, high fixed carbon, high carbon content, high H/C, low O/C, and high HHV should be preferred. Meanwhile, high ash recovery and high stable carbon contents (from fixed carbon) can be a good indicator of soil amendments. Generally speaking, bagasse char obtained at 500 °C, and a heating rate of 1 °C/min or 10 °C/min has met all the criteria. Indeed, a lower heating rate promotes higher char yield and higher HHV. However, in the present study, the HHV of char from the pyrolysis of 500 °C and the heating rate of 10 °C/min (27.85 MJ kg) is already higher or comparable to the HHV of char produced

on the same temperature and heating rate $< 10\,°C/min$ by other studies (Mesa-Perez et al., 2005; Carrier et al., 2011). Carrier et al. (2011) found that the optimum HHV of bagasse slow pyrolysis (27.67 MJ/kg) was obtained at $T > 450\,°C$ and a heating rate lower than $8\,°C/min$. As a heating rate of $10\,°C/min$ also promotes higher pyrolysis liquid yield, it is reasonable to choose a higher temperature and higher heating rate in this study to co-produce the bagasse char and bagasse pyrolysis liquid. Since the temperature was a dominant factor influencing the char properties, char yield, and liquid yield, we evaluated the two types of pyrolysis liquid produced as a candidate for anti-fungal and anti-termite agents.

Table 5.4: Proximate and ultimate analysis of bagasse char at different pyrolysis conditions

Process conditions	Proximate analysis (wt.%)			AR[c] (wt.%)	Ultimate analysis (wt.%)				O/C	H/C
	VM[a]	Ash	FC[b]		C	H	N	O		
400 °C; 1 °C/min; 30 min	25.67 ±1.15	10.79 ±0.12	63.54	86.63	69.50 ±0.14	3.81 ±0.03	0.5 ±0.03	26.14	0.28	0.66
400 °C; 1 °C/min; 60 min	24.31 ±0.58	11.72 ±0.78	63.97	88.81	70.23 ±0.90	3.66 ±0.04	0.58 ±0.05	25.53	0.27	0.63
400 °C; 10 °C/min; 30 min	25.80 ±0.06	12.81 ±0.26	61.39	95.86	70.35 ±0.07	3.32 ±0.00	0.65 ±0.02	25.68	0.27	0.57
400 °C; 10 °C/min; 60 min	24.56 ±0.54	13.1 ±0.51	62.29	97.91	69.40 ±0.42	3.46 ±0.07	0.62 ±0.01	26.52	0.29	0.60
500 °C; 1 °C/min; 30 min	14.33 ±0.21	13.00 ±0.85	72.67	87.80	73.53 ±0.40	3.07 ±0.00	0.53 ±0.04	22.87	0.23	0.50
500 °C; 1 °C/min; 60 min	13.01 ±0.31	13.99 ±0.49	73.01	94.99	75.70 ±0.00	3.08 ±0.04	0.61 ±0.00	20.61	0.20	0.49
500 °C; 10 °C/min; 30 min	16.01 ±0.36	15.50 ±0.79	68.50	98.58	72.90 ±0.57	2.74 ±0.03	0.62 ±0.03	23.74	0.24	0.45
500 °C; 10 °C/min; 60 min	16.43 ±0.06	13.07 ±0.57	70.50	84.52	71.95 ±0.78	2.85 ±0.01	0.57 ±0.06	24.63	0.26	0.48

[a] Volatile Matter
[b] Fixed Carbon
[c] Ash Recovery

Table 5.5: Coefficient of regression between pyrolysis parameters and the quality of char based on multivariate analysis

Dependent variable	Independent variable	Estimate	std. error	t-value	$Pr\ (>\|t\|)$	R^2
Volatile matter content	Intercept	67.055	1.918	34.953	2.83×10^{-17}	0.976
	Temperature	-0.103	0.004	-25.892	$4.24 \times 10^{-15*}$	
	Heating rate	0.139	0.044	3.143	$5.93 \times 10^{-3*}$	
	Holding time	-0.036	0.013	-2.711	$1.48 \times 10^{-2*}$	
Ash content	Intercept	3.464	1.876	1.847	8.04×10^{-2}	0.657
	Temperature	0.019	0.004	4.973	$8.44 \times 10^{-5*}$	
	Heating rate	0.156	0.043	3.6428	$1.73 \times 10^{-3*}$	
	Holding time	0.003	0.013	0.260	7.98×10^{-1}	
Carbon content	Intercept	55.417	2.379	23.296	3.42×10^{-13}	0.806
	Temperature	0.037	0.005	7.677	$1.43 \times 10^{-6*}$	
	Heating rate	-0.111	0.053	-2.089	$5.42 \times 10^{-2*}$	
	Holding time	0.008	0.016	0.496	6.27×10^{-1}	
Higher Heating Value	Intercept	23.883	0.350	68.144	3.96×10^{-26}	0.935
	Temperature	0.010	0,001	13,870	$4.83 \times 10^{-12*}$	
	Heating rate	-0,065	0,008	-8,463	$3.30 \times 10^{-8*}$	
	Holding time	-0,002	0,002	-0,967	3.44×10^{-1}	

* Correlation is significant at confidence level 0.05.

5.4 Characteristics of pyrolysis liquid

Pyrolysis liquid was obtained in a dark brown color with a pungent, smoky odor. Previously, Demirbas (2007) has stated that the pyrolysis liquid consisted of two distinct parts: an aqueous phase consisting of a mixture of light oxygenates; and tar, a non-aqueous phase containing insoluble organics of high molecular weight. At the time of the experiment, the liquid obtained was not entirely in a separated phase (the soluble tar was presented and mixed with the aqueous phase). The heavy tar was presented, and it can be separated from the aqueous phase by the decantation. However, not all the heavy tar was successfully recovered at the end of pyrolysis experiments. Some of them were trapped in the condensation system; however, this amount is not significant (1 %). To avoid ambiguity, the term of pyrolysis liquid used in this study represents the total condensed liquid obtained from the pyrolysis experiments (crude pyrolysis liquid).

Fig. 5.2 demonstrates the FTIR spectra, representing the functional group of the pyrolysis liquid. According to the spectra obtained, pyrolysis liquid was confirmed to have various chemical components, including oxygenated compounds, such as carboxylic acids, alcohols, phenols, aldehydes and ketones, and other chemical components such as alkanes, alkenes, and aromatics. The spectra of pyrolysis liquid obtained from the slow pyrolysis at the temperature of 400 °C and 500 °C were similar. The peak between 3400 cm^{-1} and 3200 cm^{-1} presents the O–H stretching vibration corresponding to alcohols and phenols' content. The weak peaks observed between 3000 cm^{-1} and 2800 cm^{-1} (C–H stretching) imply the presence of alkanes. The C=O stretching vibrations between 1780 cm^{-1} and 1650 cm^{-1} indicate the presence of ketones, aldehydes, and carboxylic acids (Demiral et al., 2008; Islam et al., 2010). Peaks at 1513 cm^{-1} (C=C stretching vibration) correspond to the presence of alkenes and aromatics. Peaks at around 1365 cm^{-1} signify the presence of alkane due to the C–H vibrations (Temiz et al., 2010). The region between 1300 cm^{-1} and 900 cm^{-1} (C–O stretching and O–H deformation vibration) was reported to correspond to the presence of alcohols, carboxylic acids, ethers, esters, and phenols, while for the region between 900 cm^{-1} and 700 cm^{-1} (C–H bending) corresponds to the existence of aromatic compounds. The spectra obtained were in accordance with the study carried out by Varma and Mondal (2017).

The main organic compounds present in the organic fraction of pyrolysis liquid are given in Tab. 5.6. Chemical analysis using a GC–MS allowed the quantification of 56 chemical compounds, where the total organic contents quantified were 29.63 % and 25.63 % for pyrolysis liquid produced at 400 °C and 500 °C, respectively. Indeed, the pyrolysis liquid contained some

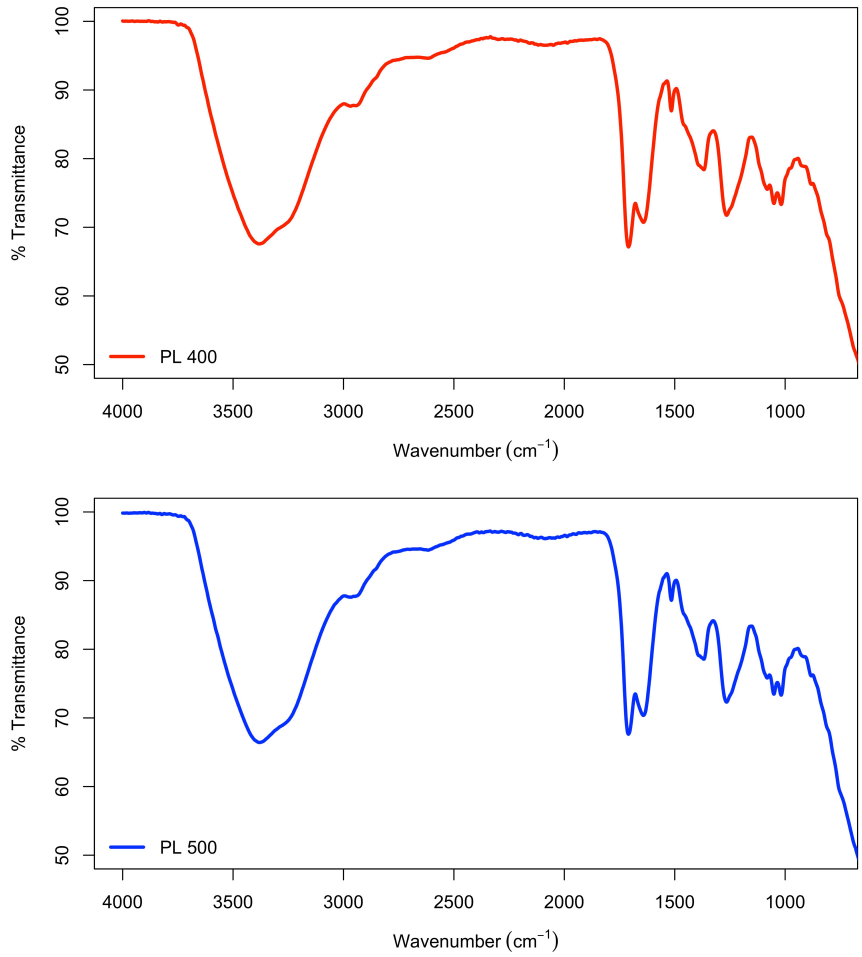

Figure 5.2: FTIR spectra of pyrolysis liquid (PL) at the temperature of 400 °C and 500 °C

non-volatile compounds that are not GC-eluted, in which the non-quantified fraction represented 28 %–32 % of the liquid products. The said compounds could not determined in this study.

The chemical composition of the pyrolysis liquid is influenced by the content of cellulose, hemicellulose, and lignin in biomass. The holocellulose generated furans and carbohydrates, whereas the lignin led to the formation of phenolic compounds (Demirbas, 2007). According to the analysis, pyrolysis liquid consisted of carboxylic acids, alcohols, aldehydes, ketones, furans, and anhydrosugars, whereas the acetic acid, glycolaldehyde, 1-hydroxy-2-propanone, methanol, formic acid, and levoglucosan were the principal compounds. Excluding the water, acetic acid was the significant compound com-

Table 5.6: Main organic compound (%) presented in the organic fraction of pyrolysis liquid

Compound name	Pyrolysis liquid (%)		Classification
	400 °C	500 °C	
Acetic acid	8.48	7.22	Acid
Glycolaldehyde	3.35	3.18	Aldehyde
1-hydroxy-2-propanone	3.32	2.91	Ketone
Methanol	2.28	1.90	Alcohol
Levoglucosan	1.79	1.75	Sugar
Formic acid	1.70	1.60	Acid
Furfural	1.19	0.45	Furan
1-acetyloxy-2-propanone	0.87	0.78	Ketone
2-butanone,1-hydroxy-	0.82	0.73	Ketone
2-hydroxy-2-cyclopenten-1-one	0.66	0.61	Ketone
DGP*	0.63	0.52	Sugar
Acetaldehyde	0.48	0.39	Aldehyde
3-methyl-1,2-cyclopentanedione	0.41	0.38	Ketone
Propionic acid	0.37	0.31	Acid
Formaldehyde	0.33	0.26	Aldehyde
2,6-dimethoxyphenol	0.30	0.27	Guaiacol
2-methoxy-4-vinylphenol	0.24	0.18	Guaiacol
Phenol-2-methoxy	0.22	0.20	Guaiacol
Phenol	0.21	0.22	Phenol
Phenol-2-methoxy-4-methyl	0.16	0.14	Guaiacol
Phenol-4-ethyl-2-methoxy	0.15	0.12	Guaiacol
Phenol-3-methyl+Phenol-4-methyl	0.11	0.11	Phenol

* DGP = 1,4:3,6-dianhydro-α-D-glucopyranose.

posing the pyrolysis liquid, presenting 7.22 %–8.48 % of the liquid. Sugarcane bagasse is reported to be high in the content of xylose (15.5 %–28.9 %) (Bezerra and Ragauskas, 2016), which contribute to the formation of acetic acid by the elimination of acetyl groups from the xylose unit (Demirbas, 2007; Temiz et al., 2013a). Demirbas (2007) studied the mechanism of the pyrolysis reaction of biomass. For example, methanol resulted from the methoxyl groups of uronic acid, whereas furfural came from xylose dehydration. Additionally, the degradation of xylan produced water, methanol, 1-hydroxy-2-propanone,1-hydroxy-2-butanone, 2-furfuraldehyde, acetic, propionic, and formic acid.

There is only a slight variation of the chemical compounds of pyrolysis liquid produced at the temperature 400 °C and 500 °C. However, higher or-

ganic content was found for the pyrolysis liquid produced at 400 °C, which also possessed a higher content of furfural (1.19 %). An increase in pyrolysis temperature contributed to the increase of phenolic compounds and decrease to the organic acid content (Kartal et al., 2004). Further, no polycyclic aromatic hydrocarbon compounds (PAHs) were found, or they were insignificant (less than 1 ppm). The PAHs content must be taken carefully into account because of their toxicity towards the environment and human health (Guo et al., 2011). In contrast to creosote, pyrolysis liquid presented in this study could be considered to be more environmentally advantageous. According to the European standard EN 13991 (2004) the maximum content of benzo(a)pyrene in creosote class B is 50 mg/kg. Cordella et al. (2012) stated that PAHs are formed with a higher proportion at a higher temperature (650 °C, 100 °C/min). Additionally, phenol formation increases as the continuous secondary degradation occur with the rising temperature (Demirbas, 2007).

Pyrolysis liquid has 42.34 ± 0.24 % and 42.30 ± 0.14 % of water content at 400 °C and 500 °C temperatures, respectively. Temiz et al. (2013a) reported that bio-oil made from giant cane has a water content of 34 %. Variation of water content is affected by the moisture content of biomass and dehydration reaction during pyrolysis. In addition, the condenser temperature, which is maintained at 0 °C during the pyrolysis process also likely to contribute to the high levels of water, acids, alcohol, and ketones (Li et al., 2020). The pH was recorded at 2, in which the acidic characteristic was due to the presence of the organic acid, aldehydes, and phenols (Varma and Mondal, 2017).

Chapter 6

Conclusion

Slow pyrolysis is an attractive method for converting the unstable biomass which contains high volatile matter, such as sugarcane bagasse, to a stable energy-rich product, even with limited yield but results in the favorable calorific value improvement. Moreover, the recovery of liquid products results in high mass yield. Pyrolysis temperature and heating rate had a significant influence on the char properties and the yield of char and pyrolysis liquid, where a high-quality char and high yield of pyrolysis liquid can be obtained at a temperature of 500 °C and a heating rate of 10 °C/min. The yield of char and pyrolysis liquid was 28.97 % and 55.46 %, respectively.

In this study, apart from its utilization for fuel due to the high carbon content (70.50 %) and HHV (27.85 MJ/kg), bagasse char is also potential to be used as soil amendments, as it has a high ash recovery (up to 98 %). For the pyrolysis liquid, water, acetic acid, glycolaldehyde, 1-hydroxy-2-propanone, methanol, formic acid, levoglucosan, furfural, followed by some phenol compounds and guaiacol derivatives, were found as the principal compounds. No polycyclic aromatic hydrocarbon compounds (PAHs) were found in the GC-MS analysis, or they were insignificant (less than 1 ppm). Due to its various chemicals, pyrolysis liquid seems to be potentially useful for wood protection agents.

Part III

Pyrolysis liquid performances for wood protection

Chapter 7

Introduction

This part presents the potential application of pyrolysis liquid for wood protection. As has been previously reported, the utilization of pyrolysis liquid is already of interest in many areas such as biocide, insecticide, fungicide, plant growth stimulant, and source of valuable chemicals (Tiilikkala et al., 2010; Pimenta et al., 2018; Mathew and Zakaria, 2015). Due to its large composition of bioactive chemicals, such as organic acids, phenols, ketones, aldehydes, furans, and guaiacols, pyrolysis liquid was presumed to protect the wood against fungi and termite (Temiz et al., 2013a). Barbero-López et al. (2019) reported that pyrolysis distillates from spruce bark, birch bark, and fiber hemp at 275 °C–350 °C temperatures provide inhibition to the growth of wood-decaying fungi. Pyrolysis liquid made from rubberwood and bamboo at 400 °C showed better anti-fungal activity towards white-rot, brown-rot, and sapstain fungi (Theapparat et al., 2015). Oramahi et al. (2018) also studied the pyrolysis liquid from oil palm trunk at a 350 °C as an anti-termite.

In this study, we used the crude pyrolysis liquid as it is obtained from the pyrolysis experiments. Before applying it to wood, pyrolysis liquid was first tested to determine whether it has activity against fungi and termites in the Petri-dish tests. The pyrolysis liquid used in the screening test was obtained from the pyrolysis process at a 400 °C and 500 °C temperatures, 10 °C/min of heating rate, and holding time of 60 min. For the termite test, a quick method of measuring the remained paper area consumed by termites was developed. The paper area loss measurement was chosen instead of the evaluation based on weight loss, considering the pyrolysis liquid volatility. Besides, Grace et al. (1986) stated that filter paper is susceptible to the mass changes caused by absorbing or releasing moisture from and towards its environment, thus can affect the accuracy of the measurement. Therefore, we developed an alternative and robust measurement method by calculating the paper's remaining area.

The wood treatment test was then continued by applying the pyrolysis liquid produced at a temperature of 500 °C, a heating rate of 10 °C/min, and a holding time of 60 min. As the preliminary test, we were interested in evaluating the effect of different drying temperatures on the treated samples, as reported in some previous studies (Tab. 7.1). The effect of leaching was

also investigated, along with tests on chemical analysis and the effect of leachate products on fungal growth. Lastly, the samples after leaching were tested for their efficacy towards *Reticulitermes flavipes* termites.

Table 7.1: Various drying temperatures used for wood treated with pyrolysis liquid products reported in different studies

Pyrolysis type	Temperature (°C)	Time	Biomass	References
Slow	40	3 days	Macadamia nutshells	Kartal et al. (2011)
Slow	65	24 hours	Giant cane	Temiz et al. (2013a)
Slow	Ambient	3 weeks	Pineapple waste	Yahayu et al. (2017)
Fast	60	n/a	Eucalyptus fine	Lourençon et al. (2016)
Fast	Air drying	24 hours	Pinewood	Robinson et al. (2011)

After determining the desirable drying temperatures for wood samples, the impregnation process was done using pyrolysis liquid at different concentrations. In this step, the efficacy and the threshold of the pyrolysis liquid's concentration towards decay fungi and termites were evaluated. The effect of leaching and evaporation were also investigated.

Chapter 8

Materials and Methods

8.1 Anti-fungal and anti-termite test

8.1.1 Fungal inhibition test

Pyrolysis liquid produced at a temperature of 400 °C and 500 °C, a heating rate of 10 °C/min, and a holding time of 60 min were tested for its anti-fungal activity. The fungal inhibition test was evaluated using two types of wood-decaying fungi: *Coniophora puteana* (brown-rot, strain BAM Ebw. 15) and *Trametes versicolor* (white-rot, strain CTB 863 A) in the malt-agar medium. The medium was prepared by mixing 40 g of malt (Quaron) and 20 g of agar (Biomerieux) in 1 L of deionized water (water quality 3) and sterilized using an autoclave at 121 °C for 20 min. To determine the Minimum Inhibitory Concentration (MIC), various concentration (v/v) of pyrolysis liquid (0.05 %, 0.10 %, 0.15 %, 0.20 %, and 0.25 %) were tested by diluting them directly in the malt agar solution. Right after the malt agar solution (40 ml) was distributed into Petri-dishes (diameter of 9 cm), the pyrolysis liquid solution was introduced using a micropipette. Afterward, the mixture was stirred until it homogenized and left until it solidified. Four replicates were used for each treatment. A mycelium piece from a growing fungal culture (diameter of 5 mm) was placed centrally, and then the medium was incubated at (22 ± 2) °C and (70 ± 5) % relative humidity (RH). The inhibition rate (I_r) was determined by comparing the diameter of fungal growth on the treated medium with the control (Petri-dishes containing only malt-agar medium), following the method described by Kartal et al. (2011) (Eq. 8.1).

$$I_r(\%) = 1 - \frac{D_t}{D_c} \tag{8.1}$$

where D_c is the colony diameter of mycelium from the control Petri-dishes (mm), and D_t is the colony diameter (mm) of mycelium from tested the Petri-dishes containing the pyrolysis liquid.

8.1.2 Termites non-choice test/toxic effect

Termites non-choice test was evaluated using the pyrolysis liquid produced at the temperature of 400 °C and 500 °C, a heating rate of 10 °C/min, and a holding time of 60 min. The non-choice test was conducted against *Reticulitermes flavipes* (ex. *santonensis*) termites using a Joseph filter paper (grammage 25 g/m^3) made of pure cellulose (diameter of 42.5 mm). Pyrolysis liquid was diluted in ethanol (Honeywell) (v/v) at a 5 % and 10 % concentration and treated to the filter paper by immersing them for 60 s. Two control were also prepared by soaking the filter paper in deionized water and ethanol, separately. Six replicates were performed for each treatment. Prior to the test, all of the treated filter papers were air-dried for at least 10 min or 20 min for paper treated with water.

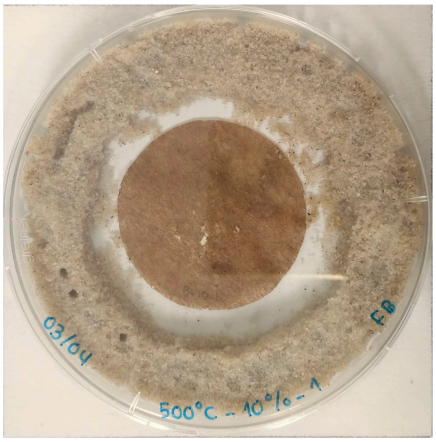

Figure 8.1: Termites test device for the choice test using one Joseph filter paper (diameter of Petri-dish = 9 cm)

A 9-cm diameter of Petri dish was filled with approximately 30–40 g of the wet Fontainebleau sand (4 vol. of sand/1 vol. of deionized water. The Joseph papers were placed on the plastic mesh to avoid water saturation. The test device is illustrated in Fig. 8.1. Then, a total of 20 termite workers were introduced in each petri dish and put in a dark climatic chamber at 27 °C, RH >75 %, for 4 weeks, watered and observed regularly. The mortality rate of termites (M_r) (Eq. 8.2) and the paper area loss were determined. A quick method of measuring the remained paper area consumed by termites was developed and described further in the subsection 8.1.4.

$$M_r(\%) = \frac{n}{20} \times 100 \tag{8.2}$$

where n is the number of dead termites, and 20 is the number of initial termites added in the test.

8.1.3 Termites choice test/repellent effect

Termites choice test was evaluated using the pyrolysis liquid produced at the temperature of 400 °C and 500 °C, a heating rate of 10 °C/min, and a holding time of 60 min. Two sets of Joseph filter paper (grammage 25 g/m^3) made of pure cellulose (diameter of 42.5 mm) were used to evaluate the repellent effect of pyrolysis liquid toward *R. flavipes*. Each paper was treated with only ethanol or pyrolysis liquid diluted in ethanol (Honeywell) (v/v) at a concentration of 5 %, 10 %, and 20 %. Meanwhile, another was set-up as control (treated with deionized water). The control and treated paper were placed inside a 140-mm diameter Petri-dish, which were separated approximately 15 mm apart (Fig. 8.2). Then, a total amount of 20 termites workers were introduced in each Petri-dish.

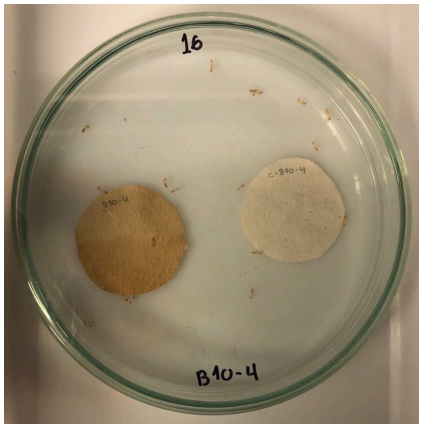

Figure 8.2: Termites test device for the repellency test using two Joseph filter papers (diameter of Petri-dish = 14 cm)

The number of termites workers that made contact with paper were counted every 5 min in a 60 min observation (n = 12 counts), following the experimental work described by Oramahi and Yoshimura (2013). The mortality of termites (Eq. 8.2) was also determined at the end of the test. Four replicates were performed for each treatment.

8.1.4 Method development for paper area measurement

8.1.4.1 Image analysis using image segmentation and k-means clustering

Following the experimental work described in the subsection 8.1.2, the total remaining paper area consumed by termites were measured through *k-means* clustering method that was built into the *Scikit-Learn*, a machine learning package written in Python, an open-source general programming language (Van Rossum and Drake Jr, 1995; Pedregosa et al., 2011). This technique is one of the widely used clustering algorithms intended to distribute n objects into k number of clusters with a central point, also known as the mean, nearest to all of the other data in that cluster.

The principal algorithm of *k-means* clustering can be written as:

$$\phi = \Sigma_{j=1}^{k} \Sigma_{i=1}^{n} ||x_i(j) - c_j||^2 \tag{8.3}$$

where ϕ is the total of intra-cluster variance, which would become the objective function, k is the number of clusters requested, n is the number of data points, $x_i(j)$ is the data point i, assumed to be in one of the k clusters (thus, it is in cluster j), and c_j is the centroid for cluster j, or the varied parameter of the function. The aim here is to minimize the ϕ value until the c_j points do not have to be changed anymore.

The algorithm consisted of the following principal steps:

1. determine k number of initial centroids, possibly where $min(x_i) < c_j < max(x_i)$,
2. calculate the euclidean distance of each data point to both centroids. Assign each data points to the centroid closest to them,
3. calculate the true centroid of true mean of all objects in each cluster,
4. if the true mean of each cluster is not equal to the initially guessed centroids, use the new true mean as new centroids, and repeat the steps above using these new centroids,
5. do the steps 2–4 continuously until the new true centroids equal to the previous ones, which indicate that the convergence has been obtained.

The automated segmentation protocol and paper area measurement was outlined in Fig. 8.3 and described below. Firstly, we put the remaining filter paper, usually having the color white or grey, on a clean surface with color in contrast to the filter paper. Some possible surface or background color

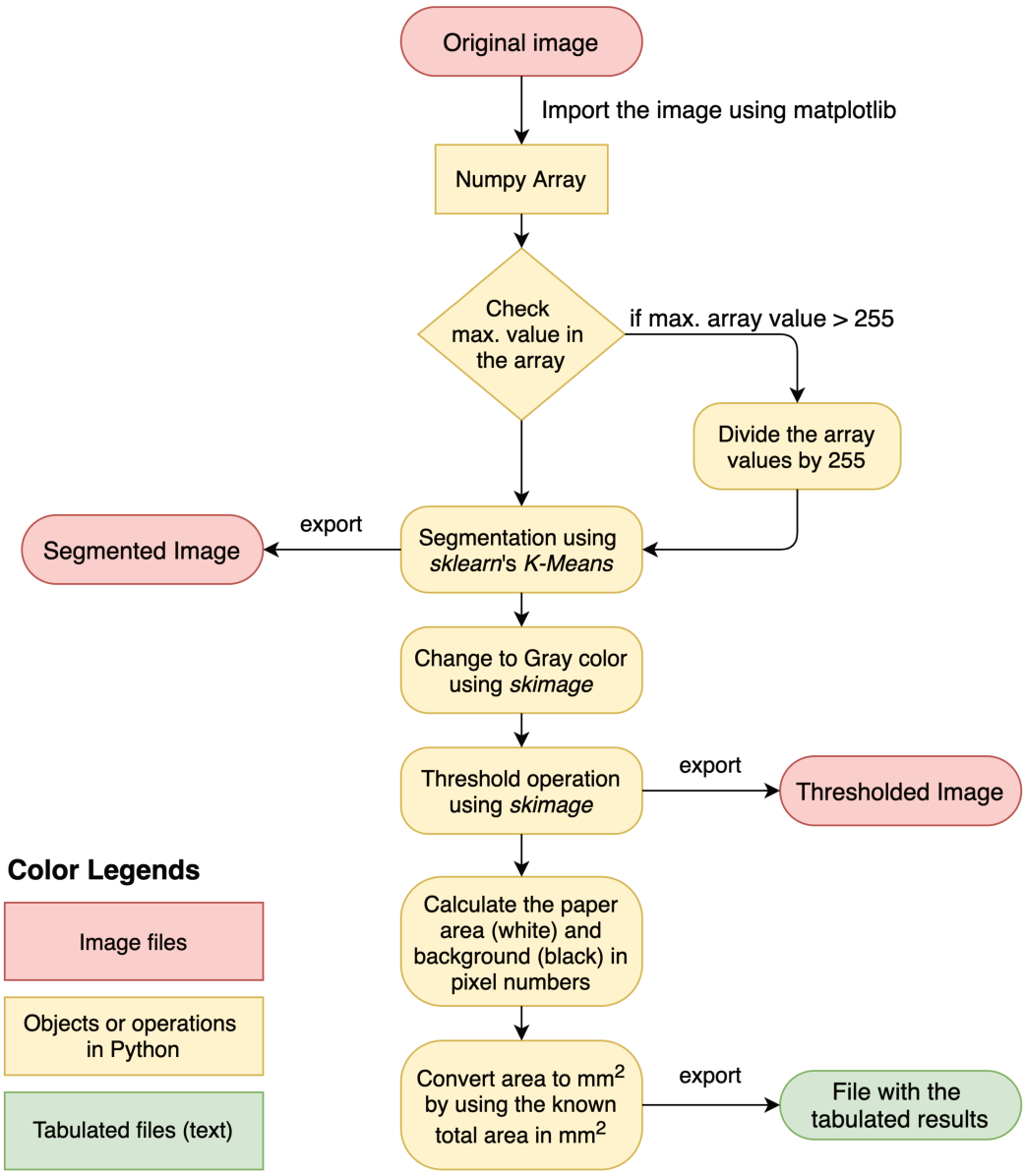

Figure 8.3: Workflow of the image processing using Python from the original image to the exported results

choices would be red, blue, green, or even black. In our example here, we used the color red. Then we took the pictures of the paper using a known and uniform scale. This would be the image acquisition step, and it would produce original images, mentioned in Fig. 8.3.

Next, we started the program by running it, similar to launching a Python script. The code was written in two versions: with GUI (graphical user interface), where the user will be presented with dialog windows asking, consecutively: (1) to select the repository or folder containing the original, acquired image, (2) to select the reference image, which means the filter paper photo which was not consumed by termite at all, (3) to select the folder where the classified images would be saved, and (4) the name of the output file, written in comma-separated values (CSV) format. A degree of flexibility could be experienced here. In the non-GUI version, the code will, by default, seek the following:

- folder containing acquired image: *"Data/"*, with images having *".tif"* extension,
- reference picture: image file named *"ref.tif"*,
- output folder to save the classified images with the name: *"Output/"*
- output CSV file named *"Results.csv"*

For the non-GUI version, the choices of name and extension for each of the parameters above are also modifiable, but manually by editing the *.py* script file.

At the start of program's running, the code would import the original image as a *numpy* array. This is possible by reading each pixel's color as the array's values and the x and y coordinates of each pixel as the row and column index numbers. The next step is checking if the picture is in black and white or not. If it is not yet in black and white, the maximum values of the array would be > 255, and in that condition, we divide the values of each pixel with 255 to lower the euclidean distances of each pixel. This would be useful to accelerate the algorithm.

Afterward, the segmentation would take place using *k-means* clustering method. Because the objective here was classifying the image into two categories: the filter paper and the background, we put the value of $k = 2$. Each pixel's colors would be categorized into one of those two, and in the end, each pixel's values would be replaced by the centroids of each category. The last step would be threshold operation, which would convert each pixel's value into white (0) for filter paper and black (1) for the background. Overall,

these three operations–importing the image, clustering or segmentation, and threshold–could be visualized in Fig. 8.4.

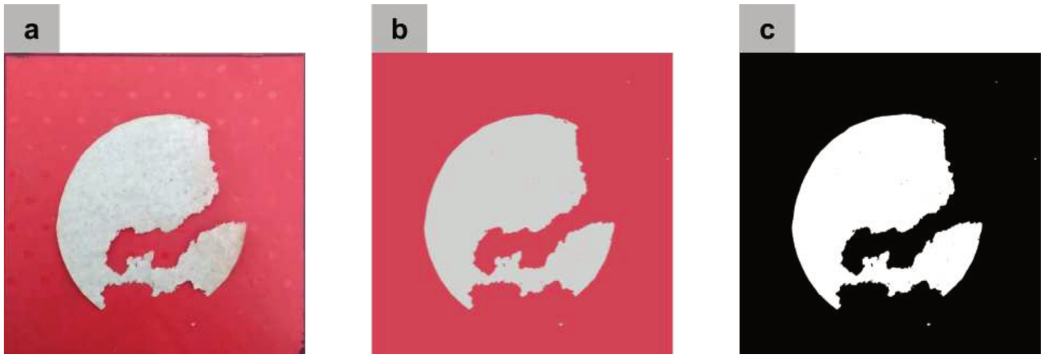

Figure 8.4: Steps of image processing, from original picture (a) to segmented (b) and thresholded image (c)

The last step is calculating the area of the filter paper. This was done by counting the number of white pixels (N_p) and converting them to mm unit. This is where knowing and having a uniform scale during the image acquisition is important. For example, if we acquired the filter paper with a red surface with the dimensions of 60 mm × 60 mm as 1600 × 1600 pixels, that means we have a scale $r_p = 26.67$ pixel per mm. Thus, the area of the remaining filter paper could simply be calculated by (8.4):

$$A_p = N_p / r_p \tag{8.4}$$

where A_p is the area of the remaining filter paper in mm^2. Further, we could calculate the percentage of remaining paper area by simply dividing the A_p with the original paper area (A_o). In our case, it would be 1466.25 mm^2.

The output of this program would be the classified image (in PNG format) and a comma-separated value file with the area of the remaining filter paper from each original image.

Following the image analysis, by taking the value of the remaining paper area and the reference paper area (the area of filter paper in pristine, original condition), the mean paper loss area (A_{pl}) was obtained as follows (Eq. 8.5):

$$A_{pl} = \frac{A_{\text{ref}} - A_p}{A_{\text{ref}}} \times 100\,\%, \tag{8.5}$$

where A_p is the remaining filter paper area obtained through image analysis.

8.1.4.2 Memory analysis

The final step is the memory and time analysis of our code. To do this, we prepared the version of the program without the GUI and used it to do image processing on 3, 5, 7, 9, 11, 13, and 15 acquired images, consecutively. During each of our program's running process on these images, the computer memory used was recorded using *mprof*, a memory profiling package built-in Python. The memory was measured once per 0.1 s. This would give us two parameters: the total running time (t_{tot}) of the program, the evolution of memory over time, and the maximum amount of memory (M_{max}) used by the program for each total number of the image (N_{image}).

The t_{tot} and M_{max} parameters were then compared towards the N_{image} using simple linear regression analysis to see if there is any clear relationships between the three parameters. We hypothesized a linear relationship with the N_{image} as the independent parameter, such as the normal condition for the image analysis program. This could give us a clear visualization and information on the amount of computer memory needed to use this program and the total number of images that could be acceptably processed at one time.

8.2 Wood treatment

8.2.1 Wood samples preparation

Conditioned portion $(20 \pm 2)\,^{\circ}\mathrm{C}$ and $(65 \pm 5)\,\%$ of beech wood (*Fagus sylvatica*) and pine sapwood (*Pinus sylvestris*), were cut into a dimension of $(2.5 \times 1.5 \times 0.5)$ cm (L × R × T). Prior to impregnation, the samples were oven-dried at 103 °C until they reached their constant mass.

8.2.2 Wood impregnation and drying procedures

8.2.2.1 Impregnation procedure

Oven-dried beech wood samples (six replicates per treatment) were impregnated with the crude pyrolysis liquid (without dilution) by a single vacuum pressure impregnation. In a beaker, wood samples, together with the pyrolysis liquid, were put into a desiccator. The samples were kept immersed during the treatment (30 mbar vacuum for 20 min, followed by 2 h at ambient pressure). The samples were then removed and blotted with tissue paper to remove the excess of the product from the wood surface. The retention (R in $\mathrm{kg\,m^{-3}}$) and the impregnation rate (IR in %) of pyrolysis liquid after

impregnation was determined with the following formula (Eq. 8.6 and Eq. 8.7):

$$R(\mathrm{kg\,m^{-3}}) = \frac{M_w - M_o}{V} \tag{8.6}$$

$$IR(\%) = \frac{M_w - M_o}{M_o} \times 100 \tag{8.7}$$

where M_w is the wet weight of samples after impregnation (kg), M_o is the initial dry weight samples (anhydrous state) before impregnation (kg), and V is the volume of samples at conditioned state before impregnation ($\mathrm{m^3}$).

For all the following experiments, the same impregnation procedure was used.

8.2.2.2 Drying procedure and visual observation using a light microscope

Five different drying temperatures were tested: 20 °C, 40 °C, 60 °C, 80 °C, and 103 °C. For ambient temperature, samples were dried for three weeks, for temperature 40 °C samples were dried for one week, and for temperature 60 °C, 80 °C, and 103 °C, samples were dried for 24 h. The weight of the samples after drying was then recorded to determine the weight percent gain (WPG in %) using the following equation (Eq. 8.8):

$$WPG(\%) = \frac{M_d - M_o}{M_o} \times 100 \tag{8.8}$$

where M_d refers to the dry weight of samples after treatment (g), and M_o is the initial dry weight samples (anhydrous state) before treatment (g).

Finally, all the samples were reconditioned at (22 ± 2) °C and (65 ± 5) % relative humidity (RH). The microstructure of treated wood samples was captured using a digital camera Nikon DS Fi1 connected to a light microscope (Olympus BX6) with 100 × enlargement.

8.2.2.3 Impregnation using different concentrations of pyrolysis liquid

For the rest of the impregnation test, the drying temperature for the treated samples was first determined based on the work described above. After obtaining the desirable drying temperature (103 °C), the treatment was continued by impregnating the samples of beech wood and pine wood using different concentration of pyrolysis liquid diluted in ethanol (5 %, 10 %, 15 %, 20 %,

25 %, and 50 % (v/v)). The impregnation procedure remained the same, where twelve replicates were used for each treatment.

8.2.3 FTIR analysis of treated and untreated wood

The untreated and treated beech wood samples from each drying temperature were milled to form a fine and homogenous powder. All samples were then analyzed using a Perkin Elmer Frontier spectrometer equipped with an Attenuated Total Reflection (ATR), as previously described in the subsection 4.3.2. FTIR spectra were obtained at a nominal resolution of 4 cm^{-1} for 4 scans in the range of 4000–650 cm^{-1}. The spectra were treated using RStudio using the package of MALDIquantForeign (Gibb and Strimmer, 2012; R Core Team, 2019).

8.2.4 Leaching procedure

8.2.4.1 Leaching test

The leaching test (Fig. 8.5) was carried out according to the standard NF X 41-568 (2014). Half of the total samples that were impregnated from each treatment were subjected to six successive leaching periods (1 h, 2 h, 4 h, and 8 h, 16 h, and 48 h). The samples were put into a closed container where they were immersed in deionized water (1 vol of wood/5 vol of deionized water). In the first period, the samples were submitted to continuous stirring, and the water was changed/replaced after 1, 2, and 4 h. Afterward, the samples were removed and kept at (20 ± 2) °C and (65 ± 5) % RH for 16 h. The leaching process was then continued to the next periods for 8, 16, and 48 h, with water replacement conducted between each period.

Controls of untreated beech wood (six replicates) were also leached following the same steps. After all the leaching periods completed, all wood samples were re-dried according to their initial drying temperature (ambient, 40 °C, 60 °C, 80 °C, or 103 °C) until reaching their constant mass. The weight percent gain after leaching ($WPGL$ in %) and the leaching rate (LR in %) were calculated using the following equations (Eq. 8.9 and 8.10):

$$WPGL(\%) = \frac{M_l - M_o}{M_o} \times 100 \tag{8.9}$$

$$LR(\%) = \frac{M_d - M_l}{M_d - M_o} \times 100 \tag{8.10}$$

where M_l is the dry weight of samples after leaching (g), M_o is the initial dry weight of samples (anhydrous state) before treatment (g), and M_d is the dry

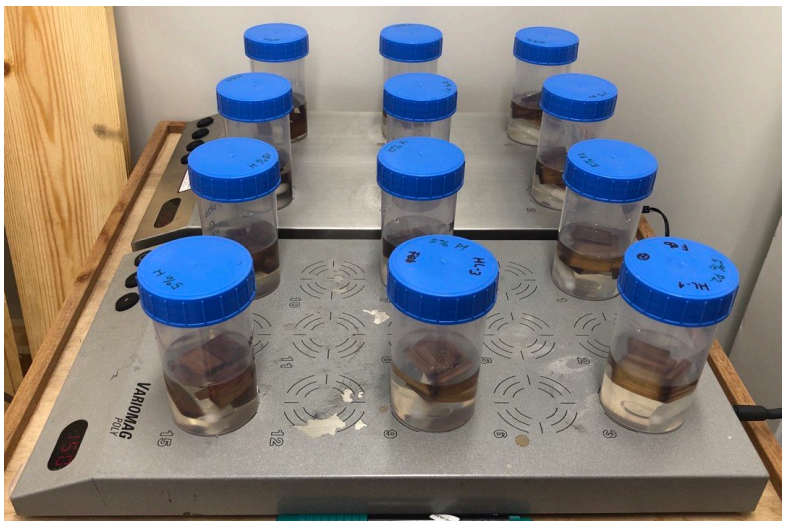

Figure 8.5: Leaching process

weight of samples after treatment (g).

8.2.4.2 Water absorption

Using the same samples dried at different temperatures and their control specimens, the wet weight after each leaching cycle was recorded to obtain the result on the water absorption. This step is conducted to get an idea of pyrolysis liquid's hydrophobic properties as described by Lourençon et al. (2016). The water absorption (WA in %) was calculated according to Eq. 8.11.

$$WA(\%) = \frac{W_a - W_b}{W_b} \times 100 \tag{8.11}$$

where W_a is the wet weight of samples before water replacement (g), and W_b is the wet weight of samples after water replacement (g) in every leaching period.

8.2.5 Evaporation test

Twelve samples of beech treated with 100% pyrolysis liquid and dried at 103 °C were used for the evaporation test. Specimens were subjected to an air flow of 1 m/s at 40 °C for a week. Afterward, the samples were oven-dried at 103 °C, and the percentage of weight loss after evaporation (WLE in %)

was determined (Eq. 8.12).

$$WLE(\%) = \frac{M_d - M_e}{M_d} \times 100 \tag{8.12}$$

where, M_d is the dry weight of samples before evaporation (g), and M_e is the dry weight of wood samples after evaporation (g).

8.3 Analysis of the leachate products

8.3.1 Chemical analysis of the leachate products using GC-MS

The leachate products from different samples after different drying temperatures were collected from the leaching process and analyzed using GC-MS. Detailed on the GC-MS procedure has previously described in subsection 4.3.3.

8.3.2 Fungal inhibition test using leachate products

A simple measurement was conducted to determine whether the leachate solution collected from different samples contains substantial active compounds to inhibit fungi. The malt-agar medium (4 % malt, 2 % agar) was prepared using the collected leachate products from every leaching process. The pH of leachate solution was previously adjusted to 7 by adding NaOH (Sigma-Aldrich) 1 M to allow the solidification of the medium. Two mycelium pieces from a growing fungal culture (diameter of 5 mm) of brown-rot (*Coniophora puteana*, strain BAM Ebw. 15) and white-rot (*Trametes versicolor*, strain CTB 863 A) were placed on the right and left edge of the 9 cm diameter of a petri dish. The medium was then incubated at (22 ± 2) °C and (70 ± 5) % relative humidity (RH). The malt-agar medium prepared in the distilled water was used as control. Four replicates were used for each treatment. The radial growth of mycelium was measured after eleven days of exposure.

8.4 Fungal resistance test and correction factor

8.4.1 Fungal resistance test

The fungal tests (Fig. 8.6) were conducted following a screening test method (Grosse et al., 2019), derived from EN 113-1 (2020) using two types of wood-decaying fungi: a white-rot (*Trametes versicolor*, strain CTB 863 A), and

two brown-rots (*Coniophora puteana*, strain BAM Ebw. 15 and *Rhodonia placenta*, strain FPRL 280). Samples of beech wood were exposed to *T. versicolor*, while the samples of pine sapwood were exposed to *C. puteana* and *R. placenta*, separately. The malt-agar medium was prepared by mixing 40 g of malt (Quaron) and 20 g of agar (Biomerieux) in 1 L of deionized water (water quality 3) and sterilized using an autoclave, at 121 °C for 20 min. The sterile culture medium (65 ml) then poured into a culture flask. Two small pieces of mycelium from a growing fungal culture were inoculated inside the culture flask and incubated for two weeks at (22 ± 2) °C and (70 ± 5) % RH to allow full colonization of the medium by the mycelium.

Figure 8.6: Fungal test device with wood specimens

Wood samples were sterilized in two cycles using an autoclave at 121 °C for 20 min and 10 min, respectively. Three of the treated samples from leaching or non-leaching treatment (six replicates per treatment) and one control (untreated sample) were placed in each culture flask. Virulence controls were also performed using twelve specimens of untreated beech and pine sapwood samples. Incubation was carried out at (22 ± 2) °C and (70 ± 5) % RH. After eight weeks of fungal exposure, the mycelium was carefully brushed and removed from the samples and weighed to evaluate their moisture content (MC in %) (Eq. 8.13). The specimens were finally dried at 103 °C, and the weight loss (WL in %) was determined (Eq. 8.14):

$$MC(\%) = \frac{M_b - M_c}{M_c} \times 100 \tag{8.13}$$

$$WL(\%) = \frac{M_a - M_c}{M_a} \times 100 \tag{8.14}$$

where, M_a is the dry weight of wood samples before being exposed to fungi (g), M_b is the weight of wood samples after being exposed to fungi (before being dried) (g), and M_c is the dry weight of wood samples after being exposed to fungi (g).

For the fungal test results, WL will be corrected with the correction factor as described in EN 113-1 (2020).

8.4.1.1 Fungal correction factor

The same treatment using the same procedure (six replicates per treatment) was conducted without the presence of fungi (only samples put in the malt-agar medium) to determine the correction factor by evaluating the weight loss of the samples at the end of the test. This test was conducted to obtain the samples' weight loss caused by a non-fungal attack (caused by leaching in the culture flask).

8.5 Termites resistance test

Termite resistance test (Fig. 8.7) was evaluated according to a non-choice screening test (Mubarok et al., 2019), derived from the European standard EN 117 (2013). It is the same procedure as described for the filter paper test (see subsection 8.1.2). Each wood sample before and after leaching (three replicates per treatment) was exposed to 50 workers of *R. flavipes* (ex. *santonensis*) termites in a Petri dish with 9 cm of diameter. One nymph and one soldier were also introduced to each Petri dish. Three replicates of untreated beech wood were also set up, as termite virulence controls, following the same procedure. The Petri dishes were then put in a dark climatic chamber at T = 27 °C and RH >75 %. After four weeks, the samples were removed, cleaned, and dried according to their initial drying temperature until reaching their constant mass.

A visual rating, according to the EN 117 (2013), but adjusted to the sample size, was also given to each sample (Tab. 8.1). Finally, the termite survival rate was quantified, and the wood samples' weight loss (WL in %) were determined through the following equation (Eq. 8.15)

$$WL(\%) = \frac{M_a - M_b}{M_a} \times 100 \tag{8.15}$$

where, M_a is the dry weight of wood samples before being exposed to termites (g), and M_b is the dry weight of wood samples after being exposed to termites (g).

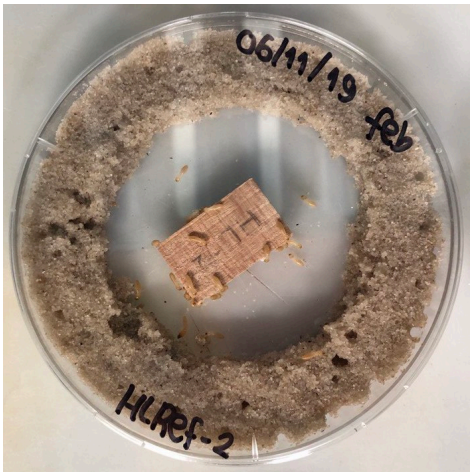

Figure 8.7: Termites test device with wood specimen

Table 8.1: Assessment on the visual rating described in the EN 117 (2013)

Visual rating	Assessment
0	No attack
1	Attempted attack
2	Slight attack
3	Average attack
4	Strong attack

8.6 Data analysis

A t-test analysis was used to compare the data from each specimen and treatment. The data were analyzed in order to see their groupings (the same groups are indicated by the same letter) at a significance level of $p < 0.05$. The analysis was conducted using Microsoft Excel, R, and RStudio (R Core Team, 2019).

Chapter 9

Results and Discussion

9.1 Anti-fungal and anti-termites activity

9.1.1 Effect of pyrolysis liquid in inhibiting fungi

The two types of pyrolysis liquid (400 and 500 °C) revealed their efficacity to inhibit the growth of *C. puteana* and *T. versicolor* (Fig. 9.1) in the Petri-dish test. Fig. 9.2 shows the comparison of the fungal growth between the treated and untreated samples. Pyrolysis liquid produced at 400 °C slightly tends to be more active, delaying the fungal growth at lower concentration, likely because of the relatively higher organic contents. According to the GC-MS analysis (Tab. 5.6), pyrolysis liquid at 400 °C contains higher organic acid and furfural than the pyrolysis liquid obtained at 500 °C. At a 0.15 % concentration, pyrolysis liquid at 400 °C caused a 100 % inhibition of *C. puteana*. Also, to inhibit the fungal growth completely, pyrolysis liquid at a concentration of 0.20 % and 0.25 % was required to suppress the growth of *C. puteana* and *T. versicolor*, respectively. The different effect of pyrolysis liquid towards the fungi was likely correlated to the different metabolic rates or the enzyme released by the fungi (Barbero-López et al., 2019).

It is not easy to compare the results with other studies since the high variability of pyrolysis liquid influenced by pyrolysis parameters and the nature of biomass used. However, mostly, at a concentration of less than 1 %, pyrolysis liquid has an excellent inhibition activity against various types of wood-decaying fungi. Barbero-López et al. (2019) found that the MIC values for the complete inhibition were between 0.5 % and 1 % by using the liquid product from the pyrolysis of tree bark and fiber hemp at the temperature of 275 °C–350 °C. Meanwhile, Kartal et al. (2011) reported the tar oil made from the slow pyrolysis of macadamia nut shells effectively inhibited the brown-rot fungi, white-rot, and sap-staining fungi tested at the concentration of 0.20 %.

The anti-fungal activity of pyrolysis liquid was likely the results of the synergetic effect from the various chemical compounds. The inhibition can also occur probably because of the compounds affect the enzymatic activity of the fungi. Several authors have reported that propionic acid (Barbero-López et al., 2019), acetic acid (Oramahi et al., 2018), and furfural (Pimenta

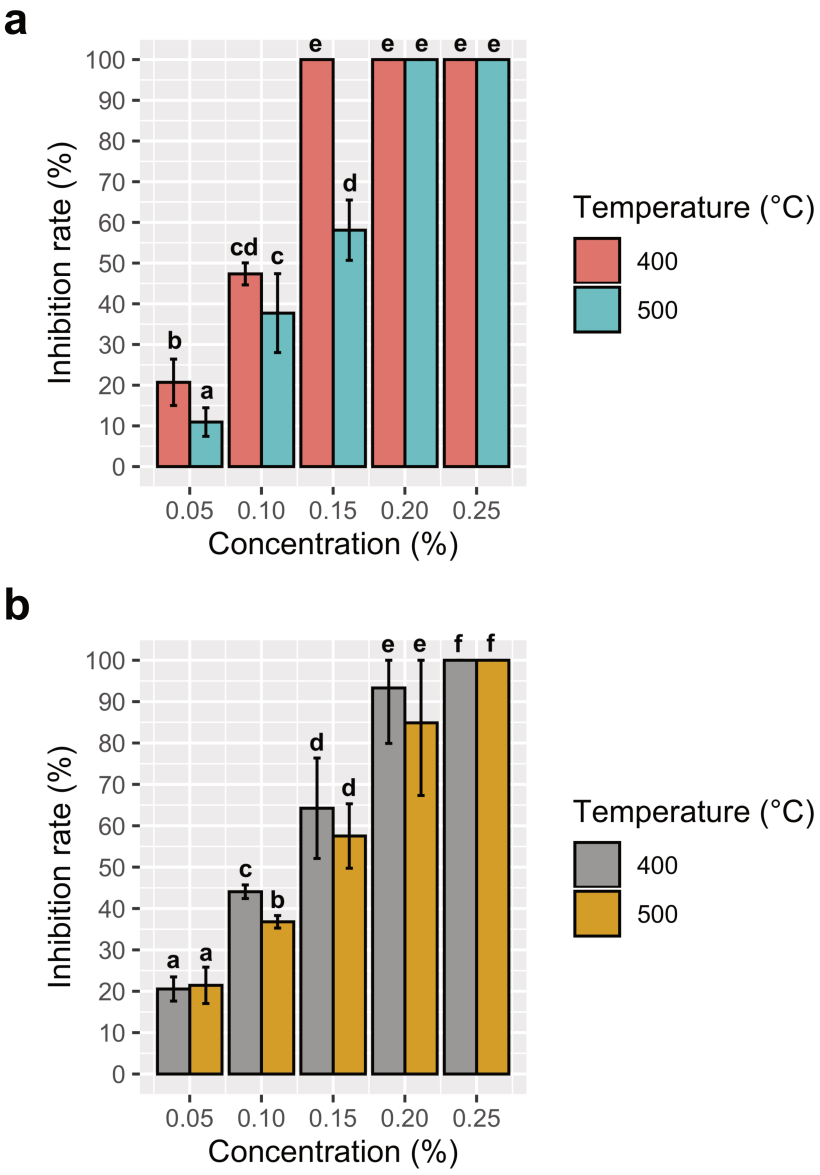

Figure 9.1: Inhibition rate of *C. puteana* (a) and *T.versicolor* (b) at different concentrations (bar followed by the same letter are not significantly different)

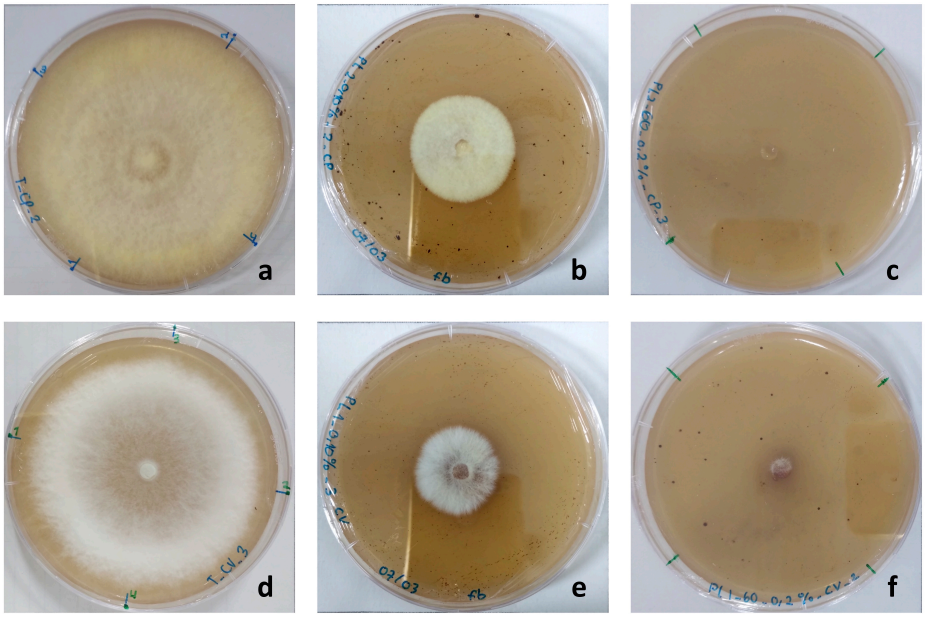

Figure 9.2: Growth of *C. puteana* (a = control; b = pyrolysis liquid at 0.10 % concentration; c = pyrolysis liquid at 0.20 % concentration) and *T. versicolor* (a = control; b = pyrolysis liquid at 0.10 % concentration; c = pyrolysis liquid at 0.20 % concentration)

et al., 2018) exhibited anti-fungal activity. Barbero-López et al. (2019) reported that at the concentration of 0.1 % or below, propionic acid alone could completely inhibit fungal growth such as *C. puteana*. Guaiacols derivatives, which were also found in this study, such as phenol-2-methyl, phenol-3-methyl, phenol-4-methyl, phenol-2-methoxy-4-methyl, and phenol-4-ethyl-2-methoxy were also responsible for the ability of pyrolysis liquid to inhibit fungi (Mourant et al., 2007; Mohan et al., 2008).

9.1.2 Effect of pyrolysis liquid in termite's non-choice test

The effect of pyrolysis liquid on the paper area loss and mortality of *R. flavipes* are presented in Fig. 9.3. Control paper samples treated with deionized water and ethanol represent the equal portion of paper area loss (76.22 % and 79.3 %, respectively) with a low rate of mortality (8.33 % for both controls). Results show that paper treated with ethanol was proved not to affect the termites feeding activity. Fig. 9.4 shows the remaining paper area consumed by termites. At a 5 % concentration, termites consumed less paper

(18.01 %–28.15 %), with a small number of termites survived after a 4-week test. Statistically, pyrolysis liquid obtained at 400 °C is more effective when applied at a 5 % concentration. However, using a 10 % concentration, both pyrolysis liquids caused complete mortality, even if, in this non-choice test, termites still consumed a little portion of the paper (5.56 %–7.03 %). A higher rate of termite mortality showed the toxic effect of pyrolysis liquid.

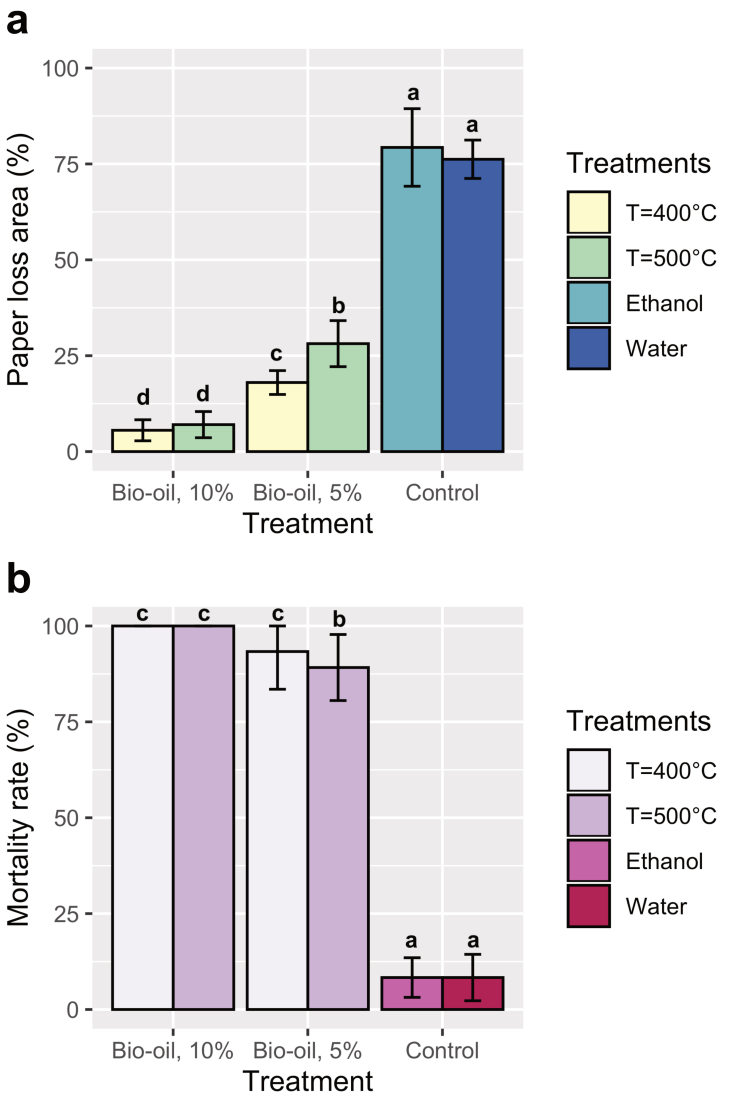

Figure 9.3: Percentage of paper loss area and termite's mortality (bar followed by the same letter are not significantly different)

When termites were subjected to the treated paper on the first day of

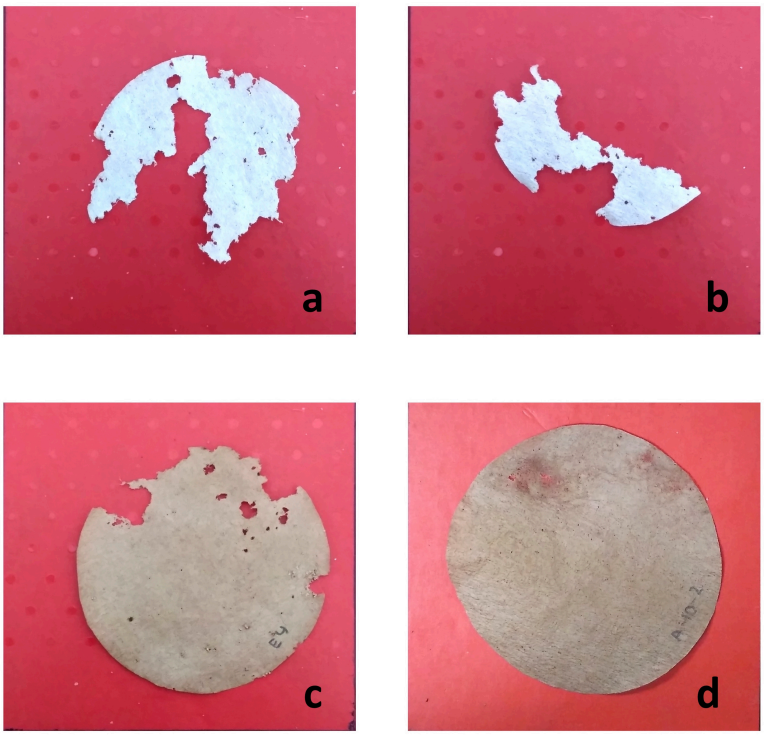

Figure 9.4: Paper consumed by termites (a = control (water); b = control (ethanol); c = pyrolysis liquid at 5 % of concentration and d = pyrolysis liquid at 10 % of concentration)

experimentation, termites seemed to stay away from the treated samples, probably because of the unpleasant odor from the pyrolysis liquid. It has been known that pyrolysis liquid has a smoky flavor characteristic due to the presence of ketones, phenol, guaiacol, and syringol (Yasuhara and Sugiura, 1987; Mathew and Zakaria, 2015). The volatile compounds released during the experimentation was believed to repel the termites as reported by Oramahi and Yoshimura (2013). However, since the results showed that some termites have to consume the treated paper to die, the repellency is not enough, and the ingestion is necessary to make the termite die. Pyrolysis liquid produced from the biomass pyrolysis has been reported to have activity against *Reticulitermes speratus*, *Coptotermes formosanus*, *C. curvignathus*, and *Odontotermes* sp. (Mattos et al., 2019). The presence of formaldehyde in the pyrolysis liquid, akin to that of carbamate, can affect insects' nervous system (Wititsiri, 2011). Acetic acid and phenols also contribute to the termiticidal activity. Yatagai et al. (2002) stated that formic acid showed strong termiticidal activities against *R. speratus*.

9.1.3 Effect of pyrolysis liquid in termites' choice test

The termite's choice test was conducted to examine the repellency effect of pyrolysis liquid towards termites. The number of termites in contact with paper was recorded, and their average and median values were presented in Tab. 9.1. The control paper (paper treated with deionized water) showed a high termite's preference compared to the paper treated with pyrolysis liquid. Pyrolysis liquid is significantly repelling the termites from the paper, while only a small number of termites observed made contact with the corresponding samples. Pyrolysis liquid produced at 400 °C had a slightly high repellency than the one produced at 500 °C. However, statistically speaking, they do not differ significantly. At the lowest concentration tested in this study (5%), pyrolysis liquid had a repellent effect towards *R. flavipes*.

Table 9.1: Number of termites in contact with paper during the 60 minutes of repellency test

Treatment	Concentration (%)	Number of termites in contact with paper	
		Median	Mean
Control*	0*	12	12.35 ± 4.24 (a)
	0*	6	6.40 ± 3.86 (b)
Ethanol	0*	2	13.89 ± 6.89 (a)
	0	17	7.19 ± 7.41 (b)
PL 400 °C	0*	16	14.48 ± 5.07 (a)
	5	0	1.00 ± 0.00 (c)
	0*	15	14.00 ± 5.17 (a)
	10	0	1.00 ± 0.00 (c)
	0*	13	12.70 ± 6.30 (a)
	20	0	1.00 ± 0.00 (c)
PL 500 °C	0*	13	12.77 ± 4.78 (a)
	5	1	2.96 ± 2.65 (c)
	0*	16	13.75 ± 5.36 (a)
	10	0.5	1.38 ± 0.49 (c)
	0*	14.5	11.98 ± 7.11 (a)
	20	0	1.14 ± 0.38 (c)

* Paper treated with deionized water

Indeed, for the control treatment, termites were made an unequal contact with the paper (the two corresponding papers were treated in the same manner). During a 60 min test, termites tend to randomly choose the paper when they first introduced to the Petri-dishes, and they were observed to stay in the same place afterward. At the beginning of the test, we also hypothesized

that the ethanol-treated paper would not give any significant differences toward termite's preferences, as the results on the termite's non-choice test support our assumption. In this case, the data showed that termites were indeed made an equal contact in regard to the ethanol and control paper in all the treated medium (in the range of 12.35 to 13.89 termites). While it seems that termites tend to prefer ethanol-treated paper to the control paper, it is worth noting that the number of termites in contact with the control paper in the control and ethanol treatments was still in the same statistical group range (6.40 and 7.19, respectively). The standard deviation was also found high for the ethanol-treated paper because from the four sets of experiments, there was one of them in which termites prefer the control paper to ethanol-treated paper. The same trend can be observed with the treatments of pyrolysis liquid at the temperature of 500 °C when using a 5 % concentration, where some termites were made contact with the treated paper at the beginning of the test and then left the paper at the end.

Previous study conducted by Oramahi and Yoshimura (2013) has shown that wood vinegar made from pyrolysis of *Vitex pubescens* had repellent effect against *C. formosanus* and *R. speratus* workers. The termites exhibited significant avoidance when exposed to paper treated with 10%, 50%, and 100% concentration of wood vinegar.

9.1.4 Program viability of paper area measurements

The use of automatic segmentation, the *k-means* clustering algorithm, is feasible and simple to treat a thin substrate's image, filter paper on termites' test. The machine learning capability to differentiate the paper from the background allows us to measure the area in a high degree of precision accurately. However, a curious phenomenon could sometimes be observed during the measurement process, which was the presence of white speckles on the classified images. This could happen if the background's surface were not clean enough during the acquisition of the images. Thus, it underlined the necessity of making sure the cleanliness of the surface and camera lenses.

Fig. 9.5 shows the evolution of memory utilization over time obtained by recording the program's memory utilization. Several things could be noted from these data. The first is the fact that the program used a significant amount of memory, even from the very beginning, rising from 0 to almost 500 megabytes (MB) very quickly. Even for a process that only analyzed three images ($N_{\text{img}} = 3$, Fig. 9.5a), the maximum memory used exceeded 1000 MB. This should not be a surprise, seeing that Machine Learning is a branch of data science that actually still necessitates high-performance computers. It was also why many machine learning and deep learning packages available

in the market during this thesis's writing also included integration to the Graphical Processing Unit card of the computer (GPU) to accelerate the process.

As observed from the Fig. 9.5, the maximum memory use also increased with the increase of the number of images processed. This led us to the second step of the process analysis, which was the running time and maximum memory analysis (Fig. 9.6). By putting the N_{img} together with t_{tot} and M_{max}, we could see a clear linear relationship between the parameters ($r^2 = 0.951$ for t_{tot} and $r^2 = 0.974$ for M_{max}). This could give us an expectation of how long our code would conduct an image analysis given an N number of acquired images and the number of memories it would take to process them. This is an important point because it would be related to the type and performance of the computer that we use and would allow us to plan a strategy not to saturate our machine's memories too quickly.

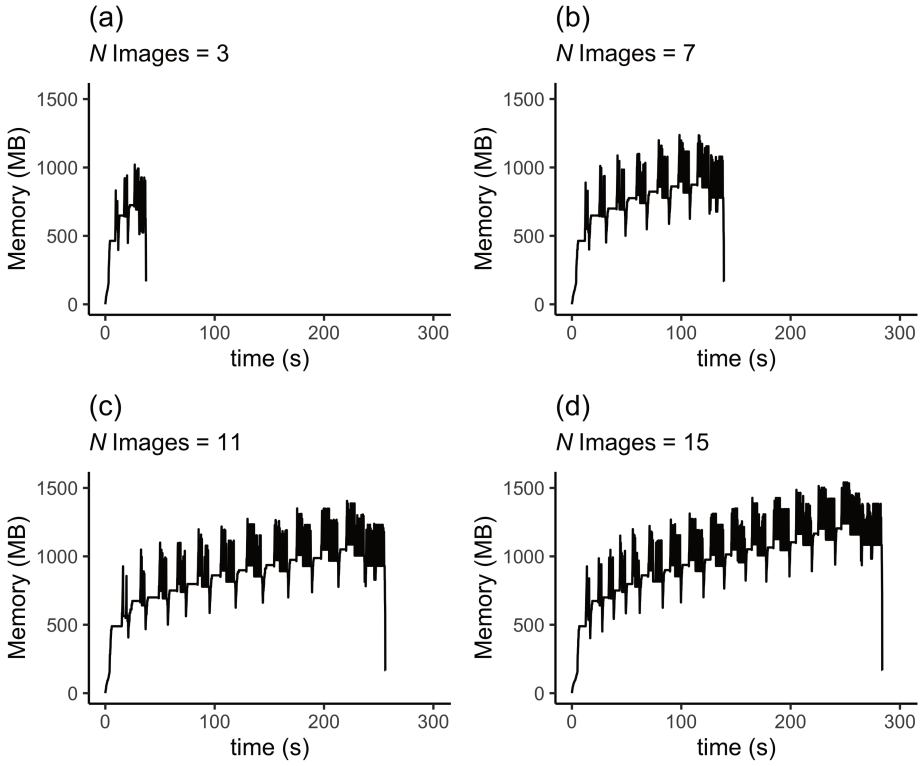

Figure 9.5: Evolution of memories used by the code (non-GUI version) over time for various total number of images

As presented, this program allows calculating the surface of paper degraded by termite. It is a practical, easy and quick tool that can be easily

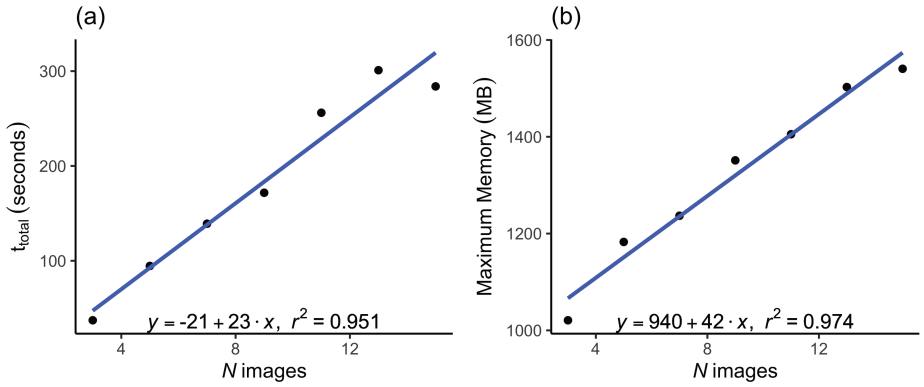

Figure 9.6: Relationships between total number of processed images, processing time, and maximum memories used

implemented in a laboratory. Moreover, it is more accurate than the conventional method, for example by using a tracing graph paper, which need to use categories/classes to describe the degradation (e.g., degraded by 10%, 25%, 50% or 100%) (Sankara et al., 2020). Additionally, measuring the surface area avoids the mass loss error problem due to the hygroscopicity of the filter paper made of cellulose and avoids the error in weighing a really small weight (Grace et al., 1986).

9.2 Wood treatment using pyrolysis liquid

9.2.1 Effect of different drying temperatures on beech wood samples

9.2.1.1 Retentions and microscope observation

Fig 9.7 shows the untreated and treated beech wood (with 100% pyrolysis liquid) after being dried at different temperatures. The higher the drying temperature, the darker the wood. The air-dried samples had more pungent odor than other specimens.

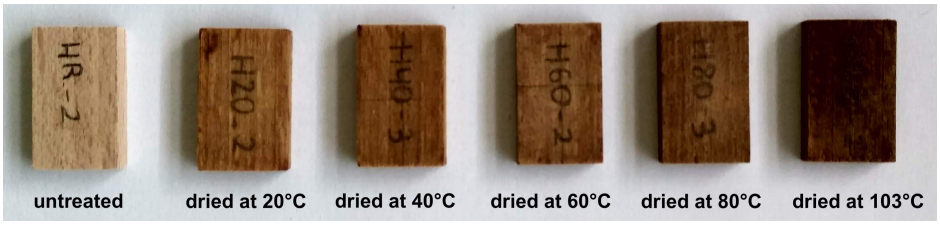

Figure 9.7: Untreated and treated beech wood samples after drying

After being impregnated into 30 samples of beech wood, the average of pyrolysis liquid retention was recorded at 734.23 ± 20.59 kg/m^3. Excluding the water contained in the pyrolysis liquid, the retention is 423.65 ± 11.88 kg/m^3. During the oven-drying process, water and the volatile compounds from the pyrolysis liquid were released. Further, at the drying temperatures used in this study, most volatile components of pyrolysis liquid—such as methanol, acetaldehyde, formaldehyde, 2-propanol, and formic acid—are able to evaporate (Chhiti et al., 2012; Brown and Stein, 2018).

Fig. 9.8 presents the microscopic observation of the untreated beech wood and treated beech wood after dried at 103 °C. According to the visual observations, higher drying temperature (above 60 °C) seems to promote the agglomeration of pyrolysis liquid inside the microstructure of wood. Such agglomeration is even more noticeable in the tangential section, which fills the wood rays. As a comparison, we did not find the same agglomeration when dried the samples at ambient temperatures. Kim et al. (2012) stated that the chemical components of pyrolysis liquid were able to penetrate into the wood cell lumen and agglomerate forming large clusters when the volatiles were evaporated during the oven drying process. In another study, Lourençon et al. (2016) also reported that the liquid product of pyrolysis acts by coating the surface of vascular microstructures of the wood.

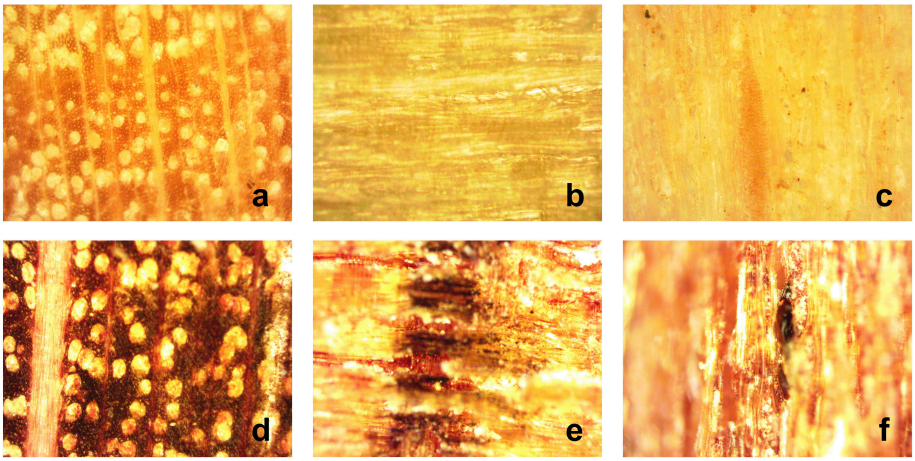

Figure 9.8: Microscopic observation using a light microscopy: (a) untreated beech wood at longitudinal section; (b) untreated beech wood at radial section; (c) untreated beech wood at tangential section; (d) treated beech wood – 103 °C at longitudinal section; (e) treated beech wood – 103 °C at radial section; (f) treated beech wood – 103 °C at tangential section.

9.2.1.2 FTIR analysis

The FTIR spectra of the untreated and treated beech wood samples were presented in the fingerprint region (1800 to 800 cm^{-1}) (Fig. 9.9). The peaks observed for the untreated beech wood at this range, included peaks at 1732 cm^{-1} (C=O stretching) which presenting the acetyl groups in hemicelluloses, 1593 cm^{-1} (C=C stretching) presenting the aromatic skeletal in lignin, 1232 cm^{-1} (C–O stretch in lignin and xylan), and 1032 cm^{-1} (C–O stretching). Meanwhile, peaks at 1459 cm^{-1}, 1372 cm^{-1}, and 1158 cm^{-1} correspond to C–H deformation in carbohydrates and lignin, C–H deformation in cellulose and hemicellulose, and C–O–C vibration in cellulose and hemicellulose, respectively (Grosse et al., 2018). Indeed, the FTIR spectra of treated beech wood reflect the compositions of the pyrolysis liquid and beech wood spectra (Lourençon et al., 2016). The absorbance peaks at 1732 cm^{-1}, 1650 cm^{-1}, and 1593 cm^{-1} seem to decrease with the increase of drying, which may be related to the pyrolysis liquid content inside the wood. The C=O stretching vibrations with absorbance between 1650 and 1780 cm^{-1} indicate the presence of ketones, aldehydes, and carboxylic acids from the pyrolysis liquid (Demiral et al., 2008; Islam et al., 2010). However, no peak was presented as a result of the interaction between pyrolysis liquid and wood, which means that no chemical reactions occurred between them as previously confirmed

by Lourençon et al. (2016).

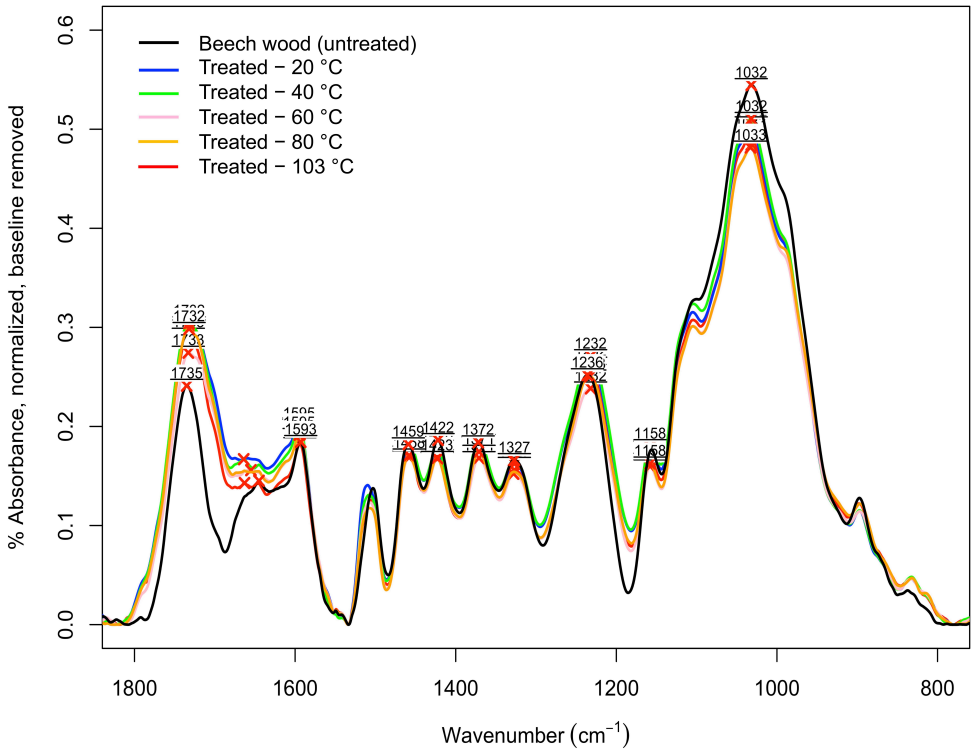

Figure 9.9: FTIR analysis of untreated and treated beech wood

9.2.2 Effect of different drying temperatures on leaching

9.2.2.1 Leachability of treated samples

Fig. 9.10 shows the weight percent gain before (WPG) and after subjected to water-leaching (WPGL), as well as the leaching rate (LR) of the treated samples, with their statistical grouping presents in Tab 9.2. The difference in drying temperature gave a significant difference to the WPG, except for the samples dried at 40 °C and 60 °C. Results show that the amount of evaporated volatile compounds positively correlated with the drying temperatures. Pyrolysis liquid appears to be highly water-leachable from wood. The decrease of pyrolysis liquid content inside wood after the leaching process was even more apparent, characterized by the differences of their WPG and WPGL. However, it should be noted that at low drying temperature (below 103 °C), the weight of specimens still contain moisture. Our preliminary results indicate that at the drying temperature of 103 °C, the leaching

rate was significantly lower compared to other samples. It is presumed that the presence of agglomerates caused the lower leaching rate, as they can act by blocking the water flow inside the wood, as reported by Lourençon et al. (2016).

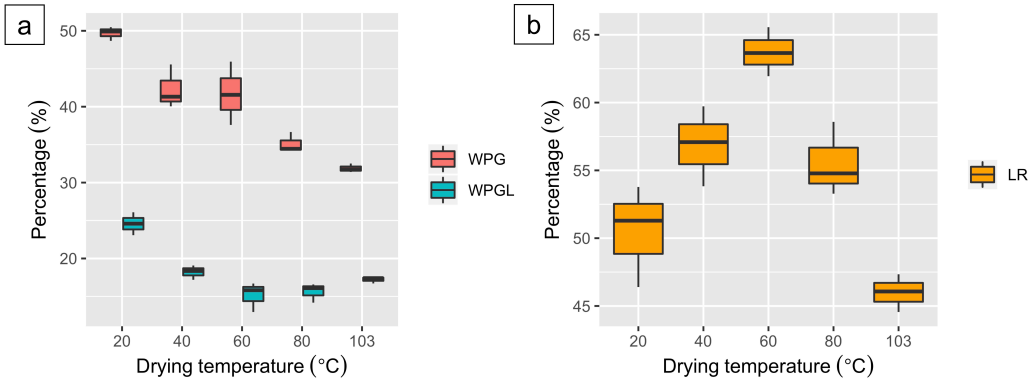

Figure 9.10: Weight percent gain before and after leaching (a) and leaching rate (b) of the treated samples when dried at different temperatures

Table 9.2: Statistical group of treated beech wood dried at different temperatures for their WPG, WPGL, and LR values

	20 °C	40 °C	60 °C	80 °C	103 °C
WPG	a	b	b	c	d
WPGL	a	b	b	b	b
LR	bc	ab	a	b	c

9.2.2.2 Analysis of the leachate compounds

The compounds leached from different treated samples is illustrated in Fig. 9.11 and Tab. 9.3. According to the GC-MS analysis, some portion of phenols, guaiacols, and ketones were leached from all the treated wood. The lower the drying temperatures, the higher portion of compounds detected by GC-MS. In this case, considering that during the drying process several compounds have been released, it is understandable that the samples dried at the temperature of 20 °C had the highest quantified compounds that were leached (77.2 mg/L). Acetaldehyde was the major compound leached from the treated sample dried at 20 °C. Tab. 9.3 demonstrates the analysis results of some species quantifiable in the leachate products. However, it

should be noted that the quantification is also limited due to the higher portion of water, thus reducing the concentration of the species in the leachate products. The results presented in this analysis showed that 3-methyl-1,2-cyclopentanedione, 2,6-dimethoxyphenol, and phenol were the three significant compounds that leached from all the treated-wood.

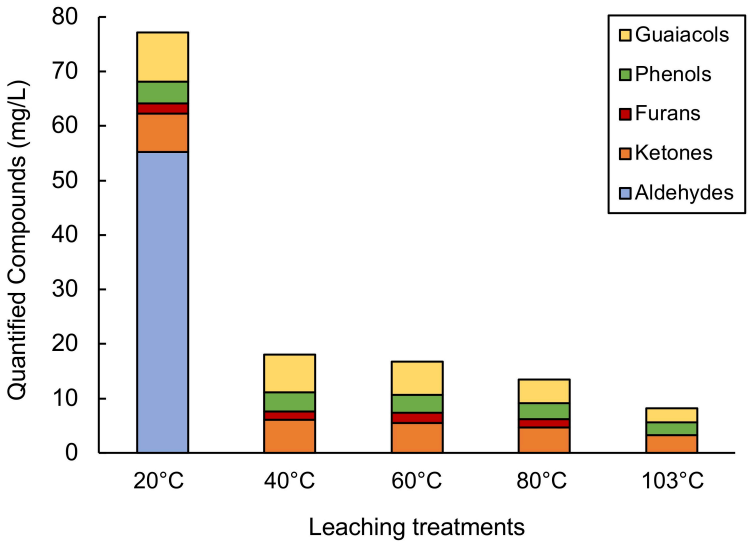

Figure 9.11: Compounds leached from the treated-wood specimens that dried at different temperatures

Table 9.3: Compounds leached according to the GC-MS analysis

Group	Compounds	Quantified compounds (mg/L)				
		20 °C	40 °C	60 °C	80 °C	103 °C
Aldehyde	Acetaldehyde	55.20	-	-	-	-
Ketones	3-methyl-1,2-cyclopentanedione	7.05	6.13	5.43	4,64	3.29
Furans	2(5H)-Furanone	1.85	1.48	1.89	1.57	-
Phenols	Phenol	2.77	2.21	2.09	1.76	1.08
Phenols	3,4-dimethylphenol	1.24	1.26	1.24	1.21	1.20
Guaiacols	Phenol-2-methoxy	1.56	1.32	1.33	1.17	-
Guaiacols	Phenol-2-methoxy-4-methyl	1.15	1.14	1.09	-	-
Guaiacols	2,6-dimethoxyphenol	5.36	4.52	3.67	3.06	2.57
Guaiacols	Acetosyringone	1.02	-	-	-	-

Previous studies highlighted the leachability as the main drawback of pyrolysis liquid when used as wood preservatives (Mohan et al., 2008; Temiz et al., 2013a). Temiz et al. (2010) reported that a significant quantity of

phenolic compounds was leached during the leaching process, which was confirmed by a UV-Vis analysis. However, detailed chemical identification was not performed. A study conducted by the same author three years afterward utilized the combination of epoxidized linseed oil (ELO) to reduce the leachability of pyrolysis liquid through secondary impregnation. Their results indicated that the number of compounds determined in the leachate products was decreased from 74 to 21 when the samples were treated with 10% pyrolysis liquid and with the combination of ELO. The catechol and syringol were the most abundant compound found in the leachate products for both treatments, respectively (Temiz et al., 2013a).

9.2.2.3 Effect of leachate products in fungal inhibition test

Tab 9.4. presents the results of the radial measurements from the four-set data test. The higher the drying temperature, the higher radial growth of mycelium, which means that it had less effect on fungi. This study also showed that *T. versicolor* has grown faster than *C. puteana*. However, when comparing the treated and untreated samples, the leachate products were more effective against *C. puteana* for all treatments. Indeed, from subsection 9.1.1, results suggested that pyrolysis liquid was more effective against *C. puteana* compared to *T. versicolor*.

Table 9.4: Radial growth of *C. puteana* (CV) and *T. versicolor* (TV) in the medium of leachate products

Fungi	Samples	Radial growth (mm)					
		20 °C	40 °C	60 °C	80 °C	103 °C	Control
CP	1	0	3	0	3	8.5	30
	2	0	0	3	8.5	12	27
	3	0	0	0	10	12	23
	4	0	5	1.5	11	13	27
TV	1	18	19	26	35	27	34
	2	20	21	20	23	38	36
	3	20	21	25	24	31	38
	4	21	27	23	25	35	36

For *C. puteana*, no growth was observed for the treatment using leachate products from the samples dried at 20 °C, showing strong fungal activity. Further, for the leachate samples dried at 40 °C and 60 °C, half of the test samples showed no growth. As also shown in Fig. 9.12, all treatments for *T. versicolor* showed the mycelium growth, but slower for the treatments using lower drying temperatures. At 103 °C, the effect of the leachate products was

not giving a significant difference to the growth of control. Results suggested that the leachate products were more tolerant to *T. versicolor* compared to *C. puteana*. Also, it is worth nothing that phenol-2-methoxy-4-methyl, a specific compound with anti-fungal activity, were not presented (or perhaps low in quantity) in the leachate products 80 °C and 103 °C as presented in Tab. 9.3.

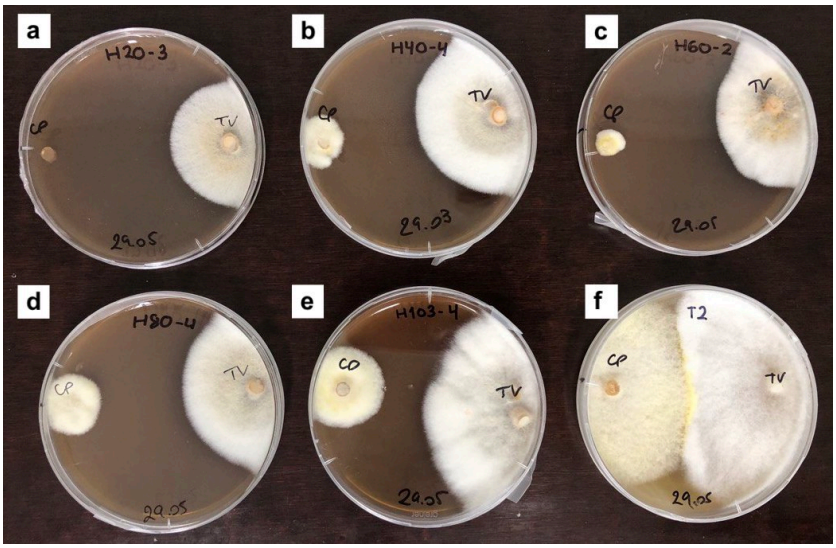

Figure 9.12: The growth of *C. puteana* and *T.versicolor* at different leachate products: (a) 20 °C; (b) 40 °C; (c) 60 °C; (d) 80 °C; (e) 103 °C; (f) control

9.2.3 Resistance towards termites

The results of the termite resistance test are shown in Tab. 9.5 and the images of the samples after the test are presented in Fig. 9.13. Strong wood degradation (visual rating 4) and high termite worker survival (84 %) were observed for the control samples, thus validating the test. As expected, all the treated samples have high resistance against termites (visual rating 0 to 1), with a considerably lower weight loss compared to the control treatment. No surviving termites were found for the samples dried at 60 °C, 80 °C, and 103 °C, while only a very low termite survival rate was found for the specimens dried at 20 °C and 40 °C. Although the pyrolysis liquid was found to be leachable, it seems that the remaining product left in the samples is still sufficient to protect the wood.

During the experiments, we also noted that the termites were directly affected very rapidly when exposed to the treated samples. Termites tend to

Table 9.5: Performance of wood treated with pyrolysis liquid after drying at different temperatures against termites (leached specimens)

Samples	Weight loss (%)	Survival rate (%)	Visual rating (%)				
			0	1	2	3	4
Treated – 20 °C	2.68 ± 0.29 (c)	0.67 ± 1.15 (a)	33.33	66.67	0	0	0
Treated – 40 °C	1.39 ± 0.11 (a)	0.67 ± 1.15 (a)	33.33	66.67	0	0	0
Treated – 60 °C	1.67 ± 0.05 (b)	0	33.33	66.67	0	0	0
Treated – 80 °C	1.37 ± 0.11 (a)	0	33.33	66.67	0	0	0
Treated – 103 °C	1.86 ± 0.15 (b)	0	0	100	0	0	0
Control	9.95 ± 1.33 (d)	84 ± 2.00 (b)	0	0	0	0	100

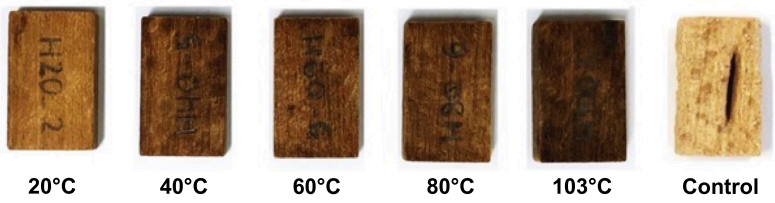

Figure 9.13: Beech wood samples at the end of termites' test

abstain from getting closer to the samples, and most of them hid under the sand. After two days of the test, most of the termites remained less active and gathered with one another, while significant termites were found dead in the first week of the test. Very small wood degradation were observed for all treatments (visual rating 0-1).

9.2.4 Weight loss after evaporation test

After being treated with 100 % pyrolysis liquid, the weight loss of beech wood samples caused by the evaporation test is lower compared to leaching, and its effect is considered negligible (Tab. 9.6). Following this found, pyrolysis liquid seems to be significantly able to be removed from the wood samples, only if the samples were exposed in high moisture or humidity condition.

Table 9.6: Weight loss of beech wood samples after the evaporation test and the leaching process

Treatment	Weight loss (%)
Evaporation	0.54 ± 0.06
Leaching	7.29 ± 0.71

9.3 Wood screening test

As previously described in the methodology section, the screening test was conducted using various concentrations of pyrolysis liquid diluted in ethanol. Specimens treated with the pyrolysis liquid before and after leaching were exposed to *T. versicolor*, *C. puteana*, and *R. placenta*. The correction factor for the fungal test was also presented. The whole examination aimed to determine the efficacy threshold of pyrolysis liquid using various concentrations. The samples' detailed characteristics after impregnation, leaching, and the biological performances for all of them are provided in Appendix B.

9.3.1 Percentage of weight gain and leaching rate

The weight percent gain before (WPG) and after leaching (WPGL) is presented in Fig. 9.14. At lower concentrations (5 %, 10 %, 15 %, and 20 %), the WPG for both samples are lower than 10 %. The average WPG for beech wood samples was recorded at 2.37 % for the lowest loading treatment and 33.75 % for the highest loading treatment. For pine, the values were 2.23 % and 29.22 %, respectively. Compared to beech, pine wood samples have a lot of variation in their data distribution, possibly attributed to their anatomical characteristics (e.g., presence of the resin canal). Meanwhile, the average WPG for beech is higher possibly due to its high permeability to the impregnation. Compared to Lourençon et al. (2016), our WPG is lower. In their study, WPG of using 50 % concentration was about 57 %. The WPGL of samples was considerably reduced proportionally to the initial loading of pyrolysis liquid. For the highest concentration, WPGL was reduced to 23.62% and 20.05% for the beech and pine samples, respectively.

As illustrated in Fig. 9.15, the leaching rate was found high. The leaching rate showed the percentage of pyrolysis liquid that leached in the water. From the boxplot presented, therefore, it could be seen that the higher the concentration, the lower the leaching rate, as it is related to the amount of pyrolysis liquid in the wood. Almost half and more than half of products were theoretically removed during leaching for the concentration below 100 %. The lowest leaching rate was observed at 30.11% for beech samples and 31.86% for pine samples. Those values are already corrected by subtracting the values from the untreated samples. When leaching the untreated samples, some extractives could be removed. The weight loss caused by leaching for the untreated beech and pine is (1.12 ± 0.41)% and (1.57 ± 0.51)%, respectively.

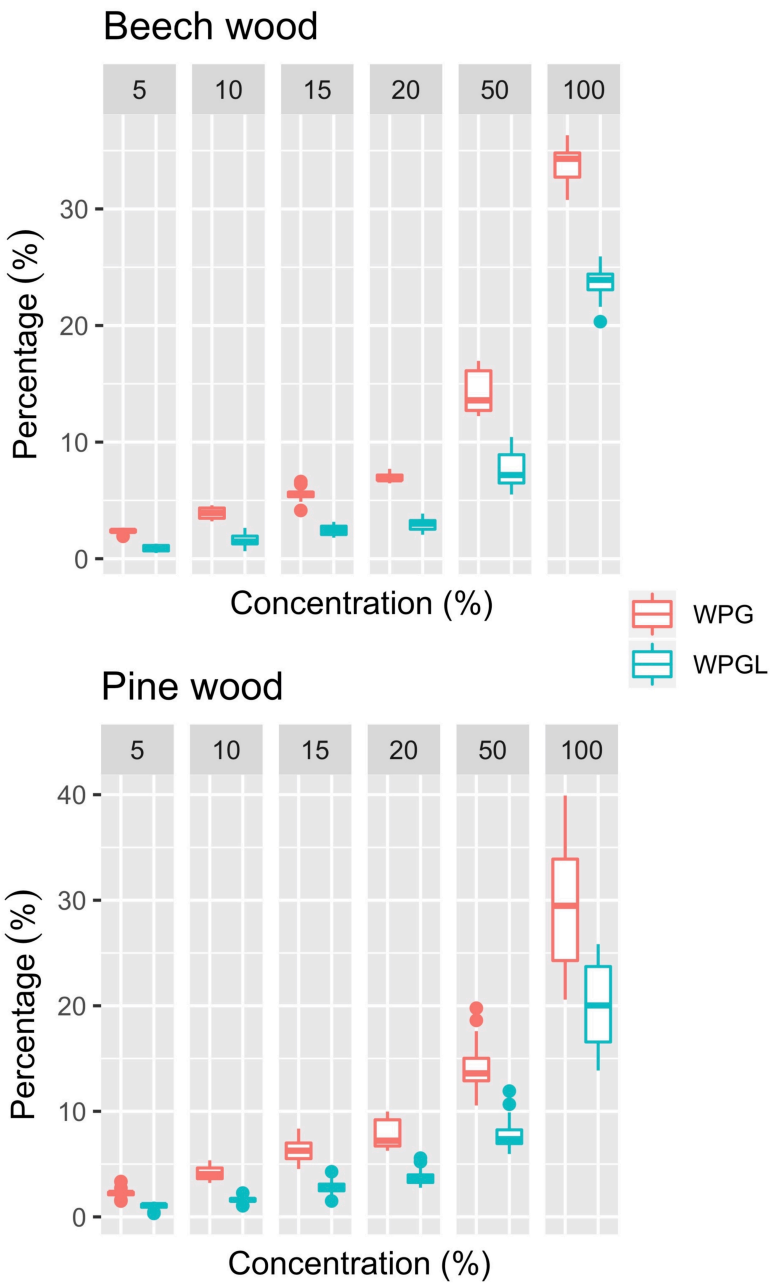

Figure 9.14: Weight percent gain before (WPG) and after leaching (WPGL) for beech wood and pine wood samples at various concentrations of pyrolysis liquid

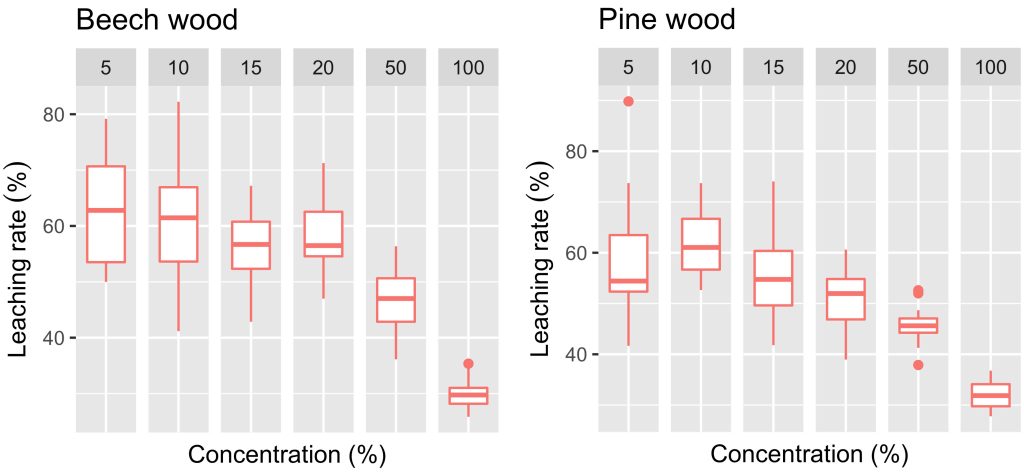

Figure 9.15: Leaching rate for beech wood and pine wood samples at various concentrations of pyrolysis liquid

9.3.2 Correction factor for the fungal test

Fig. 9.16 shows the weight loss after the correction factor test with their moisture content recorded at the end of the test. For the highest loading treatment, the weight loss recorded for the unleached samples in this test is similar or even higher than the weight loss caused by the leaching process (see Annex. B). For beech samples, the weight loss for the correction factor is (10.31 ± 0.56) % and for the leaching is (6.93 ± 0.48)%. Meanwhile, for pine samples, the weight loss for the correction factor and due to leaching is (8.40 ± 1.59)% and (6.18 ± 0.78)%, respectively. Such findings support the fact that the pyrolysis liquid is highly leachable when exposed to high moisture and humidity. Moreover, the relative humidity in the test media was known to be at approximately 90 %. It is also interesting to note that at the end of the test, the media which the samples had the highest loading of pyrolysis liquid were observed to have the darkest color, meaning that a high portion of products was leached out into the malt-agar medium (Fig. 9.17).

Following the results, the correction factor test is thus crucial to prevent the false-positive result on the weight loss caused by the fungal attack. Using the slow pyrolysis liquid from macadamia nutshell, Kartal et al. (2011) previously reported that the weight losses due to the fungal attack in leached specimens were less than those observed in unleached specimens; still, they did not conduct the correction factor for the fungal test. In another study, Tomak et al. (2011) reported that when using treated wood with a high

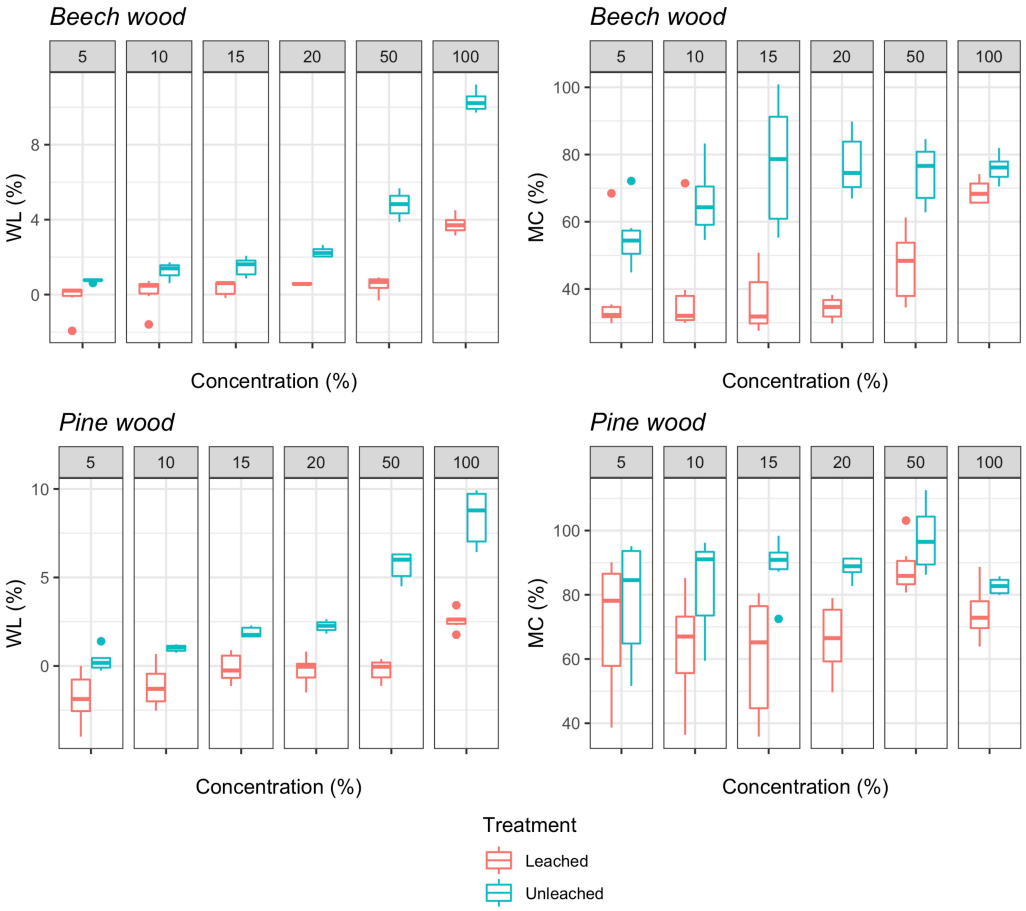

Figure 9.16: Weight loss and moisture content of treated beech and pine wood after the correction factor test

Figure 9.17: Darkest color on the malt agar medium from samples treated with the highest loading of pyrolysis liquid at the end of the test: (a) pyrolysis liquid at 10% and (b) pyrolysis liquid at 100%

loading of vegetable oils, they observed high weight losses after exposed to the decay test. The oils were found to be leached out during exposure to high moisture conditions and not caused by the fungal attack. Indeed in the case of plant oils, which are often correlated as a hydrophobic substance, the drying is due to the polymerization by oxidation. However, when applied in large quantities, it will hinder the diffusion of air (oxygen) through the wood, so it requires a longer time for polymerization to occur (Koski and Ahonen, 2008).

In some cases, there was a tendency that the moisture content or the water uptake during the test for the leached samples are lower than the unleached ones suggesting that the leaching process removed the hydrophilic substances but possibly left the hydrophobic molecules (see again Fig. 9.16). According to the microscopic observation illustrated in Fig. 9.18, some agglomeration can still be observed in the treated samples after leaching, especially those that treated using the highest loading. For the specimens diluted in ethanol, some agglomeration can still be observed, notably at the radial section. Some researchers like Lourençon et al. (2016) and Temiz et al. (2013b) reported the hydrophobic properties of the liquid product from the pyrolysis process by the fact that the treated samples caused lower water absorption than those of the untreated ones. We believed such a claim is true when tested the water absorption using samples from the leaching test (see Appendix.

C, Fig. 1), as described by Lourençon et al. (2016). However, the results are more noticeable when high loadings were applied (we did not present the data using lower concentrations due to its low readability). Further, Panov et al. (2010) also stated that when exposed under high relative humidity, the oil-treated wood swells to the same extent as the untreated wood but at a longer time to reach equilibrium. This could possibly means that the effect of pyrolysis liquid on reducing the water absorption is solely based on the agglomeration of products that hinder the water from easily penetrating the wood, as Koski and Ahonen (2008) stated in the case of water repellent. In the end, it is also important to note that the pyrolysis liquid product may differ from one another presented in the literature. Some products are described to have higher viscosity and not soluble in water, such as presented by (Temiz et al., 2013b).

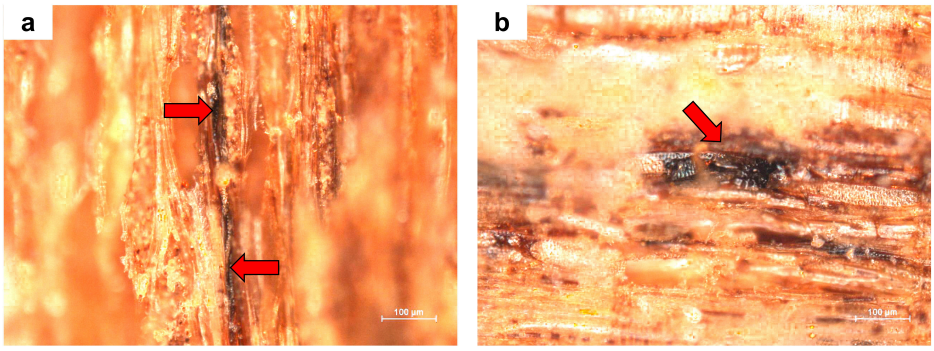

Figure 9.18: Microscopic observation of treated wood samples after leaching (a) tangential section treated with 100% concentration of pyrolysis liquid, and (b) radial section treated with 50% of radial section

9.3.3 Decay resistance test

The results for the decay weight loss, its moisture content, and the samples after exposure (at 50% concentration) are shown in Fig. 9.19–9.24. For the control samples (virulence), the average of weight loss is always above 20%, thus validate the tests. There were significant differences in the samples that were leached or not, as expected. However, some treatments using lower loading were not significantly effective to protect the wood from the fungal attack.

Although the weight losses of the control samples were considerably higher than those of the treated ones, pyrolysis liquid at lower concentration (5 % to 20 %) has low effectiveness towards *T. versicolor*. Some samples were even

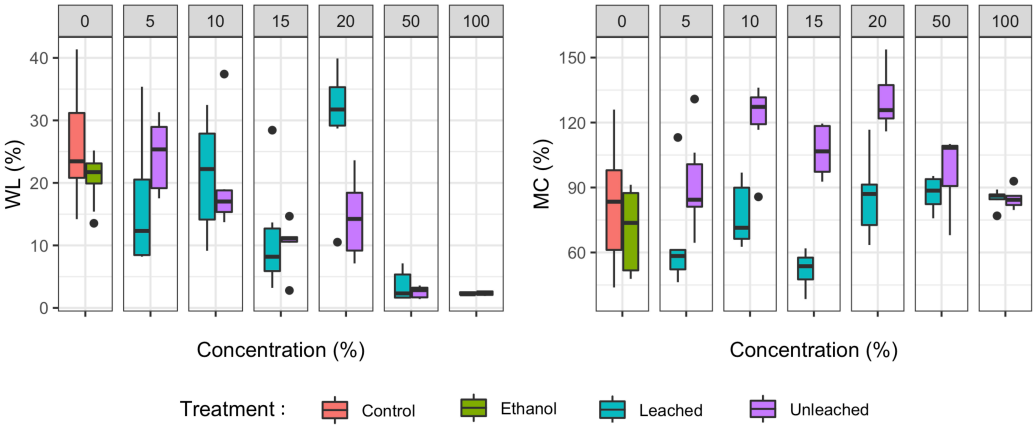

Figure 9.19: Weight loss of beech specimens and their moisture content after exposed to *T. versicolor* (WL is corrected with the correction factor)

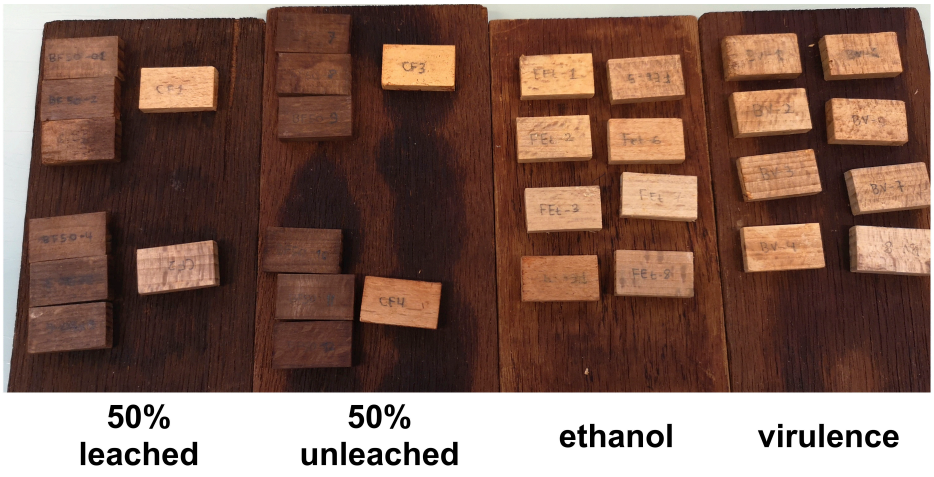

Figure 9.20: Beech samples at the end of decay test (exposed to *T. versicolor*)

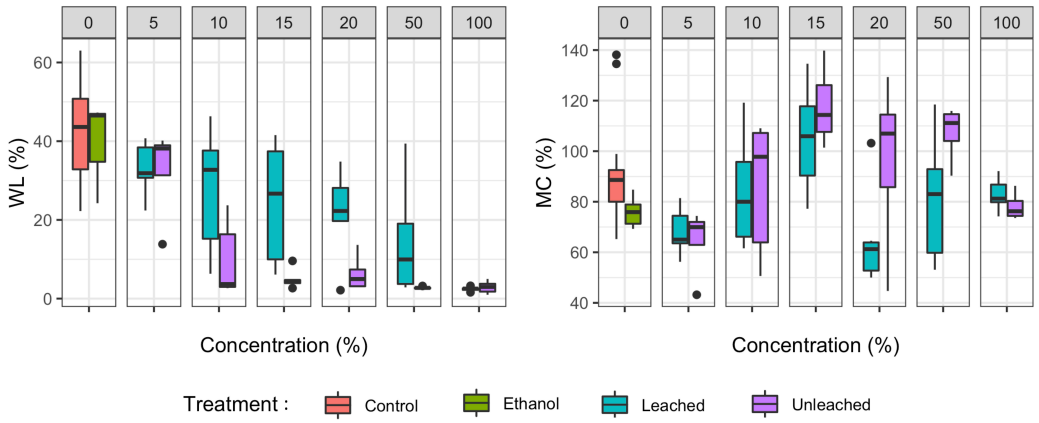

Figure 9.21: Weight loss of pine specimens and their moisture content after exposed to *C. puteana* (WL is corrected with the correction factor)

Figure 9.22: Pine samples at the end of decay test (exposed to *C. puteana*)

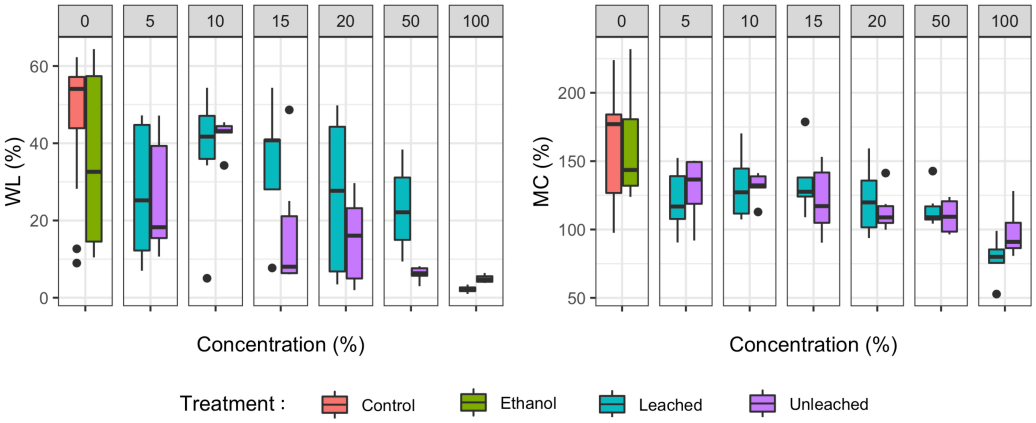

Figure 9.23: Weight loss of pine specimens and their moisture content after exposed to *R. placenta* (WL is corrected with the correction factor)

Figure 9.24: Pine samples at the end of decay test (exposed to *R. placenta*)

attacked similarly to the control samples. High variations on the resulting data could show that the treatments do not give enough protection to the wood. However, when treated wood with high loadings (50 % and 100 %), both concentrations give excellent protection towards decay, even for the leached samples.

For *C. puteana*, pyrolysis liquid seems to be more effective and consistent with their weight loss proportion when starting to use it at 10 % of concentration (retention = 50.44 kg/m^3). Moreover, it has been shown that *C. puteana* seems to be less tolerance to pyrolysis liquid, compared to *T. versicolor*. Meanwhile, for *R. placenta* the effect is noticeable when using pyrolysis liquid starts at 15 % (retention = 82.62 kg/m^3). Using the concentration of 50 % for both fungi was less effective when samples were leached. It is possible that some of the active ingredients, such as phenolic compounds, which are always mentioned to be responsible for the anti-fungal activity, have been removed during leaching, thus decreasing the effectiveness of pyrolysis liquid. Despite the efficacy of pyrolysis liquid, it is also important to remember the high leachability of treated wood during the test for those treated at the highest loading. It is possible that the pyrolysis liquid was leached out, then causing the fungi around the samples to die, thus slow down the fungal attack.

Indeed, the results are promising when using the highest loading, as reported in precedent studies. Lourençon et al. (2016), for instance, treated the pine wood samples to reach the WPG of 57–80 % to cause complete mortality of the fungal colony of *T. versicolor*, while Kartal et al. (2011) treated the pine samples with 100 % of pyrolysis liquid (retention = 460 kg/m^3). It is thus reasonable to use the high loading (concentration of 50% to 100%) of pyrolysis liquid to wood to maintain its efficacy. However, due to its high leachability presented in this study, pyrolysis liquid seems not effective to be used as a stand-alone method for wood protection against fungi. It is probably a potential treatment to combine with other products such as water repellent.

9.3.4 Termites resistance test

Tab. 9.7 shows the test results for the wood treated with pyrolysis liquid at 25 % and 50 % of concentration. Fig. 9.25 presents the samples at the end of the test. Specimens treated with ethanol are similar to the untreated ones, showing that ethanol did not significantly affect the termites' preferences. However, the weight loss and the survival rate for the control groups were lower than those presented in Tab. 9.5 due to different test time and termites. Some termites from different colonies could be bigger in their size or already

full at the beginning of the test, thus affecting their eating preferences. For that reason, the virulence samples are important to carry on in every test.

Table 9.7: Performance of wood samples treated with pyrolysis liquid against termites before and after leaching

Treatments	Weight loss (%)	Survival rate (%)	Visual rating (%)				
			0	1	2	3	4
25 % – Leached	1.49 ± 0.67 (a)	0 (a)	0	100	0	0	0
25 % – Unleached	3.58 ± 0.30 (b)	0 (a)	0	66.67	33.67	0	0
50 % – Leached	1.45 ± 0.08 (a)	0 (a)	33.67	66.67	0	0	0
50 % – Unleached	3.86 ± 0.47 (b)	0 (a)	0	100	0	0	0
Control – Ethanol	6.96 ± 1.82 (c)	57.33 ± 7.57 (b)	0	0	0	0	100
Control	6.88 ± 0.69 (c)	58.00 ± 5.29 (b)	0	0	0	0	100

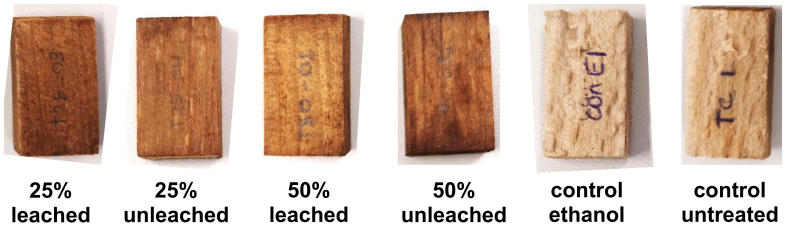

Figure 9.25: Beech wood samples treated with different concentration of pyrolysis liquid at the end of the termites' test

Following the results, although the visual rating for the specimens treated with 50 % of pyrolysis liquid provides the lowest attack (visual rating 0 to 1), there are no significant differences observed in the weight loss for both concentrations. However, the leaching treatments give the significantly lowest weight loss compared to the specimens that were not leached. For this phenomenon, Kartal et al. (2011) previously suggested that leaching treatment could remove some beneficial compounds for the organism (e.g., source of food) or perhaps the leaching process making the distribution of bio-oil inside the wood becomes uniform. Another possibility could be caused by the product that leached out during the test, yet, the weight loss data for the termites' test was not corrected as the fungal test. Indeed in the standard, termites results were assessed only based on the visual rate. For that, the test using samples after fungal correction factor (see Fig. 9.16) were reused and exposed to termites to compare the results.

Overall, pyrolysis liquid is found effective against *R. flavipes* at both concentrations. Compared with the result presented in Tab. 9.5 (samples treated with 100% pyrolysis liquid after leaching), the weight loss and survival

rate were similar with those treated at 50% of concentration. In another study, Temiz et al. (2013a) reported that at a concentration of 20 % (retention = 108 kg/m^3), bio-oil made of giant cane (*Arundo donax* L.) is highly effective when tested against the same termites (no weight loss and zero survival rate).

9.3.5 Termites test using samples from the correction factor

The treated beech wood and pine wood samples from the fungal correction factor experiments were reused for the termites' test. It is clear that some content of pyrolysis liquid had been removed due to the weight loss observed during the correction test (see again in Fig. 9.16).

For the beech samples (Tab. 9.8), the treatments with low concentrations (5% to 20%) did not show any protection against termites. However, the samples treated at 100% showed good protection with a weight loss of 2% (visual rating 1) and zero termites' survival. For the pine samples (Fig. 9.26 and Tab. 9.9), the treatments at concentration of 5% to 50% failed to give the protection against temites, except for the specimens treated at the highest concentration (100%). The weight loss recorded for such treatment was observed at 3.18-4.03%, with the visual rating from 1 to 4. The protection for the pine is lower than the beech samples probably due to different initial retention of pyrolysis liquid for both samples. Following the results on the biological tests, it is imperative to improve the stability of pyrolysis liquid to prevent leaching by means of fixation.

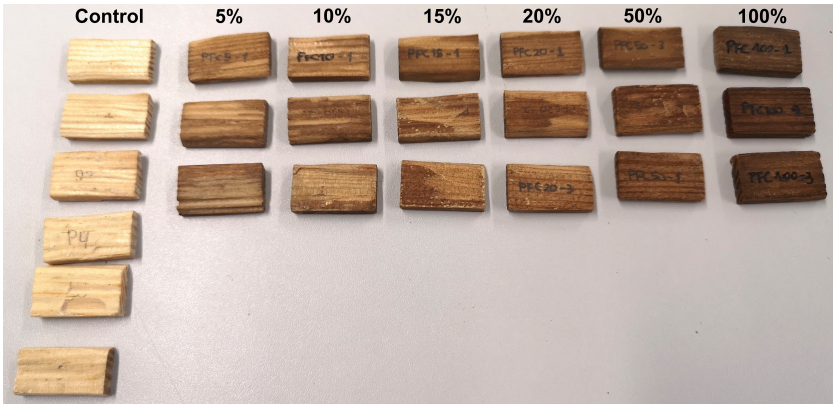

Figure 9.26: Samples of pine at the end of termites' test (leached specimens)

Table 9.8: Performance of wood treated with pyrolysis liquid against termites (using beech samples from the correction factor test)

Treatments	Weight loss (%)	Survival rate (%)	Visual rating (%)				
			0	1	2	3	4
BCF - 5% leached	9.86 ± 2.91 (ab)	90.67 ± 3.06 (a)	0	0	0	0	100
BCF - 5% unleached	9.98 ± 0.90 (ab)	54.67 ± 11.02 (bc)	0	0	0	0	100
BCF - 10% leached	10.81 ± 0.86 (a)	86.67 ± 10.26 (a)	0	0	0	0	100
BCF - 10% unleached	9.89 ± 0.39 (ab)	64.67 ± 1.15 (abc)	0	0	0	0	100
BCF - 15% leached	9.97 ± 1.00 (ab)	82.67 ± 12.22 (ab)	0	0	0	0	100
BCF - 15% unleached	9.27 ± 0.39 (ab)	66.67 ± 9.24 (abc)	0	0	0	0	100
BCF - 20% leached	8.58 ± 0.46 (ab)	60.67 ± 14.05 (abc)	0	0	0	0	100
BCF - 20% unleached	7.94 ± 0.75 (ab)	61.33 ± 6.43 (abc)	0	0	0	0	100
BCF - 50% leached	6.84 ± 1.12 (bc)	38.67 ± 6.43 (c)	0	0	0	0	100
BCF - 50% unleached	3.94 ± 0.73 (cd)	4.00 ± 4.00 (d)	0	0	33.33	33.33	33.33
BCF - 100% leached	2.06 ± 0.29 (d)	0 (d)	0	100	0	0	0
BCF - 100% unleached	2.00 ± 0.96 (d)	0 (d)	0	100	0	0	0
Control Beech	9.69 ± 1.12 (ab)	70.50 ± 15.70 (ab)	0	0	0	0	100

Table 9.9: Performance of wood treated with pyrolysis liquid against termites (using pine samples from the correction factor test)

Treatments	Weight loss (%)	Survival rate (%)	Visual rating (%)				
			0	1	2	3	4
PCF - 5% leached	12.94 ± 0.22 (a)	80.67 ± 3.06 (ab)	0	0	0	0	100
PCF - 5% unleached	11.93 ± 0.68 (ab)	72.67 ± 16.17 (ab)	0	0	0	0	100
PCF - 10% leached	12.22 ± 0.77 (a)	81.33 ± 8.33 (ab)	0	0	0	0	100
PCF - 10% unleached	12.47 ± 0.77 (a)	84.67 ± 6.11 (ab)	0	0	0	0	100
PCF - 15% leached	11.65 ± 1.54 (ab)	90.00 ± 4.00 (a)	0	0	0	0	100
PCF - 15% unleached	10.36 ± 1.83 (abc)	52.00 ± 7.21 (bc)	0	0	0	0	100
PCF - 20% leached	11.79 ± 1.93 (ab)	79.33 ± 4.62 (ab)	0	0	0	0	100
PCF - 20% unleached	8.78 ± 0.73 (bc)	58.00 ± 9.17 (ab)	0	0	0	0	100
PCF - 50% leached	12.80 ± 1.38 (a)	75.33 ± 5.03 (ab)	0	0	0	0	100
PCF - 50% unleached	8.23 ± 1.65 (c)	52.00 ± 15.62 (bc)	0	0	0	0	100
PCF - 100% leached	4.03 ± 1.08 (d)	19.33 ± 18.15 (cd)	0	33.33	0	0	66.67
PCF - 100% unleached	3.18 ± 0.98 (d)	6.00 ± 10.39 (d)	0	66.67	33.33	0	0
Control Pine	11.41 ± 0.82 (ab)	80.83 ± 14.81 (ab)	0	0	0	0	100

Chapter 10

Conclusion

Bagasse pyrolysis liquid contains various chemicals, such as acetic acid, formic acid, propionic acid, phenols, and guaiacol derivatives, exhibiting anti-fungal and anti-termite properties. At low concentration (0.25 % in a culture media), pyrolysis liquid was able to inhibit the growth of *C. puteana* and *T. versicolor*. It also has a repellent effect on the termites, discourages the consumption activity when the paper is treated at a higher concentration of pyrolysis liquid. Filter paper treated with 10 % of pyrolysis liquid caused 100 % of termite mortality, while only 5.65 %–7.03 % of the treated filter papers consumed by termites at such concentration. Due to its efficacity against fungi and termites, pyrolysis liquid is potentially interesting for the formulation of wood protection systems.

The measurement of remained paper area in termite's bioassay using the k-means clustering method is rapid, precise, and simple to conduct. Although it clearly necessitated the utilization of a high level of random access memory, we have estimated the relationships between the number of processed images and the needed memory, thus allowing us to make a compatible strategy in choosing the number of images that could be analyzed at once based on our machine's capacity.

When treated with pyrolysis liquid only, the retention was 734.23 ± 20.59 kg/m^3. By excluding the water from the pyrolysis liquid, the retention was 423.65 ± 11.88 kg/m^3. In this case, it is possible to use vacuum/pressure systems without any problem. Treated wood which oven-dried at 103 °C shows lower leaching and promote agglomeration of pyrolysis liquid product inside wood cells. However, there was no indication of any chemical reaction between wood and pyrolysis liquid as shown on the FTIR results. Pyrolysis liquid is highly leachable in water, in which phenolic and guaiacol compounds were detected by GC-MS in the leachate products. The leachate products showed the lowest activity against fungi at highest drying temperature.

Pyrolysis liquid was not sufficiently compelling to protect wood against fungi when applying at low concentration (5–20%). The performance under leaching test even decreases the efficacy of pyrolysis liquid. Moreover, the fungal correction factor test suggested that pyrolysis liquid remains leachable from the wood when exposed to high humidity. A good improvement of

treated wood was observed when treated the samples at high loadings (50 and 100%). In the case of the termites' test, results suggest that pyrolysis liquid is effective when applied at concentration 25%; however, considering the instability of pyrolysis liquid, the treated wood's performance is believed to be decreased over time when exposed to high humidity.

Part IV

Conclusion and Perspective

Chapter 11

Conclusion and Perspective

11.1 General Conclusion

The valorization of biomass waste to generate bio-active chemicals is interesting given that biomass is the cheapest and most abundant resource found in large volumes, especially those that come from agricultural residue. Slow pyrolysis as a biomass thermochemical conversion method is promising for co-producing char and pyrolysis liquid in the perspective of energy densification and valorization of by-product. The recovery of condensable organic vapor for further utilization reduces the impact of air pollution, considering the conventional practice of slow pyrolysis is only intended for char generation.

In this study, sugarcane bagasse was pyrolyzed using different parameters, such as temperature (400 °C and 500 °C), heating rate (1 °C/min and 10 °C/min), and holding time (30 min and 60 min). The char generated from the process improves the properties of biomass to be used for energy. Simultaneously, the liquid product's recovery for another utilization offers an alternative route in wood protection application.

Pyrolysis temperature and heating rate had a significant influence on the char properties and the yields of products. The yield of char decrease with the increase of pyrolysis temperature but results in the favorable calorific value improvement; while at the same time generating a high mass of liquid yield. At the temperature and heating rate of 500 °C and 10 °C/min, the yield of char and pyrolysis liquid was 28.97% and 55.46%, respectively. Apart from its utilization for fuel due to the high carbon content (70.50 %) and HHV (27.85 MJ/kg), bagasse char is also potential to be used as soil amendments, as it has a high ash recovery (up to 98 %).

Pyrolysis liquid produced at different temperatures differs slightly on their proportion of chemical compositions; however, water, acetic acid, glycolaldehyde, 1-hydroxy-2-propanone, methanol, formic acid, levoglucosan, furfural, followed by some phenol compounds and guaiacol derivatives, were found as the principal compounds. Pyrolysis liquid produced at 400 °C results in slightly higher total organic contents quantified by GC–MS. From the quantification of 56 chemical compounds, the total organic contents quantified were 29.63 % and 25.63 % for pyrolysis liquid produced at 400 °C and 500 °C,

respectively.

Pyrolysis liquid, which used to be a by-product of the slow pyrolysis, is a potent candidate for wood protection agents against fungi and termites. Results indicate that at low concentration (0.25 % in a culture media), pyrolysis liquid was able to inhibit the growth of *C. puteana* and *T. versicolor*. Also, it has a repellent effect on termites and is very toxic when the paper is treated at a high pyrolysis liquid concentration (10%). Various chemicals, including acetic acid, formic acid, propionic acid, phenols, and guaiacol derivatives, have been reported to exhibit anti-fungal and anti-termite activity. The synergistic effect between those compounds is likely to be responsible for its efficacy. Further, in contrast to creosote, a by-product from coal distillation, pyrolysis liquid contains no polycyclic aromatic hydrocarbon compounds (PAHs), or they were insignificant (less than 1 ppm).

Pyrolysis liquid contains considerably high water content; however, it decreases viscosity and a pre-heating process before the application can be avoided. Once incorporated in wood through vacuum impregnation, the retention of pyrolysis liquid when used alone was 734.23 ± 20.59 kg/m^3. By excluding the water from the pyrolysis liquid, the retention is 423.65 ± 11.88 kg/m^3. Different drying temperatures of wood samples after being treated with pyrolysis liquid (e.g., ambient, 40, 60, 80, and 103 °C) gave significant differences in the product's loading in wood, while the high temperature (at 103 °C) seems to promote agglomeration of pyrolysis liquid product inside wood cells; however, there was no indication of any chemical reaction between wood and pyrolysis liquid as shown on the FTIR results.

Pyrolysis liquid is highly leachable in water. Compounds such as 3-methyl-1,2-cyclopentanedione, phenol, 3,4-dimethylphenol , phenol-2-methoxy, phenol-2-methoxy-4-methyl, and 2,6-dimethoxyphenol were detected in the GC–MS quantification using the leachate products collected from the different drying temperatures. The leachate products also showed some activity against *C. puteana* and *T. versicolor* when incorporated in a culture media in the fungal growth inhibition test. Samples dried at ambient temperature indicates the strongest activity, notably against *C. puteana*.

Pyrolysis liquid was not sufficiently compelling to protect wood against fungi when applying at low concentration (5-20%). The performance under leaching test even decreases the efficacy of pyrolysis liquid. Moreover, the fungal correction factor test suggested that pyrolysis liquid remains leachable from the wood when exposed to high humidity. A good improvement of treated wood was observed when treated the samples between 50 and 100%. In the case of the termites' test, results suggest that pyrolysis liquid is effective when applied at concentration 25%; however, considering the instability of pyrolysis liquid, the treated wood's performance is believed to be decreased

over time when exposed to high humidity.

In addition to those scientific results, the experiments on the termites' test using filter paper allowed us to develop a rapid, simple, and precise calculation on the paper area measurement using the k-means clustering method. Although it necessitated the utilization of a high level of random access memory, we have estimated the relationships between the number of processed images and the needed memory, thus allowing us to make a compatible strategy in choosing the number of images that could be analyzed at once based on our machine's capacity.

11.2 Perspective

Due to its anti-fungal and anti-termite properties, pyrolysis liquid is potentially interesting for the formulation of wood protection systems. However, some issues related to its acidity nature and leachability need to be highlighted prior to use it for wood protectants. Despite its good efficacy against fungi and termites, the use of pyrolysis liquid as a stand-alone method does not seem very promising, considering its high instability once it is integrated into the wood. Wood treated with pyrolysis liquid remains highly leachable when exposed to water or high humidity, indicating that future studies should be conducted to find out how to decrease its leachability. Further study is worth carrying out, particularly in investigating the formulation strategies (fixation using the minimum product through formulation for extended efficacy through life and minimizing the impacts on human health and the environment), such as through co-impregnation with water repellents such as linseed oil and resin acid.

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Appendix

A. Data recapitulation: Specimens treated with crude pyrolysis liquid at different drying temperatures

Abbreviations:

IR = Impregnation rate
WPG = Weight percent gain
WPGL = Weight percent gain after leaching
WL = Weight loss
WLL = Weight loss caused by leaching
LR = Leaching rate
WLE = Weight loss caused by evaporation
WLCF = Weight loss after the fungal correction factor test
ER = Evaporation rate
MC = Moisture content

Table 1: Beech samples treated with crude pyrolysis liquid at different drying temperatures

Treatment	Retention (kg/m^3)	IR (%)	WPG (%)	WPGL (%)	WLL (%)	LR (%)	WL termites (%)
Beech-20 °C	743.34 ±16.48	119.79 ±6.73	48.94 ±1.71	24.58 ±1.51	16.77 ±1.41	50.49 ±3.75	2.68 ±0.29
Beech-40 °C	730.80 ±22.24	116.07 ±8.82	41.26 ±2.23	18.21 ±0.95	16.92 ±1.57	56.88 ±2.95	1.39 ±0.11
Beech-60 °C	729.88 ±36.63	117.03 ±13.48	42.03 ±3.47	15.15 ±1.96	18.71 ±1.15	63.72 ±1.81	1.67 ±0.05
Beech-80 °C	732.84 ±13.12	116.26 ±3.11	35.09 ±0.87	15.62 ±1.27	14.43 ±0.68	55.55 ±2.73	1.37 ±0.11
Beech-103 °C	734.27 ±6.32	115.63 ±4.25	31.31 ±1.04	17.22 ±0.44	11.12 ±0.41	45.99 ±1.39	1.86 ±0.15

Table 2: Evaporation test using beech samples

Treatment	Retention (kg/m^3)	IR (%)	WPG (%)	WLE (%)	ER (%)	WL decay (%)[a,b]	MC decay (%)[b]
Beech-103 °C	743.03 ±21.95	119.53 ±7.28	33.33 ±1.98	0.54 ±0.06	2.16 ±0.23	0.66 ±0.41	85.80 ±3.68

[a] Corrected values

[b] Virulence for *T. versicolor* (n = 12): WL = 38.83 ± 9.65; MC = 111.15 ± 39.65

Appendix

B. Data recapitulation: Specimens treated with different concentration of pyrolysis liquid

Table 3: Correction factor for the fungal test of the beech samples

Treatment	Retention (kg/m^3)	IR (%)	WPG (%)	WPGL (%)[a]	WLL (%)[a]	LR (%)[a]	WLCF (%)	MC (%)
Beech-5 %	23.35 ±1.31	73.64 ±7.75	2.41 ±0.17	1.09 ±0.22	1.28 ±0.24	59.96 ±7.74	L = -0.18 ± 0.87 U = 0.76 ± 0.08	L = 38.28 ± 14.89 U = 55.57 ± 9.33
Beech-10 %	48.53 ±2.75	78.32 ±8.52	4.19 ±0.37	1.93 ±0.48	2.11 ±0.23	54.27 ±8.83	L = 0.10 ± 0.87 U = 1.28 ± 0.43	L = 39.27 ± 16.16 U = 66.67 ± 10.39
Beech-15 %	72.27 ±3.06	76.60 ±7.34	5.50 ±0.45	2.67 ±0.38	2.67 ±0.51	52.08 ±6.75	L = 0.36 ± 0.41 U = 1.49 ± 0.50	L = 36.07 ± 9.54 U = 77.31 ± 19.21
Beech-20 %	95.61 ±3.83	76.76 ±6.54	6.81 ±0.47	3.29 ±0.43	3.33 ±0.21	53.00 ±4.33	L = 0.58 ± 0.06 U = 2.26 ± 0.27	L = 34.26 ± 3.35 U = 76.93 ± 9.34
Beech-50 %	285.26 12.58	86.98 ±8.02	12.75 ±1.03	6.31 ±0.60	5.75 ±0.49	51.87 ±3.93	L = 0.51 ± 0.46 U = 4.80 ± 0.69	L = 47.09 ± 10.84 U = 74.46 ± 9.01
Beech-100 %	747.28 ±28.71	118 ±10.51	34.28 ±2.52	23.94 ±1.06	6.93 ±0.48	28.75 ±0.94	L = 3.74 ± 0.48 U = 10.31 ± 0.56	L = 68.92 ± 3.74 U = 75.96 ± 4.08

[a] Corrected values

Table 4: Correction factor for the fungal test of the pine samples

Treatment	Retention (kg/m^3)	IR (%)	WPG (%)	WPGL (%)[a]	WLL (%)[a]	LR (%)[a]	WLCF (%)	MC (%)
Pine-5 %	24.37 ±2.00	87.19 ±7.27	2.29 ±0.19	1.01 ±0.22	1.15 ±0.12	55.70 ±9.01	L = -1.82 ± 1.47 U = 0.31 ± 0.61	L = 70.91 ± 20.91 U = 78.46 ± 18.66
Pine-10 %	50.00 ±3.42	87.30 ±9.95	3.78 ±0.41	1.55 ±0.25	2.08 ±0.29	60.34 ±6.13	L = -1.14 ± 1.21 U = 1.00 ± 0.19	L = 63.78 ± 17.19 U = 83.26 ± 15.44
Pine-15 %	75.77 ±5.52	90.15 ±16.66	5.70 ±0.87	3.00 ±0.56	2.45 ±0.35	47.97 ±4.19	L = -0.12 ± 0.83 U = 1.90 ± 0.30	L = 60.78 ± 19.69 U = 88.92 ± 8.87
Pine-20 %	107.48 ±7.22	93.00 ±20.00	7.26 ±1.19	4.31 ±0.87	3.09 ±0.54	44.30 ±4.02	L = -0.24 ± 0.81 U = 2.25 ± 0.31	L = 66.12 ± 11.48 U = 88.44 ± 3.46
Pine-50 %	304.54 ±13.65	108.00 ±17.20	15.13 ±1.97	8.09 ±1.75	5.91 ±0.44	47.04 ±4.66	L = -0.23 ± 0.60 U = 5.67 ± 0.80	L = 88.35 ± 8.20 U = 97.64 ± 10.45
Pine-100 %	594.71 ±124.20	101.28 ±23.50	27.46 ±5.93	18.91 ±4.84	6.18 ±0.78	30.96 ±1.94	L = 2.57 ± 0.54 U = 8.40 ± 1.59	L = 74.42 ± 8.72 U = 82.69 ± 2.49

[a] Corrected values

Table 5: Beech samples treated with pyrolysis liquid at different concentrations, exposed to *T. versicolor*

Treatment	Retention (kg/m^3)	IR (%)	WPG (%)	WPGL (%)[a]	WLL (%)[a]	LR (%)[a]	WL decay (%)[a,b]	MC decay (%)[b]
Beech-TV 5 %	23.28 ±1.40	69.38 ±8.02	2.25 ±0.21	0.72 ±0.22	1.53 ±0.24	69.97 ±8.19	L = 16.44 ± 10.80 U = 24.47 ± 5.93	L = 64.73 ± 24.39 U = 91.72 ± 23.33
Beech-TV 10 %	46.13 ±2.65	69.38 ±8.65	3.80 ±0.36	1.20 ±0.40	2.31 ±0.67	68.25 ±10.23	L = 21.21 ± 9.25 U = 19.89 ± 8.80	L = 77.18 ± 15.21 U = 120.99 ± 18.52
Beech-TV 15 %	75.06 ±4.47	74.03 ±8.87	5.51 ±0.59	2.22 ±0.37	3.03 ±0.57	60.41 ±4.68	L = 11.22 ± 9.18 U = 10.25 ± 3.95	L = 52.04 ± 8.65 U = 107.1 ± 12.50
Beech-TV 20 %	103.52 ±2.85	81.03 ±5.18	7.24 ±0.53	2.61 ±0.53	4.03 ±0.42	63.08 ±6.64	L = 29.79 ± 10.25 U = 14.42 ± 6.46	L = 85.81 ± 18.97 U = 130.48 ± 14.09
Beech-TV 50 %	294.26 ±21.39	91.13 ±13.75	15.42 ±2.01	9.08 ±1.37	5.30 ±0.63	41.45 ±4.34	L = 3.52 ± 2.49 U = 2.56 ± 0.95	L = 87.35 ± 7.89 U = 98.19 ± 17.70
Beech-TV 100 %	737.25 ±22.67	115.74 ±6.02	34.07 ±1.56	23.29 ±2.01	7.65 ±0.75	31.48 ±3.51	L = 2.27 ± 0.29 U = 2.33 ± 0.34	L = 84.92 ± 4.23 U = 84.84 ± 4.67

[a] Corrected values

[b] Virulence for *T. versicolor* (n = 20): WL = 26.28 ± 8.76 ; MC = 82.01 ± 24.21

Table 6: Pine samples treated with pyrolysis liquid at different concentrations, exposed to *C. puteana*

Treatment	Retention (kg/m^3)	IR (%)	WPG (%)	WPGL (%)[a]	WLL (%)[a]	LR (%)[a]	WL decay (%)[a,b]	MC decay (%)[b]
Pine-CP 5 %	23.32 ±3.22	81.56 ±19.96	2.29 ±0.51	0.80 ±0.40	1.39 ±0.44	66.32 ±15.94	L = 32.96 ± 6.92 U = 32.48 ± 10.98	L = 68.06 ± 9.44 U = 64.49 ± 12.65
Pine-CP 10 %	50.44 ±3.34	79.19 ±12.71	4.14 ±0.54	1.73 ±0.31	2.41 ±0.71	60.90 ±6.56	L = 27.79 ± 16.15 U = 9.51 ± 9.84	L = 83.88 ± 22.30 U = 86.37 ± 27.00
Pine-CP 15 %	83.20 ±4.67	92.10 ±15.37	6.34 ±0.96	2.44 ±0.66	3.56 ±0.55	63.09 ±6.47	L = 24.40 ± 15.80 U = 4.96 ± 2.39	L = 105.09 ± 21.25 U = 117.55 ± 14.58
Pine-CP 20 %	106.65 ±10.97	90.10 ±14.74	7.62 ±0.89	3.51 ±0.16	3.83 ±0.91	54.97 ±3.52	L = 21.74 ± 11.21 U = 6.22 ± 4.16	L = 65.06 ± 19.66 U = 97.27 ± 30.50
Pine-CP 50 %	275.82 ±16.87	90.45 ±8.26	14.20 ±1.16	7.78 ±0.83	5.26 ±0.44	45.38 ±1.52	L = 14.31 ± 14.24 U = 2.72 ± 0.30	L = 80.98 ± 25.17 U = 107.66 ± 9.86
Pine-CP 100 %	657.49 ±89.87	105.06 ±18.36	30.47 ±5.24	20.70 ±4.03	6.21 ±0.59	30.05 ±2.12	L = 2.45 ± 0.55 U = 2.89 ± 1.51	L = 82.79 ± 6.49 U = 77.96 ± 4.97

[a] Corrected values

[b] Virulence for *C. puteana* (n = 19): WL = 41.87 ± 11.48 ; MC = 89.23 ± 18.99

Table 7: Pine samples treated with pyrolysis liquid at different concentrations, exposed to *R. placenta*

Treatment	Retention (kg/m^3)	IR (%)	WPG (%)	WPGL (%)[a]	WLL (%)[a]	LR (%)[a]	WL decay (%)[a,b]	MC decay (%)[b]
Pine-RP 5 %	22.41 ±2.54	70.44 ±11.17	2.26 ±0.25	1.19 ±0.12	0.98 ±0.16	52.48 ±7.33	L = 27.30 ± 18.73 U = 25.86 ± 16.17	L = 121.26 ± 23.71 U = 130.31 ± 23.65
Pine-RP 10 %	52.78 ±5.06	89.73 ±22.64	4.46 ±0.84	1.53 ±0.30	2.64 ±0.62	63.94 ±6.83	L = 37.63 ± 17.38 U = 42.25 ± 4.06	L = 131.48 ± 24.77 U = 131.65 ± 10.31
Pine-RP 15 %	82.62 ±5.41	93.92 ±16.58	6.54 ±0.83	3.12 ±0.61	3.42 ±0.43	54.05 ±6.00	L = 34.36 ± 17.56 U = 17.01 ± 17.12	L = 135.50 ± 26.30 U = 121.41 ± 25.04
Pine-RP 20 %	106.83 ±10.89	91.66 ±19.34	7.73 ±1.32	3.53 ±0.92	3.77 ±0.74	54.24 ±5.16	L = 26.38 ± 21.39 U = 15.10 ± 11.67	L = 121.56 ± 25.18 U = 113.68 ± 15.05
Pine-RP 50 %	255.11 ±33.71	85.90 ±18.61	13.78 ±2.46	7.71 ±2.12	5.18 ±0.96	44.91 ±3.67	L = 23.12 ± 11.26 U = 6.22 ± 1.89	L = 115.21 ± 14.40 U = 109.69 ± 12.63
Pine-RP 100 %	682.87 ±65.72	116.89 ±26.52	33.13 ±6.50	20.55 ±3.76	7.70 ±1.39	7.70 ±1.39	L = 2.15 ± 0.87 U = 4.91 ± 1.01	L = 78.85 ± 15.40 U = 97.54 ± 17.80

[a] Corrected values

[b] Virulence for *R. placenta* (n = 19): WL = 47.53 ± 15.40; MC = 161.21 ± 37.74

Appendix

C. Water absorption during leaching test

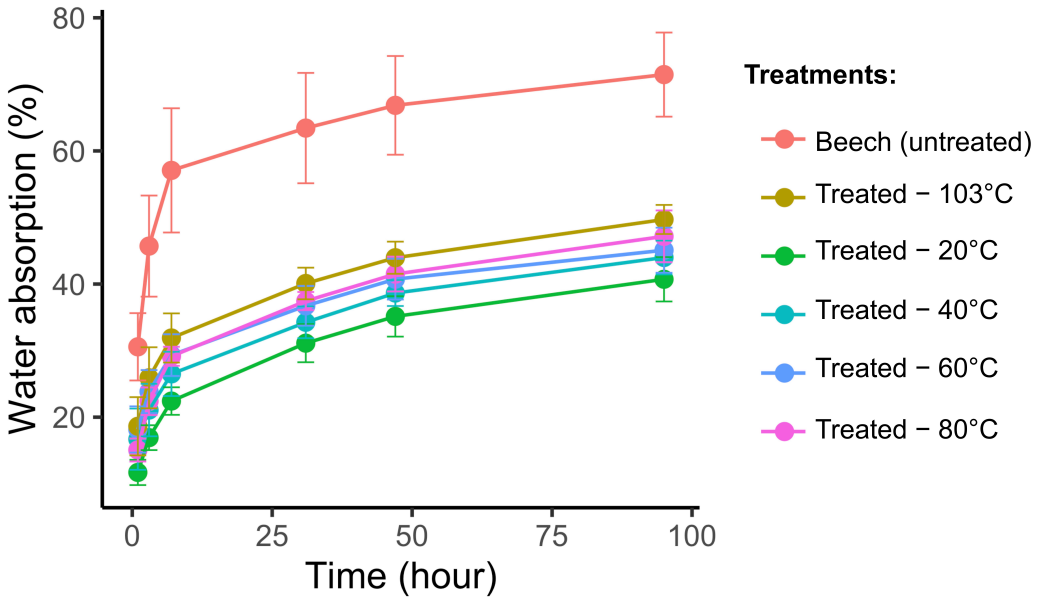

Figure 1: Water absorption during leaching test using beech samples dried at different temperatures

Résumé élargi de la thèse

I. Introduction Générale

Les résidus de biomasse végétale agricole possèdent un grand potentiel comme ressources renouvelables pour la production d'énergie et de matériaux. L'utilisation durable de la biomasse peut être implémentée en utilisant la pyrolyse avec l'objectif de la densification énergétique (conversion de la biomasse en charbon) et l'utilisation de son sous-produit comme agent protecteur du bois ou des biomatériaux. En effet, la biomasse doit être utilisée immédiatement en raison de sa propension à la biodégradation. Le potentiel de la biomasse lignocellulosique pour la production d'énergie peut être mis en œuvre grâce à la conversion de la biomasse par pyrolyse. Ce processus transforme les matières organiques en utilisant la chaleur dans un environnement pauvre en oxygène, décompose certaines molécules constitutives de la biomasse, tels que les hémicelluloses, la cellulose et la lignine, en composés plus petits, produisant des fractions solides (charbon), liquides et gazeuses (Mohan et al., 2006). En ajustant les paramètres de pyrolyse, tels que le niveau de température, la vitesse de chauffe et le temps de séjour, la quantité des produits les plus désirés peut être contrôlée (Carrier et al., 2011).

La pyrolyse lente est une conversion énergétique largement éprouvée. Dans ce processus, la biomasse est lentement chauffée pour produire du charbon de bois, et les vapeurs organiques sont souvent simplement considérées comme des déchets. (Bridgwater et al., 2007). Cependant, des études passées et récentes ont montré un certain intérêt pour la récupération de ce type de vapeurs organiques condensables en raison de sa grande composition en composés chimiques bioactifs tels que les acides, les phénols, les furanes et les guaiacols. Cette fraction liquide a une nomenclature variée dans la littérature, comme l'huile de pyrolyse, le liquide de pyrolyse, la bio-huile, la fumée liquide, et les distillats de bois (Bridgwater, 2003), et ses propriétés pourraient différer les unes des autres en fonction des paramètres de pyrolyse et de la matière première utilisée. En fait, dans de nombreux pays asiatiques, la pyrolyse lente est pratiquée depuis longtemps pour produire à la fois du charbon de bois et des produits liquides (Mathew and Zakaria, 2015). Les agriculteurs traditionnels de ces pays tirent profit du produit liquide en l'utilisant comme stimulant de croissance des plantes et comme biopesticide (Tiilikkala et al., 2010).

D'autre part, le bois a été massivement utilisé en raison de ses excellentes propriétés physiques, mécaniques et chimiques. Néanmoins, certaines essences ont des utilisations finales limitées en raison de leur sensibilité aux dégradations biologiques (champignons et insectes, en particulier). Dans ce cas, le liquide de pyrolyse pourrait être une voie intéressante pour la protection du bois. Plusieurs chercheurs ont montré que le liquide de pyrolyse possède une activité anti-fongique et anti-termite (Oramahi et al., 2018; Barbero-López et al., 2019). En outre, il a été rapporté que le liquide de pyrolyse peut être considéré comme une alternative à la créosote, ce qui est plus avantageux car il ne contient pas d'hydrocarbures aromatiques polynucléaires (HAP) (Temiz et al., 2013a), limitant ainsi l'impact sur l'environnement. Dans la littérature, l'utilisation des produits liquides de pyrolyse pour la protection du bois est relativement limitée et présente une grande variabilité en raison des différents types de matières premières et de méthodes utilisées. C'est pourquoi, nous nous sommes concentrés sur la valorisation du liquide de pyrolyse provenant de la pyrolyse lente, qui sert généralement de produit secondaire.

Dans cette étude, la bagasse de canne à sucre, un résidu de fibre qui reste après le traitement de la canne à sucre, a été utilisée comme matière première pour la pyrolyse. La biomasse est originaire de l'île de la Réunion et a été choisie comme modèle de biomasse tropicale. Le choix de la bagasse est déterminé en tenant compte de trois points : sa disponibilité, sa présence en tant que déchet ou sous-produit au lieu de matières premières, et le potentiel de sa valorisation. De plus, à notre connaissance, il n'y avait pas de précédent de recherche sur le liquide de pyrolyse obtenu à partir de la bagasse de canne à sucre pour une application de traitement du bois. La conversion de la bagasse de canne à sucre en charbon de bois pour la production d'énergie pourrait également permettre de résoudre les problèmes de saisonnalité et de biodégradabilité de cette biomasse. Étant une plante saisonnière, la bagasse doit être stockée si elle doit être utilisée en dehors de sa période de récolte maximale. De plus, étant un matériau hygroscopique, la bagasse est sujette à des changements d'humidité pendant le stockage et à la biodégradation (Breccia et al., 1997; Dong et al., 2013). Pour surmonter ces problèmes, la conversion thermochimique de la bagasse peut être appliquée en la transformant en un charbon riche en carbone, qui peut ensuite être stocké sans aucune dépertition d'énergie. En outre, jusqu'à présent, peu d'études ont porté sur un processus de co-valorisation de la biomasse couplant (i) le processus de pyrolyse pour produire de l'énergie et des gaz, et (ii) la conservation et la valorisation des composés chimiques condensables issus de ce premier processus thermochimique en composés chimiques de valeur, plus particulièrement pour leurs activités anti-fongiques et anti-termites. Les principaux objectifs

de ces travaux seront les suivants:

1. Déterminer la condition optimale du paramètre du processus de pyrolyse pour la co-production du charbon et du liquide de pyrolyse.
2. Évaluer la composition chimique et les activités anti-fongiques et anti-termites du liquide de pyrolyse sélectionné.
3. Traiter le liquide de pyrolyse dans les échantillons de bois pour étudier son potentiel de protection du bois, déterminer la température de séchage optimale, analyser ses propriétés de lessivage et obtenir le seuil de concentration efficace contre les champignons et les termites.

Cette thèse est divisée en quatre parties. La première partie est consacrée à l'analyse bibliographique sur la valorisation de la biomasse par pyrolyse et le potentiel du liquide de pyrolyse pour la protection du bois. Les deuxième et troisième parties couvrent les résultats des travaux expérimentaux menés dans cette étude. La deuxième partie présente les travaux sur les paramètres de la pyrolyse lente et leur effet sur les propriétés de carbonisation et le rendement du charbon et du liquide de pyrolyse, ainsi que la composition chimique du liquide de pyrolyse. La troisième partie présente les résultats des essais biologiques sur les anti-fongiques et les anti-termites du liquide de pyrolyse dans les boîtes de Pétri, le développement de la mesure de la surface du papier en utilisant la méthode de *k-means clustering* pour l'essai sur les termites, et le traitement du bois avec le liquide de pyrolyse tout en étudiant son efficacité contre les champignons et les termites. Enfin, la dernière partie présente la conclusion générale sur le travail et les résultats, ainsi que les perspectives pour les travaux futurs.

II. Valorisation énergétique de la bagasse de canne à sucre par pyrolyse lente

2.1 Introduction

Cette partie présente les résultats des études sur la valorisation de la bagasse de canne à sucre par pyrolyse lente. La bagasse a été convertie pour produire du charbon et du liquide de pyrolyse en utilisant un réacteur de laboratoire à lit fixe. Comme mentionné précédemment, la pyrolyse lente, qui se produit à une faible vitesse de chauffe et un long temps de séjour, produit un charbon de bonne qualité (Bridgwater, 2003). Cette technique est intéressante pour convertir la biomasse instable, qui contient plus de volatils, comme la bagasse, pour obtenir un produit stable et riche en énergie. Le charbon peut également être utilisé pour la production d'électricité ou être valorisé comme un produit de grande valeur comme le charbon actif et les amendements du sol (Pecha and Garcia-Perez, 2020).

Des études précédentes ont montré que la pyrolyse lente de la bagasse est optimale pour produire le rendement de charbon le plus élevé à une vitesse de chauffe entre 2 °C/min et 16 °C/min et à une température de plus de à 240 °C, des différences significatives de perte de masse se produisant à des températures entre 300 °C et 500 °C (Katyal et al., 2003; Carrier et al., 2011). À partir de ces résultats, nous avons pu établir les expérimentations de pyrolyse lente à une vitesse de chauffe plus basse (1 °C/min et 10 °C/min) et à une température intermédiaire (400 °C et 500 °C), car une bonne qualité de charbon pouvait être obtenue avec ces gammes de températures (Demirbas, 2007).

L'objectif de notre étude est donc d'évaluer le potentiel de la valorisation de la bagasse par pyrolyse lente. Le charbon résultant de différents paramètres de pyrolyse a été évalué en fonction de son rendement, des analyses immédiates et ultimes, et de son pouvoir calorifique pour évaluer son potentiel en tant que source d'énergie. Nous avons récupéré le liquide de pyrolyse issu du processus de condensation pour qu'il serve de candidat en tant qu'agent de protection du bois. La composition chimique des liquides de pyrolyse sélectionnés à partir du processus a également été examinée.

2.2 Matériel et méthods

La bagasse de canne à sucre (*Saccharum* spp.) avec une taille de particule inférieure à 2 mm a été utilisé pour les essais de pyrolyse. La pyrolyse a été fait à une température de 400 °C et 500 °C, à une vitesse de chauffe de 1 °C/min et 10 °C/min, et temps de séjour de 30 min et 60 min, dans un réacteur à lit fixe à l'échelle du laboratoire. Le réacteur est également équipé

d'un système de condensation qui a permis de condenser et de refroidir les produits volatils générés par la pyrolyse pour produire le liquide de pyrolyse.

L'analyse immediate, ultime et calorifique, la récupération des cendres, le rendement énergétique et la densité énergétique de la bagasse et du charbon ont été caractérisés. La composition chimique du liquide de pyrolyse (produit à 400 et 500 °C, à une vitesse de chauffe 10 °C/min, et temps de séjour de 60 min) a été étudiée à l'aide de la GC-MS et de la FTIR. La teneur en eau du liquide de pyrolyse a été déterminée à l'aide d'un titrage volumétrique Karl Fisher.

Une analyse de régression multivariée a été faite pour déterminer la corrélation de chaque paramètre et ses effets sur les valeurs de rendement et les propriétés des charbons. La température, la vitesse de chauffe et le temps de séjour étaient les paramètres indépendants. Nous avons ensuite déterminé statistiquement l'impact de chacun de ces paramètres, individuellement, en utilisant la valeur p et globalement en voyant leur valeur R^2.

2.3 Résultats et discussion

La bagasse contient 8,5% d'humidité, 82,4% de matières volatiles, 13,4% de carbone fixe, et 4,2% de cendres. La bagasse contient également un très faible ratio carbone fixe / matières volatiles en raison de la forte teneur en matières volatiles. La bagasse contient 47,3% de carbone, 5,7% d'hydrogène, 0,4% d'azote, et 46,7% d'oxygène et de soufre totaux. Le HHV était de 18,14 MJ/kg. L'analyse démontre que la biomasse étudiée est comparable aux autres bagasses de canne à sucre rapportées dans différentes études.

La température a été mise en évidence comme le paramètre le plus important, influençant le rendement en charbon et le rendement en liquide. Les deux vitesses de chauffe (1 °C/min et 10 °C/min) ont également montré un effet significatif sur le rendement en charbon et en liquide. Par ailleurs, il n'y a pas de différence significative dans les rendements des produits pour le temps de séjour de 30 min et 60 min. Dans toutes les conditions testées, la moyenne du rendement en charbon et en liquide a varié entre 28,81%–35,12%, et 49,67%–55,46%.

La température et la vitesse de chauffe ont influencé de manière significative la teneur en matières volatiles, cendres, carbone fixe, carbone élémentaire et HHV, tandis que le temps de séjour ne contribue qu'à la teneur en matières volatiles. Après avoir été pyrolysée, la bagasse carbonisée a une teneur en matières volatiles de 24,31%–25,80% à 400 °C, et de 13,01%–16,43% à 500 °C. Le carbone fixe le plus élevé a été observé à 68,50%–73,01%. La teneur en cendres varie de 10,79%–15.50%, inférieure à la teneur en cendres de l'étude conduite par Varma and Mondal (2017) (16,25%). Les taux élevés

de récupération des cendres (jusqu'à 98%) ont également montré que les cendres sont retenues dans le charbon et qu'elles sont intéressantes pour leur application en tant qu'amendements du sol (Ghysels et al., 2019). Le HHV passe également de 18,14 MJ/kg à 28,67 MJ/kg à la température la plus élevée et à la vitesse de chauffe la plus faible. Le rapport molaire O/C et H/C de la bagasse de canne à sucre était respectivement de 0,74 et 1,43.

Le liquide de pyrolyse obtenu est de couleur brun foncé avec une odeur piquante et fumée. Selon l'analyse FTIR, il a été confirmé que le liquide de pyrolyse contenait divers composants chimiques, notamment des composés oxygénés, tels que des acides carboxyliques, des alcools, des phénols, des aldéhydes et des cétones, et d'autres composants chimiques tels que des alcanes, des alcènes et des aromatiques. Les spectres obtenus étaient similaires à ceux rapportés Varma and Mondal (2017).

L'analyse chimique par GC-MS a permis la quantification de 56 composés chimiques, dont les teneurs organiques totales quantifiées étaient respectivement de 29,63% et de 25,63% pour le liquide de pyrolyse produit à 400 °C et 500 °C. L'acide acétique, le glycolaldéhyde, la 1-hydroxy-2-propanone, le méthanol, l'acide formique et le lévoglucosane sont les principaux composés. Si l'on exclut l'eau, l'acide acétique était le principal composé du liquide de pyrolyse, représentant 7,22%–8,48% du liquide. La bagasse de canne à sucre aurait une teneur élevée en xylose (15,5%–28,9%) (Bezerra and Ragauskas, 2016), qui contribue à la formation d'acide acétique par l'élimination des groupes acétyle de l'unité xylose (Demirbas, 2007; Temiz et al., 2013a).

Le liquide de pyrolyse a $42,34 \pm 0,24\%$ et $42,30 \pm 0,14\%$ de la teneur en eau à des températures de 400 °C et 500 °C, respectivement. La variation de la teneur en eau est affectée par la teneur en humidité de la biomasse et la réaction de déshydratation pendant la pyrolyse. Le pH a été enregistré à 2, dans lequel la caractéristique acide était due à la présence de l'acide organique, des aldéhydes et des phénols (Varma and Mondal, 2017).

III. Performances des liquides de pyrolyse pour la protection du bois

3.1 Introduction

Cette partie présente les potentialités d'utilisation du liquide de pyrolyse pour la protection du bois. Comme cela a été précédemment rapporté, son utilisation est déjà effective dans de nombreux domaines tels que les biocides, les insecticides, les fongicides, les stimulateurs de croissance des plantes et comme source de produits chimiques à forte valeur ajoutée (Tiilikkala et al., 2010; Mathew and Zakaria, 2015; Pimenta et al., 2018). En raison de sa grande composition en produits chimiques bioactifs, tels que les acides organiques, les phénols, les cétones, les aldéhydes, les furanes et les guaiacols, le liquide de pyrolyse était supposé protéger le bois contre les champignons et les termites (Temiz et al., 2013a). Barbero-López et al. (2019) a indiqué que les distillats de pyrolyse issues d'écorce d'épicéa et de bouleau, de fibres de chanvre obtenues à des températures de 275 °C–350 °C permettent d'inhiber la croissance des champignons de pourriture du bois. Oramahi et al. (2018) ont également étudié le liquide de pyrolyse du stipe du palmier à huile à un 350 °C comme anti-termite.

Dans cette étude, nous avons utilisé les liquides de pyrolyse bruts obtenus à partir des nos expériences de pyrolyse. Le liquide de pyrolyse a tout d'abord été testé pour déterminer le seuil d'efficacité contre les champignons et les termites. Le liquide de pyrolyse utilisé a été obtenu à partir des températures de 400 °C et de 500 °C, de la vitesse de chauffe de 10 °C/min, et du temps de séjour de 60 min. Pour le test d'efficacité vis-à-vis des termites, une méthode rapide de mesure de la surface de papier résiduel consommée par les termites a été dévéloppée.

Le traitement du bois a ensuite été réalisé en utilisant le liquide de pyrolyse produit à une température de 500 °C, une vitesse de chauffe de 10 °C/min, et un temps de séjour de 60 min. Comme test préliminaire, nous avons voulu évaluer l'effet de différentes températures de séchage sur les échantillons traités. L'effet du lessivage a également été étudié, ainsi que l'analyse chimique des eaux de lessivage et leur potentiel anti-fongique. Enfin, les échantillons après lessivage ont été testés pour leur efficacité contre les termites *Reticulitermes flavipes*.

Après avoir déterminé les températures de séchage souhaitables pour les échantillons de bois, le processus d'imprégnation a été réalisé par vide/pression en utilisant le liquide de pyrolyse à différentes concentrations. Dans cette étape, l'efficacité et le seuil de concentration du liquide de pyrolyse vis-à-vis des champignons et des termites ont été évalués. L'effet du lessivage et de

l'évaporation ont également été étudiés.

3.2 Matériel et méthods

3.2.1 Test d'inhibition fongique

Le test d'inhibition fongique a été évalué contre deux types de champignons: *Coniophora puteana* et *Trametes versicolor* dans le milieu malt-agar stérilisé (40 g de malt et 20 g d'agar dans 1L d'eau désionisée). Diverses concentrations (v/v) de liquide de pyrolyse ont été testées (0,05 %, 0,10 %, 0,15 %, 0,20 % et 0,25 %) en les diluant directement dans la solution de malt-agar.

3.2.2 Test de non-choix et de choix des termites

Un test de non-choix a été fait contre les termites *Reticulitermes flavipes* en utilisant du papier filtre Joseph. Le papier a été traité avec un liquide de pyrolyse (5 et 10% dilué dans de l'éthanol (v/v)). Deux contrôles ont été effectués en traitant le papier avec de l'eau déionisée et de l'éthanol, séparément. Une boîte de Pétri de 9 cm remplie de 30 à 40 g de sable de Fontainebleau humide (4 vol. de sable / 1 vol. d'eau déionisée) a servi de dispositif de test. Au total, vingt termites ont été introduits dans chaque boîte de Pétri. Le taux de survie et le papier restant ont été déterminés après 4 semaines d'évaluation.

Pour le test de choix (effet répulsif), deux papiers ont été utilisés en les traitant avec de l'éthanol ou du liquide de pyrolyse (5, 10 ou 20% v/v dans l'éthanol). Un autre papier a été utilisé comme témoin (traité avec de l'eau). Le papier témoin et le papier traité ont été placés dans une boîte de Petri de 14 cm de diamètre. Ensuite, un total de 20 termites ont été introduits. Le nombre de termites qui sont entrés en contact avec le papier a été compté toutes les 5 min dans une observation de 60 min.

3.2.3 Développement de méthodes pour la mesure de la surface du papier

La surface totale de papier restante consommée par les termites a été mesurée par la méthode de *k-means clustering* qui a été intégrée dans le *Scikit-Learn*, un progiciel d'apprentissage machine écrit en Python, un langage de programmation général à source ouverte.

3.2.4 Traitement du bois/imprégnation

Du hêtre (*Fagus sylvatica*) et de l'aubier de pin (*Pinus sylvestris*) ont été coupés aux dimensions (2,5 × 1,5 × 0,5) cm (L × R × T). Pour l'essai préliminaire, des échantillons de bois de hêtre anhydre (six répliques par traitement) ont été imprégnés avec le liquide de pyrolyse brut (100%) par une seule imprégnation sous vide/pression (30 mbar de vide pendant 20 min, suivie de 2 h à la pression ambiante). La rétention a ensuite été déterminée. Dans cet

essai, cinq températures de séchage différentes ont été testées (20 °C, 40 °C, 60 °C, 80 °C, et 103 °C.) La masse des échantillons après séchage a ensuite été enregistrée pour déterminer le pourcentage de gain de masse (WPG). La microstructure des échantillons de bois traité a été observée à l'aide d'un appareil photo numérique Nikon DS Fi1 connecté à un microscope optique (Olympus BX6). Les spectres FTIR du hêtre traité et non traité ont également été enregistrés.

Un autre essai d'imprégnation a été réalisé en utilisant différentes concentrations de liquide de pyrolyse (5%, 10%, 15%, 20%, 25%, et 50%) dilué dans de l'éthanol (v/v)

3.2.5 Lessivage

Le test de lessivage a été fait selon la norme NF X 41-568 (2014) où les échantillons traités ont été soumis à six périodes de lessivage successives (1 h, 2 h, 4 h, et 8 h, 16 h, et 48 h) dans de l'eau déionisée (1 vol de bois/5 vol d'eau déionisée). Le pourcentage en masse après lessivage ($WPGL$) et le pourcentage du taux de lessivage (LR) ont été déterminés.

Pour les échantillons traités qui ont séché à différentes températures, les produits de lessivage ont été collectés pour être analysés par GC-MS. Les produits de lessivage ont été utilisés pour un test d'inhibition des champignons afin de déterminer si la solution de lessivage contient des composés bio-actifs.

3.2.6 Test de durabilité contre les champignons et les termites

Le test fongique a été réalisé selon la méthode inspirée de la norme EN 113-1 (2020) en utilisant trois types de champignons responsables de la pourriture du bois : une pourriture blanche (*Trametes versicolor*) et deux pourriture brunes (*Coniophora puteana* et *Rhodonia placenta*). Le facteur de correction (de la perte de masse due à l'action fongique) a également été déterminé pour évaluer la perte de poids des échantillons causée par l'attaque non fongique (causée par la libération de produits pendant le test). Le test a été effectué pendant huit semaines.

Le test de résistance aux termites a été évalué selon un test de non choix, inspiré de la norme européenne EN 117 (2013). A l'issue de l'essai, une cotation visuelle, été attribuée à chaque échantillon, la perte de masse du bois et le taux de survie ont été déterminés. Le test a été effectué pendant quatre semaines.

3.3 Résultats et discussion

Deux types de liquide de pyrolyse ont été révélés efficaces pour inhiber la croissance de *C. puteana* et *T. versicolor*. Pour inhiber complètement la croissance fongique, un liquide de pyrolyse à une concentration de 0,20%

et 0,25% a été nécessaire pour supprimer la croissance de *C. puteana* et *T. versicolor*, respectivement. L'effet différent du liquide de pyrolyse sur les champignons a probablement été corrélé aux différents effets métaboliques ou aux enzymes libérées par les champignons (Barbero-López et al., 2019). Plusieurs auteurs ont signalé que l'acide propionique (Barbero-López et al., 2019), l'acide acétique (Oramahi et al., 2018) et le furfural (Pimenta et al., 2018) présentaient une activité anti-fongique. Les dérivés de guaicols, qui ont également été trouvés dans cette étude, tels que le phénol-2-méthyle, le phénol-3-méthyle, le phénol-4-méthyle, le phénol-2-méthoxy-4-méthyle, et le phénol-4-éthyl-2-méthoxy étaient également responsables de la capacité du liquide de pyrolyse à inhiber les champignons (Mourant et al., 2007; Mohan et al., 2008).

Pour l'essai de termites, statistiquement, le liquide de pyrolyse obtenu à 400 °C est plus efficace lorsqu'il est appliqué à une concentration de 5 %. Cependant, à une concentration de 10 %, les deux liquides de pyrolyse ont causé une mortalité complète. On a observé que les termites consommaient une petite partie du papier (5,56%–7,03%). Un taux plus élevé de mortalité des termites a montré l'effet toxique du liquide de pyrolyse. Le liquide de pyrolyse repousse de manière significative les termites, seul un petit nombre de termites entrent en contact avec les échantillons de papier traités. Les composés volatils libérés lors de l'expérimentation auraient repoussé les termites, comme le rapporte Oramahi and Yoshimura (2013). Cependant, comme les résultats ont montré que certaines termites doivent consommer le papier traité pour mourir, l'effet répulsif n'est pas suffisant, et l'ingestion est nécessaire pour faire mourir le termites.

L'utilisation de la segmentation automatique, l'algorithme de *k-means clustering*, est possible et simple pour traiter l'image d'un substrat mince comme un papier filtre sur le test des termites. La capacité d'apprentissage automatique de la machine à différencier le papier de l'arrière plan nous permet de mesurer la zone avec une grande précision. Cependant, le programme utilise une quantité importante de mémoire. Nous avons ainsi pu développer un outil facile et fiable pour mesurer la surface de papier dégradé par les termites lors d'un essai rapide.

Lorsque les échantillons de bois de hêtre sont traités, la rétention du liquide de pyrolyse brut est enregistrée à $734,23 \pm 20,59\ \mathrm{kg/m^3}$. Selon des observations microscopiques, une température de séchage plus élevée (supérieure à 60 °C) semble favoriser l'agglomération du liquide de pyrolyse à l'intérieur de la microstructure du bois. Dans l'étude précédente, Lourençon et al. (2016) a rapporté que le produit liquide de la pyrolyse agit en recouvrant la surface des microstructures vasculaires du bois. Cependant, aucun pic dans les spectres FTIR n'a été observé pour l'interaction entre le liquide de pyrolyse et le

bois, ce qui montre qu'aucune réaction chimique ne s'est produite entre eux, comme le confirme Lourençon et al. (2016).

Le liquide de pyrolyse semble être hautement lessivable du bois. Le taux de lessivage était plus faible pour les échantillons séchés à 103 °C. Selon l'analyse par GC-MS, une partie des phénols, des guaiacols et des cétones ont été lessivés. Plus les températures de séchage sont basses, plus la proportion de composés détectés par GC-MS est élevée. Le 3-méthyl-1,2-cyclopentanedione, le 2,6-diméthoxyphénol et le phénol sont les trois principaux composés qui ont été lessivés de tout le bois traité.

Pour le test d'inhibition fongique utilisant les eaux de lessivage, nous avons observé que plus la température de séchage est élevée, plus la croissance radiale du mycélium est importante, ce qui signifie qu'il a moins d'effet sur les champignons. En revanche, aucune croissance n'a été observée pour le traitement utilisant des produits de lessivage à partir des échantillons de lessive séchés à 20 °C, ce qui montre une forte activité fongique.

Pour le test biologique contre les termites et les champignons, les résultats montrent une bonne efficacité lorsque les échantillons ont été traités avec une forte charge de liquide de pyrolyse (50% et 100%). Le principal désavantage du liquide de pyrolyse pour la protection du bois est sa lessivage élevée dans l'eau ou à l'état humide, comme le montre le résultat du facteur de correction fongique ou le test de reprise d'eau.

IV. Conclusion et Perspective

4.1 Conclusion Générale

La valorisation des déchets de biomasse agricole pour générer des produits chimiques bio-actifs est intéressante étant donné que la biomasse est la ressource la moins chère et la plus abondante que l'on trouve en grand volume. La pyrolyse lente comme méthode de conversion thermochimique de la biomasse est intéressante pour la co-production de charbon et de liquide de pyrolyse dans la perspective de la densification énergétique et de la valorisation du sous-produit. La récupération de la vapeur organique condensable pour une utilisation future réduit l'impact de la pollution de l'air, considérant que la pratique conventionnelle de la pyrolyse lente est uniquement destinée à la production de charbon.

Dans cette étude, la bagasse de canne à sucre a été pyrolysée en utilisant différents paramètres, tels que la température (400 °C et 500 °C), la vitesse de chauffe (1 °C/min et 10 °C/min), et le temps de séjour (30 min et 60 min). Le charbon généré par ce processus permet de concentrer l'énergie. Simultanément, la récupération du produit liquide pour une autre utilisation offre une voie alternative pour la protection du bois.

La température de pyrolyse et la vitesse de chauffe ont eu une influence significative sur les propriétés de charbon et le rendement des produits. Le rendement du charbon diminue avec l'augmentation de la température de pyrolyse mais résulte en une amélioration de la valeur calorifique; tout en générant une masse élevée de rendement liquide. Outre son utilisation comme combustible en raison de sa teneur élevée en carbone (70,50%) et en HHV (27,85 MJ/kg), le charbon de bagasse est également potentiellement utilisable comme amendement du sol, due à une haute récupération des cendres (jusqu'à 98%).

Le liquide de pyrolyse produit à différentes températures présente une légère différence dans les proportions de leur composition chimique; cependant, l'eau, l'acide acétique, le glycolaldéhyde, la 1-hydroxy-2-propanone, le méthanol, l'acide formique, le lévoglucosane, le furfural, suivis de quelques composés phénoliques et de dérivés du guaiacol, ont été trouvés comme composés principaux. Le liquide de pyrolyse produit à 400 °C donne un contenu organique total légèrement plus élevé lorsque quantifié par GC-MS. Sur la base de la quantification de 56 composés chimiques, les teneurs organiques totales quantifiées étaient respectivement de 29,63% et de 25,63% pour le liquide de pyrolyse produit à 400 °C et 500 °C.

Le liquide de pyrolyse est un candidat potentiel pour la protection du bois contre les champignons et les termites. Les résultats démontrent qu'à

de faibles concentrations (0,25%), le liquide de pyrolyse est capable d'inhiber la croissance de *C. puteana* et de *T. versicolor*, a également un effet répulsif et toxique vis-à-vis des termites (en particulier à forte concentration (10%)). Divers composés, dont l'acide acétique, l'acide formique, l'acide propionique, les phénols, et les dérivés du guaiacol, ont été rapportés comme ayant une activité anti-fongique et anti-termites. L'effet synergique entre ces composés est probablement responsable de son efficacité. En outre, contrairement à la créosote, un sous-produit de la distillation du charbon, le liquide de pyrolyse ne contient pas de composés d'hydrocarbures aromatiques polycycliques (HAP), ou alors ils sont insignifiants (moins de 1 ppm).

Le liquide de pyrolyse a une teneur en eau considérablement élevée; cependant, cela réduit sa viscosité et le processus de préchauffage avant l'application sur le bois peut être évité. Une fois incorporé dans le bois par imprégnation sous vide, la rétention du liquide de pyrolyse était de $734,23 \pm 20,59$ kg/m^3. En excluant l'eau, la rétention est de 423,65 $\pm 11,88$ kg/m^3. Les différentes températures de séchage des échantillons de bois après avoir été traités avec le liquide de pyrolyse (ambiante, 40, 60, 80 et 103 °C) ont donné des différences significatives dans la charge du produit dans le bois, tandis que la température élevée (à 103 °C) semble favoriser l'agglomération du produit liquide de pyrolyse à l'intérieur des cellules du bois. Nous n'avons toutefois pas eu d'indication de réaction chimique entre le bois et le liquide de pyrolyse comme le montrent les résultats de FTIR.

Le liquide de pyrolyse est hautement lessivable dans l'eau. Des composés tels que la 3-méthyl-1,2-cyclopentanedione, le phénol, le 3,4-diméthylphénol, le phénol-2-méthoxy, le phénol-2-méthoxy-4-méthyle et le 2,6-diméthoxyphénol ont été détectés lors de la quantification par GC-MS en utilisant les produits de lessivage collectés à différentes températures de séchage. Les produits de lessivage ont également montré une certaine activité contre *C. puteana* et *T. versicolor* dans le test d'inhibition de la croissance fongique, où les échantillons séchés à température ambiante indiquent l'activité la plus forte, notamment contre *C. puteana*.

Selon les résultats obtenus, le liquide de pyrolyse n'était pas suffisamment efficace pour protéger le bois contre les champignons lorsqu'il était appliqué à faible concentration (5% à 20%). De plus, le test du facteur de correction fongique suggère que le liquide de pyrolyse reste lessivable du bois lorsqu'il est exposé à une forte humidité. Une bonne amélioration de l'efficacité a été observée lorsque les échantillons ont été traités à des charges élevées (entre 50% et 100%). Dans le cas du test sur les termites, les résultats suggèrent que le liquide de pyrolyse est efficace lorsqu'il est appliqué à une concentration de 25%; cependant, compte tenu de l'instabilité du liquide de pyrolyse, on pense que la performance du bois traité diminue avec le temps lorsqu'il est

exposé à une humidité élevée.

En plus de ces résultats scientifiques, les expérimentations sur les termites à l'aide de papier filtre nous ont permis de développer un calcul rapide, simple et précis sur la mesure de la surface du papier en utilisant la méthode de *k-means clustering*. Bien que cela ait nécessité l'utilisation d'un niveau élevé de mémoire vive, nous avons estimé les relations entre le nombre d'images traitées et la mémoire nécessaire, ce qui nous a permis d'élaborer une stratégie compatible pour choisir le nombre d'images qui pouvaient être analysées à la fois en fonction de la capacité de notre machine.

4.2 Perspective

Grâce à ses propriétés anti-fongiques et anti-termites, le liquide de pyrolyse est potentiellement intéressant pour la formulation de systèmes de protection du bois. Néanmoins, certaines problématiques liées à son acidité et sa lessivabilité doivent être prises en compte avant de l'utiliser pour la protection du bois. Nos résultats montrent que l'utilisation du liquide de pyrolyse comme méthode seule ne semble pas très prometteuse, en raison de sa grande instabilité une fois qu'il est intégré dans le bois. Le bois traité avec le liquide de pyrolyse reste très lessivable lorsqu'il est exposé à l'eau ou à une forte humidité, ce qui indique que des études futures devraient être menées pour trouver comment réduire sa lessivabilité. D'autres études sont nécessaires, notamment pour évaluer les stratégies de formulation (fixation à l'aide du produit minimum par la formulation pour une efficacité prolongée tout au long de la vie et la minimisation des impacts sur la santé humaine et l'environnement), comme par exemple par co-imprégnation avec des agents hydrophobes tels que l'huile de lin et l'acide résinique.

Publications and Award

Publications

1. Febrina Dellarose Boer, Jérémy Valette, Jean-Michel Commandré, Mériem Fournier, and Marie-France Thévenon. Slow Pyrolysis of Sugarcane Bagasse for the Production of Char and the Potential of Its By-Product for Wood Protection. Journal of Renewable Materials 9(1), 2021, 97-117. DOI:10.32604/jrm.2021.013147.

2. Febrina Dellarose Boer, Ahmad Alkadri, Mériem Fournier, and Marie-France Thévenon. Measuring the termite feeding on filter paper using image segmentation and k-means clustering. To be submitted to the International Journal of Metrology and Quality Engineering (IJMQE).

Communication in international congress

1. Febrina Dellarose Boer, Luc Pignolet, Jean-Michel Commandré, Kévin Candelier, Mériem Fournier, Marie-France Thévenon. Chemical composition and performances of slow pyrolysis by-product from sugarcane bagasse for wood protection. IRG51 webinar on Wood Protection 10-11 June 2020–Oral presentation + proceeding (IRG/WP 20-30752).

Communication in national congress

1. Valorization of pyrolysis by-products for the protection of biomaterials. 7ème journée du GDR 3544 Science du Bois. Cluny 20-22 November 2018–Poster.

2. Valorization of slow pyrolysis by-product from biomass waste for the protection of wood. Doctoral seminar of SIRENA. Nancy, 13 February 2020–Oral presentation.

Award

1. Ron Cockcroft Award (RCA), International Research Group on Wood Protection (IRG 51) 2020.

Title : Valorization of sugarcane bagasse via slow pyrolysis and its by-product for the protection of wood

Keywords : biomass, char, slow pyrolysis, sugarcane bagasse, pyrolysis liquid, wood protection

Abstract :

Biomass residue—such as sugarcane bagasse—has great potential in providing renewable energy sources. However, its natural properties such as low density, low calorific value, and biodegradation susceptibility can limit its utilization. To improve its energy efficiency, slow pyrolysis—the process of thermal decomposition in an oxygen-deficient environment—can be applied by transforming the biomass into carbon-rich char. In a typical slow pyrolysis scenario, biomass is slowly heated to produce mainly char, where the organic vapors are often considered secondary products. However, there is an interest to recover this by-product by condensing the organic vapor generated during pyrolysis for various purposes. Moreover, this product has a long history due to its benefits as a bio-pesticide used by traditional farmers, notably in Asian countries. In this study, bagasse was slow-pyrolyzed to co-produce char and pyrolysis liquid using a laboratory fixed bed reactor. Different parameters were tested, such as temperatures (400 °C and 500 °C), heating rate (1 °C/min and 10 °C/min), and holding time (30 min and 60 min). This study aims to evaluate the valorization potential of bagasse with the purpose of energy densification (conversion of biomass into char) and valorizing the utilization of its by-product (pyrolysis liquid) for wood protection.

Results showed that the yield of char decrease with the increase of pyrolysis temperature but results in the favorable calorific value improvement; while at the same time generating a high mass of liquid yield. The optimum pyrolysis condition to co-produce char and pyrolysis liquid was at 500 °C temperature and 10 °C/min of heating rate, yielding 28.97% char and 55.46% liquid. The principal compounds of pyrolysis liquid were water, acetic acid, glycolaldehyde, 1-hydroxy-2-propanone, methanol, formic acid, levoglucosan, furfural, followed by some phenol compounds and guaiacol derivatives. Pyrolysis liquid also exhibits anti-fungal and anti-termite activity at relatively low concentrations in the Petri-dishes bioassays. When treated to beech and pine wood, pyrolysis liquid indicates good protection towards termites (*Reticulitermes flavipes*) and Basidiomycete fungi (*Coniophora puteana* and *Rhodonia placenta*, cubic rot and *Trametes versicolor*, a fibrous rot) at concentration 50% and 100%. However, it remains leachable when exposed to water or high humidity, which indicates that future studies should be conducted to find out how to decrease its leachability.

Titre : Valorisation de la bagasse de canne à sucre par pyrolyse lente et de son sous-produit pour la protection du bois

Mots-clés : biomasse, charbon, pyrolyse lente, bagasse de canne à sucre, liquide de pyrolyse, protection du bois

Résumé :

Les résidus de biomasse, comme la bagasse de canne à sucre, ont un grand potentiel pour fournir des sources d'énergie renouvelables. Cependant, ses propriétés naturelles telles que sa faible densité, son faible pouvoir calorifique et sa sensibilité à la biodégradation peuvent limiter son utilisation. Pour améliorer son efficacité énergétique, la pyrolyse lente–processus de décomposition thermique dans un environnement pauvre en oxygène–peut être appliquée en transformant la biomasse en un charbon riche en carbone. Dans un scénario typique de pyrolyse lente, la biomasse est lentement chauffée pour produire principalement du charbon, dont les vapeurs organiques sont souvent considérées comme des produits secondaires. Cependant, il y a un intérêt à récupérer ce sous-produit en condensant la vapeur organique générée pendant la pyrolyse à des fins diverses. De plus, ce produit a une longue histoire en raison de ses avantages en tant que bio-pesticide utilisé par les agriculteurs traditionnels, notamment dans les pays asiatiques. Dans cette étude, la bagasse a été pyrolysée pour co-produire du charbon et du liquide de pyrolyse (huile de pyrolyse) en utilisant un réacteur de laboratoire à lit fixe. Différents paramètres ont été testés, tels que les températures (400 °C et 500 °C), la vitesse de chauffe (1 °C/min et 10 °C/min) et le temps de séjour (30 min et 60 min). Cette étude vise à évaluer le potentiel de valorisation de la bagasse dans le but de densifier l'énergie (conversion de la biomasse en charbon) et de valoriser l'utilisation de son sous-produit (liquide de pyrolyse) pour la protection du bois.

Les résultats ont montré que le rendement en charbon diminue avec l'augmentation de la température de pyrolyse mais entraîne une amélioration favorable du pouvoir calorifique; tout en générant une masse élevée de rendement liquide. Les conditions de pyrolyse optimales pour co-produire le charbon et le liquide de pyrolyse étaient la température de 500 °C et la vitesse de chauffe de 10 °C/min, donnant 28,97% de charbon et 55,46% de liquide. Les principaux composés du liquid de pyrolyse étaient l'eau, l'acide acétique, le glycolaldéhyde, la 1-hydroxy-2-propanone, le méthanol, l'acide formique, le lévoglucosane, le furfural, suivis de quelques composés phéno- liques et de dérivés du guaiacol. Le liquid de pyrolyse présente également une activité anti-fongique et anti-termite à des concentrations relativement faibles dans les essais biologiques sur boîtes de Pétri. Lorsqu'il est traité au bois de hêtre et de pin, le liquid de pyrolyse indique une bonne protection contre les termites (*Reticulitermes flavipes*) et les champignons Basidiomycete (*Coniophora puteana* et *Rhodonia placenta*, une pourriture cubique et *Trametes versicolor*, une pourriture fibreuse) à une concentration de 50% et 100%. Cependant, il reste lessivée lorsqu'il est exposé à l'eau ou à une forte humidité, ce qui indique que des études futures devraient être menées pour trouver comment diminuer sa lessivabilité.

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