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FABRICATION DE GRANULÉS DE LIGNINE À L'ÉCHELLE DU LABORATOIRE.

MANUFACTURE OF LIGNIN PELLETS AT LABORATORY SCALE.

Thèse de doctorat
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RÉSUMÉ

En raison de la demande croissante en énergie dans le monde, de sources d'énergie à fort potentiel sont nécessaires afin de remplacer les combustibles fossiles, tels que le pétrole, le charbon et le gaz naturel. Une forme alternative d'énergie à fort potentiel énergétique sont les pellets (également connu sous le nom de granulés). Ceux-ci peuvent être considérés comme des biocarburants renouvelables assumant qu'ils sont produits à partir de biomasse lignocellulosique. Les pellets ont une faible teneur en humidité, une forme homogène et une densité énergétique élevée car proviennent de la biomasse végétale.

La biomasse végétale est généralement composée de trois macromolécules structurales soit l'hémicellulose, la cellulose et la lignine. Cette dernière est intégrée dans la matrice des deux autres macromolécules et constitue le second biopolymère le plus abondant dans la nature. La lignine peut également être obtenue à partir des tissus et résidus lignocellulosiques qui, dans certains cas, sont abondamment disponibles et présents à grande échelle dans le monde. La macromolécule à base phénolique a aussi été associé à des applications dans la fabrication de nouveaux matériaux polymères du type composites et également dans la production de composés organiques aromatiques à base de monomère sans oublier que le pouvoir calorifique élevé de la lignine offre la possibilité d'être utilisé comme source d'énergie. La fabrication de granulés, en tant que source d'énergie alternative, représente une possibilité exceptionnelle pour la production de combustibles solides à haute densité énergétique pour le chauffage industriel.

L'objectif principal de ce travail était de développer une méthodologie pour la fabrication de granulés de lignine à partir de résidus agricoles et forestiers. Trois types de lignine ont été utilisés dans la fabrication de granulés à l'échelle du laboratoire. La matière première utilisée dans ce travail a été isolée à partir de bois de peuplier, de tiges de maïs et d'écorce de résineux à l'aide d'un processus de saccharification directe. Les granulés de lignine ont ensuite été fabriqués à l'aide de quatre types d'additifs différents (huile de maïs, acide citrique, glycérol et d-xylose) et, finalement, ils ont été stockés dans deux conditions différentes avant d'être testés. De plus, deux appareils ont été utilisés pour la fabrication de granulés, le système de granulés simple qui a été construit dans l'atelier d'usinage et le granulateur PM650 à l'échelle du laboratoire de la société Buskirk Engineering. Ces deux appareils sont situés au Laboratoire des technologies de la biomasse (LTB) de l'Université de Sherbrooke. La certification CANplus a été utilisée pour valider les paramètres de qualité physiques et chimiques. De plus, ces propriétés ont ensuite été comparées à des granulés fabriqués à partir d'écorce de bois résineux en utilisant le même granulateur. En général, la fabrication de granulés entièrement constitués de lignine a généré des échantillons avec une hydrophobicité globale plus élevée et une valeur calorifique plus élevée. Cependant, la teneur en cendres et en soufre était légèrement supérieure aux valeurs de certification CANplus attendues pour les granulés de classe A. Par conséquent, la lignine a été prétraitée avant la fabrication des granulés, améliorant ainsi la teneur en cendres et en soufre. Cette étude vise à montrer que la lignine pourrait être utilisée pour produire ce nouveau type de granulés, en attendant que le matériau initial ait une faible teneur en cendres et en humidité.

Mots-clés: Granulés de lignine, énergie renouvelables, biocombustibles solide, procédé de pelletisation.

ABSTRACT

Due to the high demand for energy globally, high-potential sources are needed to replace fossil fuels, such as oil, coal, and natural gas. An alternative form of energy with a high heating value is pellets. These can be considered renewable biofuels, assuming they are produced from lignocellulosic biomass. The pellets have a low moisture content, a homogeneous shape, and a high energy density.

Plant biomass is generally composed of three structural macromolecules: hemicellulose, cellulose, and lignin. The latter is integrated into the matrix of the other two macromolecules and constitutes the second most abundant biopolymer in nature. Lignin can also be obtained from lignocellulosic tissues and residues, which, in some cases, are abundantly available and present on a large scale in the world. The phenolic-based macromolecule has also been associated with applications in the manufacture of new composite-type polymeric materials and the production of monomer-based aromatic organic compounds, without forgetting the high caloric value of lignin offers the possibility of being used as a source of energy. As an alternative energy source, the manufacture of pellets represents a unique possibility for producing high energy density solid fuels for industrial heating.

The main objective of this work was to develop a methodology for the manufacture of lignin pellets from agricultural and forest residues. Three types of lignin were used to manufacture pellets on a laboratory-scale. The feedstock used in this work was isolated from poplar wood, corn stover and softwood bark using a direct saccharification process. Lignin pellets were then manufactured using four different types of additives (corn oil, citric acid, glycerol, and d-xylose) and ultimately, they were stored in two different conditions prior being tested. Also, two devices were used to manufacture pellets, the single pellet system built in the machine shop and the Buskirk Engineering laboratory-scale pellet mill model PM650. These two devices are in the Biomass Technology Laboratory (BTL) located at the University of Sherbrooke. The CANplus certification was used to validate the physical and chemical quality parameters. Also, these properties were then compared to pellets made from softwood bark using the same pellet mill. In general, manufacturing pellets entirely made of lignin generated samples with an overall higher hydrophobicity and higher calorific value. However, the ash and sulfur content were slightly higher than the expected CANplus certification values for Grade A pellets. Therefore, the lignin was pretreated before pellet manufacturing, improving the ash and sulfur content. This study intends to show that lignin could be used to produce this new kind of pellets, pending that the initial material has a low ash and moisture content.

Keywords: Lignin pellets, renewable energy, solid biofuel, pelletization process.

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FOREWORD

This document is presented in the form of a document thesis. This Ph.D. thesis results from a research project carried out under the supervision of professors Jean-Michel Lavoie and Bruna Rego de Vasconcelos from the Department of Chemical and Biotechnological Engineering at Université de Sherbrooke. The project focused on studying solid biofuel properties pelleting characteristics to examine the potential of using lignin to produce pellets for bioenergy purposes. Also, it is possible to find conference proceedings and a scientific article was written in English presented in appendix 1. These are respectively:

1. Rueda, S. A. J., de Vasconcelos, B. R., Duret, X., and Lavoie, J-M. Lignin pellets for advanced thermochemical process – from a single pellet system to a laboratory-scale pellet mill. Energies MDPI. 2022, 15(9), 3007. https://doi.org/10.3390/en15093007

The author of this thesis, Sergio Andres Jaimes Rueda, was responsible for the experimental work and writing the first version of this article. Professor Jean-Michel Lavoie and Bruna Rego de Vasconcelos supervised the experiments and reviewed the article.

The following list enumerates the published and submitted articles in journals and conferences resulting from this research:

1. Dantas, J. M. de M., Pimentel, M-L., Rueda, S. A. J., Chastel, C. F., Wolfaardt, F., Ghislain, T., Lavoie, J-M. (*Oral presentation in June 2022),* Marijuana residues as a gateway biomass for a green economy. 9th International Conference on Engineering for Waste and Biomass Valorisation.

2. Rueda, S. A. J. (*Virtual presentation 2021*), Fabrication de granulés de lignine à l'échelle pilote. 20 minutes de science in Matériaux Renouvelables de Québec.

3. Rueda, S. A. J., de Vasconcelos, B. R., Duret, X., and Lavoie, J-M. (*Virtual presentation 2021*), Moisture content behavior of lignin pellets from softwood bark and poplar wood. 8th International Conference on Engineering for Waste and Biomass Valorisation.

4. Rueda, S.A.J., Duret, X., and Lavoie, J-M. (*Oral presentation 2020*), Geometrical parameters characterization of lignin pellets made from poplar wood and corn stover. European Pellet Conference, Wels, Austria.

5. Rueda, S. A. J., de Vasconcelos, B. R., Duret, X., and Lavoie, J-M. (*Virtual presentation 2020*), Fabrication de granulés de lignine à l'échelle pilote. Symposium des étudiants en génie chimique et génie biotechnologie à l'Université de Sherbrooke.

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CHAPTER 1

INTRODUCTION

Despite the most recent environmental concerns related to greenhouse gas emissions combined with the different actions undertaken by numerous governments worldwide to reduce carbon intensity, the demand for fossil fuels is still high if not increasing in most countries around the globe. The necessity to find solutions to this situation is now more than ever-present and it is essential to search for alternatives to fossil fuels that would help reduce the carbon intensity (CI). In recent years, one option for reducing CI has been to increase the use of biofuels and when it comes to solid biofuels, wood is often the most used raw material, mostly because of its low ash content compared to agricultural biomass. This particularity is essential in combustion since ashes are often related to many issues, including increased corrosion in combustion equipment *(Stelte et al., 2011)*. Wood pellets are generally produced from residues of the wood industry such as sawdust and shaving and harvest residues, which are also often considered for this purpose *(Obernberger, I. & Thek, G., 2010)*. Wood is composed of three constituents: hemicellulose, cellulose, and lignin. The latter is usually embedded within a matrix of the two other macromolecules and is considered the second most abundant biopolymer in nature (after cellulose). Even though it has been the subject of much research throughout the years, its biosynthesis, chemistry, and structure remain a popular subject in the open literature. Lignin is also a natural polymer, which is, contrarily to cellulose, mostly composed of aromatic structures that involve less oxygen and more carbon. The macromolecule has also been associated with a considerable number of potential applications such as producing new composite-type polymeric materials, producing bio-based monomeric aromatics, and producing biofuels including pellets, that can be used as a solid fuel for the production of heat and/or power.

One of the important aspects of solid biofuels is the quality standards defining the pellet's physical and chemical properties, of which moisture is often a prevalent parameter. Literature offers many pieces of information aiming at determining the best moisture content in the raw material used to produce pellets since, to the best of our knowledge, no standard value is available. In most biofuels, water content remains a challenge since it affects the energy that could be generated from the fuel downstream. Biomass itself usually contains high levels of moisture, explaining why it often goes through a drying process to reach moisture levels below 15% (also recommended by the pelletizing equipment manufacturers). Such a procedure will ensure that the pellet produced will have humidity levels below 10%, as required by certifications such as CANplus *(CANplus certification, 2016)*. The moisture content influences the self-ignition capacity of the biomass as well as its calorific value since during combustion, part of the fuel energy is dedicated (or wasted in most cases) for the evaporation of water and, consequently, it is not available for other energy uses. The water content also impacts the durability of the pellets while increasing their bulk density while possibly also inducing fungi production and/or spore emissions. Open literature shows many studies where pellets were produced using different moisture contents in the raw material.

In addition, the dimension of the pellets is one of the most important parameters since it has a direct impact when feeding these biofuels into boilers. Such combustion systems are often designed and optimized based on the values suggested by *(CANplus certification, 2016)*, and

therefore, pellets exceeding these specifications can cause damages at a different level in a combustion system. For solid biofuels, the calorific value corresponds to the amount of energy released during combustion per unit mass, expressed in MJ/kg (according to the international system of units). When it comes to pellets, this parameter varies according to the origin of the biomass used as raw material. According to the CANplus certification, this value should be greater or equal 16 MJ/kg. Of course, different feedstocks could be used to reach such specifications. Ash content is also a crucial parameter for boiler design and cleaning operation since combustion of pellet with high ash contents will require a more effective and perhaps complex ash removal process. This parameter varies according to the different types of biomasses used in the manufacture of pellets, especially for tissues such as bark and grass, which may lead to higher amounts of ash after combustion. The inorganic components that are known to contribute the most to ash formation are Si, Ca, Mg, K, Na, P, S, Cl, Al, Fe, and Mn and their overall content is deemed low when comprised between 1% and 2% according to *(CANplus certification, 2016)*.

Furthermore, several methods can be considered to determine the resistance to the impact of densified materials. However, most of them evolve around the same procedure, which is dropping a solid biofuel sample several times from a previously established height onto a previously specified material of specific composition. It is necessary to record the mass of the sample before performing the drop tests, after which the samples are sieved and weighed. This method is also known as the "drop resistance" or "shattering resistance". Although many tests are used to determine the shattering resistance of densified material, there is no standard method to the best of our knowledge. As an example, many researchers *(Khankari, K.K. et al., 1989; M. I. Al–Widyan & H. F. Al–Jalil, 2001; Sah, P. et al., 1980; Shrivastava, M., et al., 1989)* used a specific shattering resistance test to determine the durability of biomass pellets and briquettes. Pellets were dropped from a known height of 1.85 m onto a metal plate four times. The impact resistance of the pellets was then defined as the percentage of the initial weight retained after dropping. *(Richards, 1990)* introduced the impact resistance index (IRI) based on the number of drops and the number of new pieces generated by the drops. *(J. A. Lindley & M. Vossoughi, 1989)* used a similar method to determine the impact strength of briquettes where each briquette was dropped from a height of 1.0 m onto a concrete surface. This procedure was performed ten times after which the percentage of weight loss was calculated.

Regarding water resistance in wood pellets, *(J. S. Lee et al., 2020)* used three types of commercial wood pellets that were exposed to water. The parameters evaluated were the durability, density, and porosity before and after exposing them to water. They found that they began to degrade when the pellets were in direct contact with water. *(Richards, 1990)* used a briquette and placed it in water to determine its resistance against water absorption and disintegration. The briquette was immersed in water for 30 min and the pressure was applied at 10 min intervals. After this, the briquette was removed from the water, wiped to remove moisture from the surface, and weighed. This study introduced a water resistance index (WRI), allowing a better comparison between samples. *(J. A. Lindley & M. Vossoughi, 1989)* also used briquettes to determine water resistance and in this case, each sample was submerged in 25 mm of water at 27 °C for 30 s after which the percentage of weight gain in the briquettes was calculated and recorded.

There are different studies on the influence of storage time on the physical properties of pellets. For example, *(Dyjakon & Noszczyk, 2019)* analyzed the influence of storage at -28 °C on the mechanical durability of commercial pellets made from different biomass. They found that the freezing and subsequent defrosting process caused a decrease in the mechanical durability as

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compared to normal storage conditions at 20 °C. In addition, pellet storage at freezing temperature did not affect mechanical durability. *(Lee, Jun et al., 2015)* conducted a study and investigated the effects of storage configuration, storage time, storage temperature, and wood pellet quality on the net calorific value and the overall investigation was carried out for 6 months. They showed that when closed storage was selected, the storage time increased by 1% and 2% (in net calorific value).

Looking at pelletization as a pretreatment method, *(Takada et al., 2020)* exposed the influence of lignin on the durability of the pellets and the use of pellets as a raw material for bioconversion. The work also suggested that during the granulation process, when the glass transition temperature of the lignin is exceeded, it becomes plasticized and acts as a glue, thus improving the durability of the pellet. In addition to lignin, other natural additives were reported for this purpose such as sugar, starch, vegetable oils, and lignin derivatives such as lignosulfonate and Kraft lignin.

Although the literature on pelletization is abundant, there are practically no studies that show the behavior of lignin (in general) as a solid biofuel, and even lesser when it comes to the fabrication of lignin pellets. In addition, works on the subject were not conclusive, so a possible utilization to develop models or validate experimental results was not possible. In this context, the present work is intended to provide a baseline for the manufacture of lignin pellets using two devices, a single pellet system and a laboratory-scale pellet mill. This section will develop the hypothesis and define the research project.

1.1   Problem statement

The production of residues is an inescapable reality of the forest production chain, constituting a tremendous environmental responsibility and requiring proper management of these residues. It also implies controlling the possible sources of contamination of water and soil and atmospheric emissions. In the current context, given the polluting emissions from fossil energy sources, it is essential to develop alternative energy sources that respond to both energy supply and sustainable development. In the current context, given the polluting emissions from fossil energy sources, it is essential to develop alternative energy sources that respond to both energy supply and sustainable development. In this case, compacted and homogeneous products can be one of the most efficient ways of making viable the use and subsequent transformation of agricultural and forestry residues. In addition, the pellet's environmental efficiency (it emits less CO_2 than fossil fuels) can be an essential factor in the composition of the energy matrix. Therefore, the development of renewable energies is necessary to meet the growing demand for energy while allowing reasonable social and economic well-being levels to be achieved with stable and secure supplies. Forest and agricultural biomass can be processed into low-carbon solid (such as pellets), liquid, and gaseous biofuels that can help displace a variable portion of fossil fuels. The conversion of organic waste into fuel and providing energy promotes the reduction of environmental damage linked to its improper disposal. According to the context presented, this research project aimed to answer the following hypotheses:

i.   Is it possible to obtain physically and mechanically stable pellets if purified lignin is used as raw material?

ii.   Will these pellets comply with the CANplus certification, a fundamental aspect of their industrialization?

1.2 Objective

The general objective of the research project is to develop and implement a strategy to optimize the lignin pellet manufacturing process to reduce the pelletizing time and preserve the quality of the final product. This goal is intended to be met through the following objectives:

1. To take advantage of lignin from agricultural and forest residues to manufacture solid biofuels.
2. To determine the physical and chemical properties of lignin pellets according to the CANplus certification.
3. To design a control strategy to reduce manufacturing time and guarantee the quality of the final product.
4. To reduce the ash content in lignin through different strategies and its subsequent use in the manufacture of pellets.

1.3 Original contributions

This project achieved the following original contributions:

1. This work proposes and develops a study for the industrial production of solid biofuel using lignin as raw material.
2. This research project develops a lignin pellet manufacturing process that provides an optimal manufacturing recipe based on the granulation process parameters such as temperature, pressure, and extrusion speed.
3. To provide and guarantee the physical and chemical quality parameters required by the CANplus standard.
4. To develop a methodology for the elimination of inorganic substances from lignin and its subsequent use in the manufacture of pellets.

Thesis organization

The document is organized as follows. Chapter 2 provides the literature review. It introduces general aspects of the transformation of biomass and the different components of lignocellulosic biomass and a brief review of biofuels is presented. Then, the fundamentals for the densification of wood and the pelletization process (the main focus of this work) are addressed. Finally, the quality parameters (physical and chemical properties of the CANplus certification) are presented to validate the pellets manufactured through the two systems used. Next, chapter 3 is presented, which provides the methodology used to develop this doctoral thesis. Chapter 4 presents the results and discussions obtained through the experiments carried out. Finally, the last chapter provides the conclusions and suggestions for future work.

CHAPTER 2

LITERATURE REVIEW

This section initially presents a brief description of the different types of biomass conversion. Next, a literature review was carried out on lignocellulosic biomass and the other biofuels currently used. The chapter was finalized with a general description of the steam-explosion process, and the different pellets used to generate electrical energy, and the current use.

2.1   Biomass transformation

Concerns about global dependence on fossil fuels has increased substantially due to political and economic fluctuations, related to changes in the price of oil in the international market, as well as environmental risks caused by its incomplete combustion leading to the release of gases that contribute to the greenhouse effect and environmental pollution. In this context, the search for renewable sources to be used as raw material for a wide range of products, many of them direct substitutes for oil, has increasingly become the objective of various research centers around the World. An alternative to minimize the damage caused to the environment by fossil fuels is photosynthetic biomass for energy generation since this raw material is presented as a strong candidate for the production of renewable biofuels and other valuable bio-products such as hydroxymethylfurfural (HMF), furfural, among others, *(S. Dutta et al., 2013)*. For environmental and economic reasons, there is a high development of processes aimed at producing biofuels from alternative energy sources. An example of these biofuels is those obtained from lignocellulosic biomass whose exploration and production on an industrial scale may in the future compete with the price of fossil fuels and, therefore, minimize the environmental impacts associated with the release of polluting gases to the atmosphere, such as carbon monoxide, nitrogen oxide, carbon dioxide, methane, and polycyclic aromatic hydrocarbons. Within the scope of the wood industry, large amounts of lignocellulosic waste are generated. The use of this waste constitutes a potential for producing liquid and solid biofuels, such as second-generation ethanol (2G) and first-generation pellets (1G). The complex characteristics of lignocellulosic biomass fibers require pretreatments to separate the fermentable sugars and make them available (in this case for the production of 2G ethanol). There are several pretreatment processes, some at a more advanced stage of development and therefore more competitive in the short term, and others at an earlier stage of development, with the potential to be competitive in the long term. The processes are divided into physical, chemical, thermal, thermochemical, biological, and even a combination *(Biswas et al., 2014; Njoku et al., 2013)*. In these processes, the substrates must be in the form of chips, dust, bark, or straw and the choice of the best method depends on the degree of separation required, the purpose for which it is proposed, and especially the type of raw material used. The method's success is related to the amount of material recovered after the pretreatment stage and, in some cases, to the degree of efficiency increase with which the cellulose is hydrolyzed *(Grethlein, 1985; Saddler et al., 1982)*.

In this case, one of the renewable energy sources with great potential for development in the coming years is biomass. This renewable source is considered one of the main alternatives to replace energy sources such as oil and coal, thus minimizing dependence on fossil fuels. The rational use of biomass could be of great environmental importance to reduce greenhouse gas emissions and the consumption of other fuels. Converting solid biomass into energy begins with collecting various residues from the forest, agricultural or urban world. Eventually, this carbon source is converted into a product through a conversion process and then transported to places of consumption where the energy will ultimately be used. The most common process for recovering second-generation biomass is combustion, both for heat and electrical energy production. Lignocellulosic biomass is an essential source of renewable energy with the potential to produce biofuels, the cogeneration of electrical energy, and the generation of chemical compounds. Table 2.1 presents the fractions concentration in the lignocellulosic biomass (ie, cellulose, hemicelluloses and lignin) for different types of biomasses.

Table 2.1 Fractions concentration in the lignocellulosic biomass

Raw material	Cellulose fraction	Hemicellulose fraction	Lignin fraction
Energy crops	0.366	0.161	0.219
Crop residues	0.380	0.320	0.170
Woody biomass	0.437	0.283	0.243

The use of lignocellulosic biomass for the generation of value-added products from its constituent fractions such as hemicellulose and cellulose require, first of all, the elimination of barriers that hinder access to chemical or biological catalysts that contribute to its transformation, being necessary to reduce the alteration of the crystalline structures of the fraction of interest, in order to obtain a higher reaction rate and better yields. Furthermore, the carbohydrates should not break down or form other products that can inhibit the action of fermentative enzymes or microorganisms. Fractionating lignocellulosic materials and using each component separately is the goal of biorefineries. However, the problem arises: each structural component (cellulose, hemicellulose, and lignin) cannot be isolated simultaneously, and solubilization usually occurs, depending on the process, and it conditions the subsequent degradation of one of these. Wood and agricultural residues have different compositions, and the formation and deposit of each of the macromolecular fractions in the cell walls vary according to the species, environmental conditions, damage (such as pruning), humidity, ultraviolet radiation, pests, etc. Considering the difference in composition and structural complexity of each plant and its respective tissues, it is, therefore, possible to subject them to different bioconversion pathways and operating conditions to find the best balance between performance and profitability. The pretreatment of the biomass allows for eliminating the lignin and extracting the hemicellulose fraction. This step is essential because lignin has a very different reactivity from the rest of the biomass components, and taking it together with hemicellulose and cellulose would give rise to secondary reactions and many unwanted products. Pretreatments include physical, chemical, thermal, biological, or even a combination, according to *(Tagliabue et al., 2008)*. Biomass pretreatment is necessary to reduce the size of the raw material (and thus facilitate subsequent processes), limit the formation of degradation products that inhibit the growth of microorganisms necessary for biological processes, minimize energy demand for subsequent reactions and, therefore, limit their cost. Scheme 2.1 shows the classification of preprocessing according to its nature.
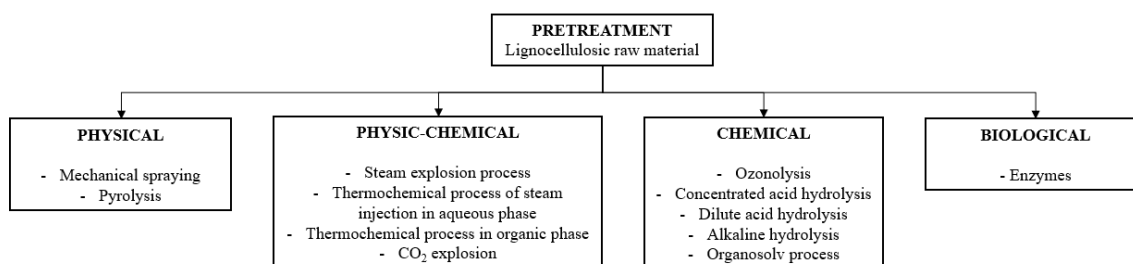
Figure 2.1 Pretreatments for lignocellulosic raw material

2.1.1 Physical pretreatments

According to *(Jackson et al., 2000)*, the physical pretreatment is carried out by subjecting the biomass to a high-pressure steam current, with temperatures between 160ºC and 260ºC, causing the decompression of the material degrading the hemicellulose, transforming the lignin, and increasing the digestibility of the cellulose. The most used physical pretreatments are: mechanical spraying and pyrolysis.

Mechanical spraying

It is characterized by reducing the size of the chips, crushed and crushed. This process involves vibrating ball mills, which are used to generate solids with a final size of 0.2-2mm. Hammer or cutter mills are also used to achieve a final particle size of 3-6mm. This type of treatment reduces the crystallinity index and the degree of polymerization of the cellulose while increasing the contact surface of the material.

Pyrolysis

Pyrolysis is a thermochemical process that converts organic matter into valuable fuel, with high yield, by heating it to a moderately high temperature and without oxygen. In slow processes and temperatures between 300ºC and 500ºC, the residual portion obtained is solid (charcoal), while in fast processes and temperatures between 800ºC and 1200ºC, mixtures of organic compounds with an oily appearance at low pH, called pyrolysis oil, are obtained. According to *(McKendry, 2002)*, due to its processing capacity, it is the most efficient method to compete with non-renewable fuel sources. From a chemical point of view, pyrolysis is a complex process. Generally and according to *(Bridgwater, 1999)*, the process is developed through a series of reactions influenced by many factors: the structure and composition of the raw material, the technology used, the heating rate, the cooling rate, and the process temperature.

2.1.2 Physic-chemical pretreatments

These pretreatments are characterized by a combination of the hydrolytic action of acid radicals and instantaneous decompression processes that cause the structure of the lignocellulosic material to break.

Steam explosion process

Different pretreatment methods are proposed in the literature, among them, steam explosion has proven to be one of the most promising for the fractionation of wood into its three main components, in parallel with a significant increase in the susceptibility of cellulose to acidic or enzymatic saccharification. Mason first introduced the steam explosion process in 1928 *(Mason,*

1928) to defiber the waste from the wood industry for the production of cardboard. *(Babcock, 1932)* showed that the steam explosion process could be used as a pretreatment to produce fermentable sugars and alcohol from wood. Also produced pulps through the steam explosion process and obtained good properties manufacturing paper, with operating temperatures ranging between 100 and 160 °C. The steam explosion pretreatment is based on heating wood chips at high temperatures and pressure, followed by the mechanical rupture of the materials by a fast discharge process (explosion) in a storage tank or even by a slow depressurization of the reactor until atmospheric pressure (no explosion). The plant cell wall structure is modified during the process *(Ramos, 1992)*, causing the hemicelluloses to be partially hydrolyzed and easily removed by aqueous extraction. The water-insoluble fraction remains composed of cellulose and partially modified lignin, and most of this lignin can be extracted with alkali, ethanol, or dioxane. The feasibility of steam pretreatment involves increasing the substrate's susceptibility to hydrolysis and the ease and efficiency with which the three major constituents of wood, cellulose, hemicelluloses, and lignin, are fractionated. The accessibility of enzymes to the substrate is gradually increased with the increasing severity of pretreatment conditions. However, under excessively severe pretreatment conditions, there are high levels of dehydration of sugars released from hemicelluloses and structural modification of lignin *(Ramos et al., 1992; Saddler et al., 1982)*. The increase in the severity of the pretreatment (increase in temperature and - or in the residence time of the material in the reactor) favors the hydrolysis reactions of cellulose and polyose, causes the beginning of the dehydration reactions of the pentoses and hexoses, with the formation of furfural and hydroxymethylfurfural *(Brownell et al., 1986; Silva, 1995)* and increases the condensation reactions of tannins and other substructures that make up extractable *(Lomax et al., 1994)*. Steam pretreatment also favors the hydrolysis of the more thermolabile bonds of lignin, mainly *β-O-4* bonds, leading to new bonds and the fragmentation of parts of the lignin polymer *(Tanahashi, 1990)*.

Thermochemical process of steam injection in aqueous phase
This process is equivalent to thermomechanical processes with a steam injection or steam explosion. In this case, the material is prepared in aqueous suspensions of medium consistency in which the particle size is less than 1 mm. In this way, the problems of diffusion of solids towards the interior, as occurs in the thermomechanical process with steam injection, are avoided. According to the work of *(J. Li et al., 2007; Viola et al., 2008)*, the treatments are carried out in shorter periods, which considerably reduces the degradation and recombination reactions of the solubilized products. The disadvantage of this process is that a large amount of water is consumed to move the solid throughout the reactor, consequently increasing steam consumption as well as energy-related grinding.

Thermomechanical process in organic phase
This process is based on a thermomechanical part that involves the incorporation of sudden decompression, similar to those described above, although the peculiarity, in this case, is that the suspensions are made with organic solvents such as methanol, ethanol, acetone, ethylene glycol and triethylene glycol (among others), or the mixture of these solvents with 1% sulfuric or hydrochloric acid.

CO$_2$ explosion

This process is similar to the steam explosion. However, the carbon dioxide explosion relies on the fact that CO_2 forms carbonic acid, which over time increases the rate of hydrolysis. The process involves the use of around 4 kg of CO_2/kg of fiber under a pressure of around 5.62 MPa.

2.1.3 Chemical pretreatments

While physical pretreatments refer to size reduction and pressure impact, chemical pretreatments, on the other hand, will affect biomass structure using solvents that promote the degradation of cellulose and/or hemicelluloses and/or lignin.

Ozonolysis

This process involves the use of ozone, and this reaction generally occurs at atmospheric temperature and pressure. Through this technique mainly occurs the degradation of lignin.

Concentrated acid hydrolysis

According to the work of *(Taherzadeh & Karimi, 2007)*, sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are used to solubilize the sugars contained in cellulose and hemicelluloses. However, this technique has many drawbacks, such as equipment corrosion and the need to recover (or neutralize) acids. In the latter case, neutralization can be done by adding bases, using anionic membranes, or in the form of hydrogen sulfide (H_2S) from anaerobic wastewater treatment. This pretreatment requires low temperatures (for example, 40ºC) but long reaction times (2 to 6 h) and acid concentrations that vary between 30 and 70%. According to
(Kumar et al., 2009), the acid treatment effectively dissolves hemicellulose. However, it is not adequate for lignin removal. This method has the disadvantage of the solutions being toxic, corrosive, and dangerous, and the material to be used, stainless steel with high anticorrosive capacity, has a high price. Since hemicellulose hydrolyzes much faster than cellulose, its monosaccharides are exposed to the action of acid for a longer time and are therefore mainly degraded.

Dilute acid hydrolysis

Sulfuric acid is the most widely used, but other acids such as nitric, hydrochloric, and phosphoric have been reported in the scientific literature. This type of pretreatment is widely used for the solubilization of hemicelluloses, allowing the digestibility of cellulose to be increased in enzymatic hydrolysis processes or to produce furfural from solubilized pentoses. According to the work of *(Taherzadeh & Karimi, 2007)*, the acid concentration varies from 0.5 to 4% for temperatures between 160 and 220ºC and periods of a few seconds to a few minutes. High temperatures lead to the rapid degradation of sugars, promoting the formation of inhibitory compounds that, in turn, affect ethanol production during the fermentation process. Inhibitors can be generated by the degradation of monosaccharides produced during hydrolysis, the formation of compounds such as acetic acid generated from the acetyl groups of hemicellulose, or even the fragmentation of lignin *(Delgenes et al., 1996; Larsson et al., 1999; Palmqvist & Hahn-Hägerdal, 2000; Ria et al., 2002)*.

Alkaline hydrolysis

Alkaline pretreatments generally use low pressures and temperatures compared to other technologies and can separate both hemicellulose and lignin, without having significant effects

on the other components, according to *(Balat, 2011)*. This type of pretreatment can be performed under ambient conditions, but run times vary from a few hours to a few days, in contrast to the seconds or minutes typically required for dilute acid treatments. Unlike acid-catalyzed pretreatments, alkaline compounds are used as reagents, converted into salts, or incorporated into biomass. The reagents used were calcium hydroxide, sodium, and potassium hydroxides, without forgetting ammonia. In addition, this pretreatment does not require high temperatures; although it generally requires longer reaction times, it does not degrade the sugars as much, according to *(Alvira et al., 2010; Kumar et al., 2009)*. Alkaline technologies are very similar to the kraft process in that their impact is mainly at the lignin level and the acetyl and uronic acids of the hemicelluloses, thus increasing the reactivity of the remaining polysaccharides. In addition to improving the access of the enzymes to the cellulose, this type of process also improves its efficiency since the elimination of non-productive adsorption sites is reduced with the elimination of lignin. According to *(Balat, 2011)*, this treatment has the disadvantage that some bases are converted into salts and cannot be recovered, and some of these salts can be incorporated into the biomass in the treatment process.

Organosolv process
Organosolv pretreatment methods are used to break down wood into its main components. Lignin and hemicellulose are depolymerized and recovered as dry solids, while the fibrous fraction of cellulose is converted to a concentrated aqueous solution of glucose obtained by enzymatic hydrolysis according to *(Viell et al., 2013)*. A mixture of organic solvents such as methanol, ethanol, acetone, ethylene glycol, and triethylene glycol (among others) with 1% inorganic acid (sulfuric or hydrochloric acid) as a catalyst breaks the internal bonds of lignin and hemicelluloses. According to *(Kumar et al., 2009)*, other organic acids like oxalic acid and acetylsalicylic acid can also be used as catalysts.

2.1.4 Biological pretreatments
The processes (physical and chemical) described above often release and produce toxic components for the microorganisms involved in the fermentation process due to high temperatures and the use of chemicals, in addition to requiring a large amount of equipment and sometimes substantial capital investments. On the contrary, biological pretreatments generally carried out with white fungi or soft rot allow the degradation of cellulose and lignin while brown rot degrades cellulose. In turn, these fungi produce cellulose, hemicelluloses, lignin-degrading enzymes (ligninases, lignin peroxidases, polyphenol oxidases, laccases), and quinone-reducing enzymes.

2.2   Lignocellulosic biomass
Biomass is any biological material derived from living organisms. Biomass for energy is often used in the material of plant origin, but the definition of biomass can also be applied to the material of animal and plant origin. Forest biomass, agroforestry residues, herbaceous plants, aquatic plants, and crops are renewable raw materials that have the potential to be transformed into the chemical industry. Plants convert carbon dioxide and water into biochemical, primary, and secondary metabolites through photosynthesis. Biomass of plant origin can come from natural biomass produced by natural ecosystems, residual biomass generated as waste in the agricultural, forestry, and industrial sectors, and biomass produced from energy crops dedicated

to biomass production for non-food energy purposes, *(Zoghlami & Paës, 2019)*. According to *(Morales-Delarosa & Campos-Martin, 2014)*, these are the raw material for the generation of first-generation biofuels. Lignocellulosic biomass is an abundant raw material and renewable whose annual world production is estimated between 10 and 50 billion tons (dry basis), *(Galbe & Zacchi, 2002)*. However, only a tiny portion of this total volume is currently used, and this includes grain and wheat straw, rice husks, corn cobs, corn stover, sugar cane bagasse, dried fruit shells, forest harvest residues, and wood processing residues.

2.2.1 Composition

Photosynthesis reactions during biomass production promote the formation of some critical components, such as cellulose and hemicelluloses, made up of various polymerized carbohydrates. Plant fibers can be considered as composed of cellulose fibrils joined by a matrix formed by lignin and hemicellulose *(Jayaraman, 2003)*, whose function is to act as a natural barrier against microbial degradation and as mechanical protection (see figure 2.2). To better understand lignocellulosic biomass and its use, it is necessary to know the primary cell wall components. These, in turn, can be divided into three organic fractions with the following representative compositions in dry weight: 20 to 50 % cellulose, 15 to 35% hemicellulose, and 10 to 30% lignin, according to the work of *(Chundawat et al., 2011; Rinaldi & Schüth, 2009; Wyman, 1999)*.
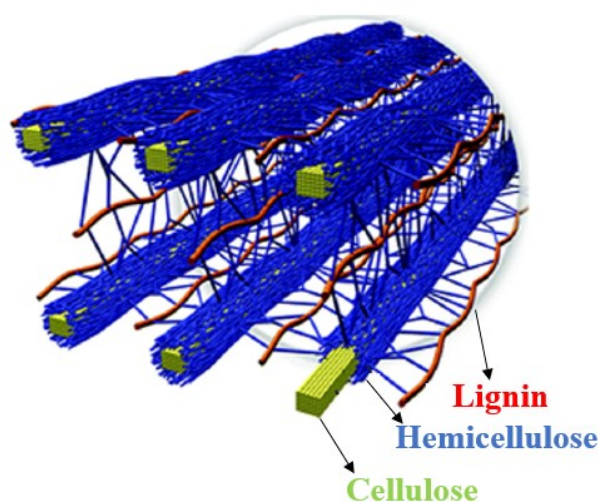
Figure 2.2 Spatial arrangement of cellulose, hemicellulose, and lignin in cell walls of lignocellulosic biomass, adapted from **(Brandt et al., 2013)**.

2.2.2 Cellulose

Cellulose is a homopolysaccharide with the formula $(C_6H_{10}O_5)n$, as shown in figure 2.3. Also, it is the main structural component of the primary cell wall of plants. It is considered the most abundant organic compound on earth, estimated at 1.5×10^{12} tons of the total annual biomass production, and is considered an almost inexhaustible source of raw materials for the growing demand for environmentally friendly products, *(Klemm et al., 2005)*.
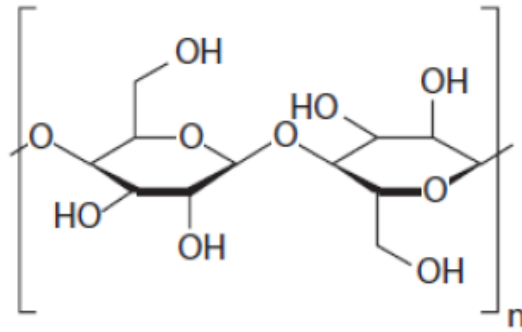
Figure 2.3 Chemical structure of cellulose where n is the degree of polymerization, according to **(Pecoraro et al., 2008)**.

Cellulose consists of two glucose molecules linked and esterified by β-1,4 glycosidic bonds that are structured in long linear chains (micro bright) linked by hydrogen bonds and intramolecular Van der Waals forces. The set forms a crystalline structure resistant to hydrolysis combined with different amorphous sections that are more sensitive to enzymatic degradation *(Béguin & Aubert, 1994; Chacón & Waliszewski, 2005)*. Cellulose is a linear polymer in which β-1,4 glycosidic linkages are linked to form cellobiose repeating units, *(Pecoraro et al., 2008)*.

2.2.3 Hemicellulose

Hemicelluloses form branched chains with a lower polymerization degree than cellulose and, therefore, generally do not have crystalline zones. In addition, hydrogen bonding is less efficient, making hemicellulose polysaccharides more accessible to attack by chemical reagents. The monomers that makeup hemicelluloses are mainly monosaccharides and derivatives such as uronic acids. The main monosaccharides found in hemicelluloses include three hexoses: glucose, mannose, and galactose, and two pentoses: xylose and arabinose, as shown in Figure 2.4 below.
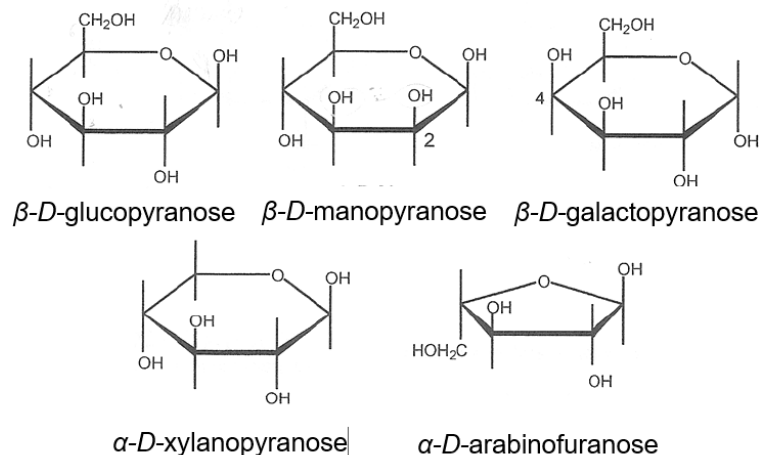
Figure 2.4 Haworth representation of the main hexoses and pentoses present in hemicelluloses, **(Brecher, 2006)**.

2.2.4 Lignin

Lignin is a hydrophobic material with a highly branched three-dimensional structure that can be classified as a polyphenol. The latter involves irregular linkages of various phenylpropane units that may contain hydroxyl and methoxy groups as substituents on the phenyl moiety. These ether bonds dominate the bond between the lignin units, which have many interconnections. This amorphous resin acts as cement between the fibrils and as a reinforcing agent in fibers. The strength of adhesion between cellulose and lignin fibers is increased by covalent bonds between the lignin chains and the components of cellulose and hemicelluloses, *(John & Thomas, 2008)*. Lignin is a unique biopolymer due to its heterogeneity and lack of a defined primary structure. Lignin is one of the most abundant organic polymers on the planet, second only to cellulose. As *(F. Lu & Ralph, 2010)* reported, the structure of lignin is defined according to the following characteristics.

   i.   Lignin is a plant polymer built from phenylpropanoid units.
  ii.   Lignin accounts for most of the total methoxylated groups contained in wood.
 iii.   Lignin when reacted with nitrobenzene in a hot alkaline solution, produce mainly vanillin, syringaldehyde and p-hydroxybenzaldehyde (concentrations vary depending on the origin of the lignins).
 iv.   When boiled in an ethanolic solution of hydrochloric acid, lignin forms monomers of the Hibbert ketone type (a mixture of aromatic ketones resulting from breaking the central ether bonds (-O-4) between lignin units).

According to *(F. Lu & Ralph, 2010)*, lignin has three basic phenylpropanic monomers (monolignols) that act as structural units, i.e., p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, as shown in figure 2.5.

Coumaryl p-alcohol   Coniferyl p-alcohol   Sinapyl p-alcohol
M_H M_G M_S
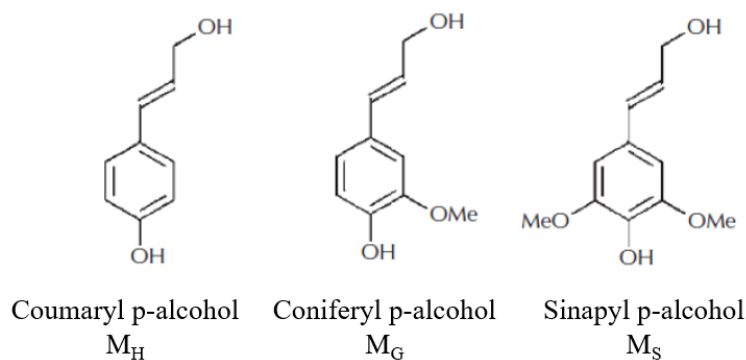
Figure 2.5 Primary structures of lignin, based in **(F. Lu & Ralph, 2010)** study.

Lignin is an aromatic polymer with heterogeneous and branched systems without defined repeating units, as *(Lewis & Yamamoto, 1990)* reported.

2.3 Biofuels

Biofuels are fuels of renewable origin that can be used as substitutes (pure or mixed in different proportions) or as additives for conventional fuels such as diesel or gasoline. Regarding fuels, the government thresholds for reducing gas tariffs and the greenhouse effect require the

progressive substitution of more fossil fuels for clean (and renewable) fuels. The increasing demand for alternative sources of clean energy has intensified research on this topic. However, the obstacle encountered during the production of the most common biofuels today is that they often compete with the food industry and require large cultivation areas. Biofuels already have very well-established technologies, while others are still under development in this context. Thus, biofuels are generally divided into four generations, depending on the biomass used and production. Each generation has advantages and disadvantages compared to the others. The difference between these generations is shown in scheme 2.6.

Biofuels			
First generation	**Second generation**	**Third generation**	**Fourth generation**
Bioethanol or butanol by fermentation of starch (wheat, barley, corn, potato) or sugars (sugarcane, beet, etc).	Lignocellulosic Biomass: agricultural and forestry residues.	Algae.	Genetically modified algae.
Advantages: simple and cheap technology, conversion technology.	Advantages: no competition for food crops.	Advantages: easy to grow algae, no competition for food crops.	Advantages: high performance and reduction of CO_2 emissions into the atmosphere.
Disadvantages: low performance and direct competition with feed prices.	Disadvantages: expensive pre-treatment of lignocellulosic materials, lignin removal for fuel production.	Disadvantages: higher power consumption.	Disadvantages: the high cost of the photobioreactor.

Figure 2.6 Different types of biofuels, scheme modified from **(K. Dutta et al., 2014)**.

2.4 Fundamental of wood densification

The heat changes the mechanical properties of the wood and causes a reduction in its mass. Below 100°C, these effects are reversible, *(Arruda et al., 2012)*. The effects become irreversible or permanent with the increase in temperature and the duration of the treatment and are mainly linked to the deterioration of the wood, resulting in loss of mass and resistance. Losses depend on moisture content, heating medium, temperature, duration, and, in some cases, the species and size of the part involved. Hydrothermal treatment (HT), carried out in a humid environment, is used to improve wood properties, dissipate internal stresses and plasticize it. It is common for compression to be carried out in the presence of moisture since it facilitates the softening of the cell wall (without breaking the cells), making the wood more malleable. Some standard processes are, for example, heat treatment followed by high-temperature drying of wood, composites, or panels. Thermo-hydro-mechanical (THM) processes, where pressure is used, are applied to wood molding, friction welding, and quality improvement through densification *(Sandberg et al., 2013)*. The VTC (Viscoelastic Thermal Compression) wood manufacturing process densifies the wood through heat, steam, and mechanical compression. It is done in a way that does not damage the cellular microstructure of the wood *(Kutnar & Šernek, 2007)*. *(Hsu et al., 1988)* showed that steam pretreatment could increase the compressibility of wood

and reduce the formation of compressive stresses during hot pressing. *(Inoue et al., 1993)* managed to fix the densified form of the wood by applying a post-treatment with steam at 200°C for 1 minute or 8 minutes at 180°C. *(Morsing, 1998)* explained that the elimination of spring back in these cases where steam is used results from the breaking of chemical bonds, which allows the rearrangement of lignin and, therefore, the formation of bonds in new rearrangements. *(Reynolds, 2005)* investigated the physical properties of densified wood and concluded that swelling below 15% can only be achieved if the densification process is carried out at 200°C and 100% humidity. Like steam, heat can also induce permanent fixation of the densified form of the material through thermal degradation of the hygroscopic components of the cell wall, especially hemicelluloses *(Morsing, 1998)*. Research in wood densification and post-treatment applied after thermo-hydro-mechanical treatment points to the possibility of treating large-sized wood used in civil construction. In smaller samples, it is possible to guarantee the homogeneity and reproducibility of the treatment and the uniformity of temperature and moisture content of the samples during densification and in the post-treatment process *(Sandberg & Navi, 2007)*. However, during the densification of more significant elements, cracks and delamination occur, problems related to the element's size.

Furthermore, amorphous polymers have a disordered molecular structure and, in their natural state, are generally transparent, brittle, and rigid. The amorphous polymers in wood are hemicellulose and lignin *(Morsing, 1998)*. At room temperature and humidity, these polymers have a glassy behavior and can be characterized as hard and brittle. However, at high temperature and high moisture content, polymers become more malleable, in a state characterized by large plastic deformations *(Kutnar & Šernek, 2007; Wolcott et al., 1990)*. The heterogeneous, low molecular weight and the non-crystalline structure of hemicellulose coexists with cellulose in the cell wall, and these are tightly bound to each other and lignin. The latter acts as an adhesive, joining microfibrils made of cellulose and covered by hemicelluloses. Due to the amorphous structure, the hydroxyl groups of hemicellulose are much more available to water than cellulose *(Kocaefe et al., 2008)*. Thus, according to these authors, the elimination of hemicelluloses reduces hygroscopicity. However, this also increases the crystalline part of the wood due to the relative increase in cellulose. When the relative amount of the hemicellulose-cellulose-hemicellulose bond is replaced by the cellulose-cellulose bond, the flexibility of the wood decreases. The viscoelastic nature of wood is of great importance in compression and densification. At low temperatures and humidity, wood behaves resistant and even brittle *(Kutnar & Kamke, 2012)*. At high temperatures and humidity, wood has a flexible and malleable behavior. The transition phase occurs between these two conditions, usually characterized by the glass transition temperature (Tg) *(Horvath et al., 2011)*, as shown in figure 2.7. Temperatures above Tg promote mobility and allow the rearrangement of the amorphous molecular structure. Consequently, large strains can occur without cell wall fractures. In addition, temperatures higher than the Tg of lignin, which is the dominant Tg, modify the absorption properties of wood *(Kutnar & Kamke, 2012)*.
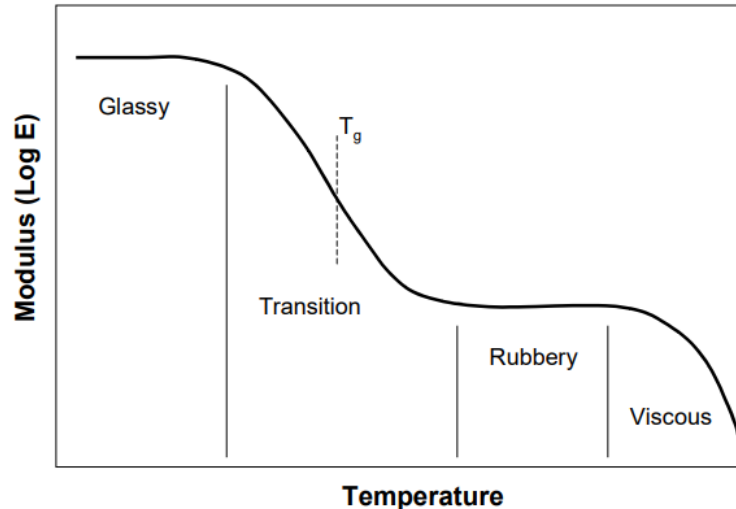
Figure 2.7 Variation of the modulus of elasticity vs temperature for an amorphous polymer from **(Lenth, 1999)**.

Furthermore, many authors studied the glass transition of cellulose, hemicellulose, and lignin and found that the moisture content of the material influences it *(Atalla et al., 1976; Back & Salmén, 1982; Bhuiyan et al., 2000; Feldman, 1985; Fengel, 1966; Irvine, 1984; Jakobson & Erinsz, 1981; Klason & Kubat, 1976; Poncsák et al., 2006; L. Salmen, 1982; N. L. Salmen, 1979; Weiland, 2000; Wikberg et al., 2002; Wikberg & Liisa Maunu, 2004; Yang & Goring, 1980; Yano et al., 1976; Yano & Hatakeyama, 1988)*. vitreous polymers, analysis techniques with DTA or the calorimetric method, and infrared spectrometry were used. The glass transition temperature (Tg) is the transition from a rigid ordered (glassy) state of the polymer to a disordered state in which the polymer chains have increased mobility (the polymer softens). In the case of some classes of natural polymers, this mobility, such as cellulose, hemicellulose, and lignin, gives rise to plastic behavior *(L. Salmen, 1982)*. The value of the glass transition temperature of wood polymers undergoes some variations depending on the technique used to measure it, not being a fixed thermodynamic point. Several factors influence the glass transition. Among them, the following can be highlighted the rate of heating (or cooling), the degree of crystallinity, the degree of polymerization, and the molecular weight, but such variations are limited to a not very wide temperature range. In the case of lignin, the moisture content has a significant effect on the softening temperature, which decreases with increasing moisture content *(Back & Salmén, 1982)*. In general, it can be stated that for cellulose, the glass transition temperature is between 200 °C and 250 °C. For hemicellulose, it is observed the range between 150 °C and 220 °C and, for lignin, the range between 180 °C and 200 °C *(Back & Salmén, 1982; Irvine, 1984)*. According to *(Goring, 1963)*, the glass transition temperature of lignin is influenced by the molecular weight due to the increase in crosslinking. Also, *(Irvine, 1984)* found that the glass transition temperature decreases as the moisture content increases.

In general, the main adverse effect of densification is the spring-back effect, which is the tendency of the material to return to its initial thickness after the stress is released. The storage of elastic strain energy causes it during the compression of semicrystalline hemicellulose microfibrils. Despite this stored energy, compressed wood maintains its shape after pressing due to the binding of deformed microfibrils with lignin and cellulose through solid covalent bonds and hemicellulose hydrogen bonds *(Skyba et al., 2009)*.

2.5 Pelletizing process

In general terms, granulation consists of densifying the biomass by applying pressure on a certain mass of particles with or without the addition of binders and temperature. In the case of wood, the addition of binders is variable due to the lignin content present in each biomass and the required quality. Pellets are granular solid fuels obtained by compacting biomass in a perforated matrix coupled to a press. Pelletizing optimizes the characteristics of the biomass, generating materials of homogeneous size and shape, which contributes to the reduction of volume, storage and transportation costs *(Warajanont & Soponpongpipat, 2013)*. Among the factors that influence granulation, the temperature and the pressure exerted on the biomass stand out. Among the factors related to the raw material, the moisture content, the shape and particle size, and the chemical composition stand out. Furthermore, these factors also affect the quality of the densified biomass *(Shaw, 2008)*. In the pelletizing process, the pellets go through various stages of production, both upstream and downstream of their extrusion through the die, as exemplified in scheme 2.8.
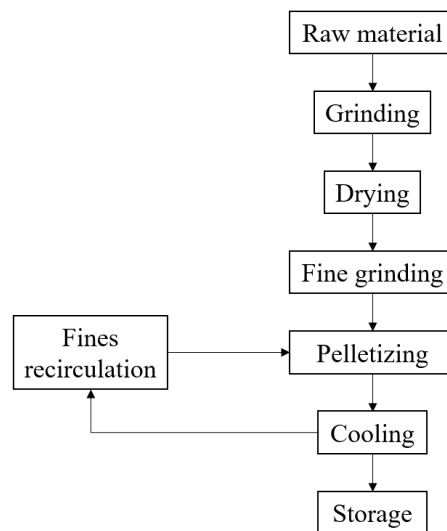
Figure 2.8 Diagram of the pellet manufacturing process

After receiving the raw material at the facilities, the following steps include grinding the material to reduce its granulometry and drying to adjust the moisture content. These steps can be optional when the raw material is already in the form of sawdust and without excess moisture. The drying process can be carried out naturally or using dryers. The first option can reduce energy costs, but the disadvantages are long drying times, the occupation of large spaces, and difficulties in regulating moisture content. The next step is the fine grinding of all the material to standardize the dimensional granulometry of the sawdust, a factor that will influence the density of the final pellets. Once these steps are guaranteed, the material is pelletized. This operation consists of pressing the raw material through rollers, followed by extrusion through a perforated die with circular holes. At the die outlet, the pressed material is cut by blades and adjusted to measure to obtain a final product with the desired dimensions. In general, this process occurs at high temperatures, between 110 - 130 °C, due to friction and pressure in the order of 210 to 450 MPa, caused by force in the roll-die system *(N. P. K. Nielsen et al., 2009)*. In general, both components (die and rollers) are steel. The high temperature reached during the

17

process helps aggregate the particles since, when heated, the lignin in the wood acquires certain plasticity. However, natural glue additives, such as corn, are sometimes used to facilitate the pressing process and improve the pellets' energy balance and strength. Subsequently, the cooling process must be ensured so that the lignin of the biomass hardens and the pellets adapt their typical rigid shape. If this step results in significant amounts of fines, then the pellets should be screened, and the fines sent back to the granulation stage. Once cooled, the pellets can be stored in silos, sold in bulk, packaged in 15 kg bags, or 500 to 1000 kg big bags. Storage, whether at the factory or the customer, must be in a dry place to maintain durability due to low moisture content.

2.5.1 Raw material

The use of forest biomass for energy purposes, in general, presents a tremendous variation in terms of its chemical and physical composition, which directly influence the energy properties, the combustion process, and the use of the by-products generated from the transformation of wood, for example, densification. The density and moisture content of the raw material are the main characteristics that influence granulation. The density influences the energy density of the pellets. In addition, materials with higher density require equipment with greater power and higher energy consumption. The moisture content influences the formation of pellets due to the heat transfer process with the consequent plasticization of the lignin and the reduction of the energetic properties of the fuel *(Tumuluru et al., 2011)*. One of the leading chemical constituents to be evaluated in wood for pellets production is the lignin content. It releases a more significant amount of energy than the other main compounds of the plant (cellulose and hemicelluloses) and collaborates with the compaction process. At temperatures above 70ºC, lignin begins to plasticize, becoming malleable and allowing better adhesion between the particles during the densification process, resulting in pellets with better mechanical properties *(Kaliyan & Morey, 2010)*.

2.5.2 Pelletizing equipment

Usually, closed dies are used to study the effect of pressure on a laboratory scale that produces a single pellet, with a configuration similar to the one shown in figure 2.9, since this allows tests to be carried out at fixed pressure levels in the pellets that the forming pressure is independent of the other process parameters. Although in the industrialized production of pellets, the pelletizing pressure is always a parameter dependent on the other process parameters, there are few studies in which an open die is used at the laboratory level to simulate the pelletizing/extrusion process *(Munoz-Hernandez et al., 2006)*.
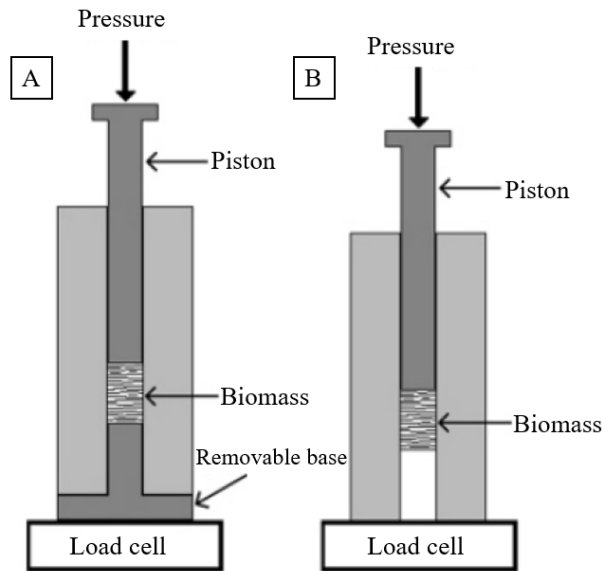
Figure 2.9 Diagram of a single-pellet system: A) configuration for pellet production with a removable base, B) configuration without a removable base to measure the resistance of the pellet to movement inside the channel **(Holm et al., 2006)**.

On an industrial level, pellets are usually produced in a machine with a die and rollers that force the raw material into the channels of the die as seen in figure 2.10. During pelletizing, a fraction of the material is forced into the die channels by the rollers, and with each pass of the rollers creates layers of compressed material that make up the pellet in a semi-continuous manner. Due to the friction between the channel surfaces and the biomass, a counter pressure is formed, and energy is generated in the form of heat *(Stelte et al., 2012)*. The pressure exerted by the roller (P_R) has the same direction in the opposite direction to the counter-pressure generated in the channel (P_X), figure 2.10. Under steady-state conditions, the two pressures are in equilibrium. When the pressure in the channel exceeds the pressure that the roller can generate, the channels become blocked since the rollers cannot generate enough pressure to push the material through the channels. Therefore, the optimal magnitude of P_X must take into account the pressure necessary to produce stable pellets of good quality and the energy expenditure by the pelletizing machine. High P_X further increases the risk of fires due to excess heat developed by friction. The back pressure of the channel is mainly affected by the type of material used, the geometry of the channel, the humidity of the material, the temperature of the material, and the particle size of the material *(Stelte et al., 2011)*. In order to study the back pressure generated in the channel, some authors such as *(Holm et al., 2006, 2007, 2011; N. P. K. Nielsen et al., 2009; Stelte et al., 2011)* have used a configuration similar to the one shown in figure 2.9 in which biomass is introduced into a chamber with a plug to compact the biomass and generate a single pellet (figure 2.9A). The base is removed, and the pressure necessary to move the pellet is recorded through the channel (figure 2.9B). The studies mentioned above show that the back-pressure increases as the humidity of the sample decreases, the temperature decreases, the grain size decreases, and the length of the pellet increases (which in an industrial machine would mean an increased length of the channel).
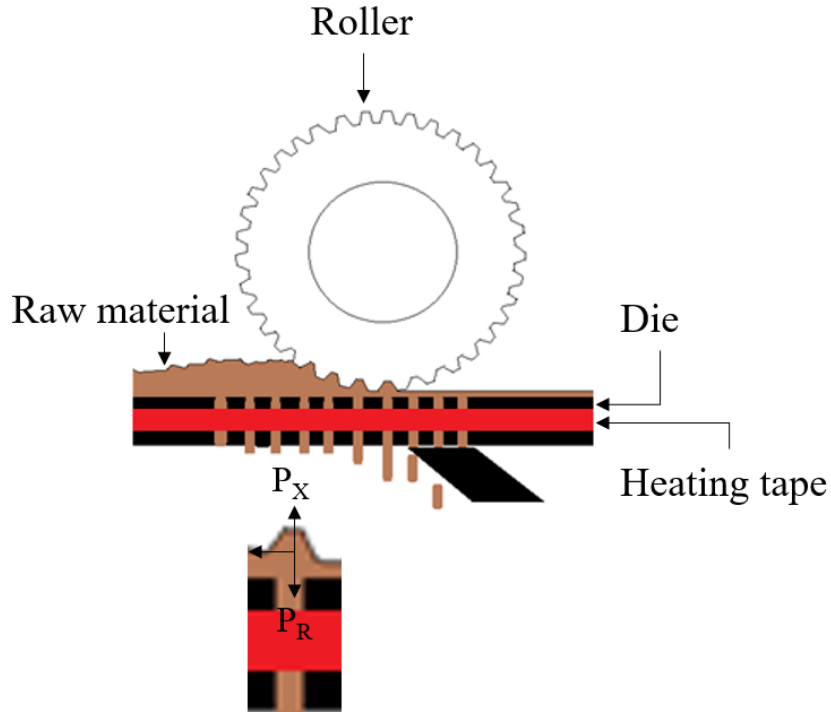
Figure 2.10 Diagram of the pelletizing channel of a roller pellet mill, adapted from **(Stelte, W. et al., 2012)**.

2.5.3 Processing parameters

Moisture content

Water plays a crucial role in the pelleting process *(N. P. K. Nielsen et al., 2009)*. It has been found that it is the factor that most influences the quality of the pellets. The water contained within the biomass acts simultaneously as an agglomerating agent and as a lubricant *(Kaliyan & Vance Morey, 2009)* and helps to generate Van der Waals forces by increasing the contact area between the particles *(Grover & Mishra, 1996)*. Water helps the adhesion process when water-soluble components are found, such as sugars, proteins, or starches. Several studies have found that the agglomerates' durability increases as the biomass's moisture content increase until an optimum is reached, after which the durability decreases *(Kaliyan & Vance Morey, 2009)*. In general, good results have been obtained with humidity in the range of 8 to 15%, although the optimal range depends on the specific biomass used, finding values of 10 to 15% for wheat straw *(Smith et al., 1977)*, 8 to 9% for alfalfa *(Hill & Pulkinen, 1988)* and 11 to 12% for corn by-products *(C. A. Stevens, 1987)* among others. At humidities more significant than 25%, the densification process is complex, probably due to the incompressibility of the water, since the moisture trapped inside the particles can prevent the complete crushing of the product and, therefore, the release of natural binders contained within the particles *(Pickard et al., 1961)*. If the raw material does not have a good moisture absorption capacity during the conditioning process, the water can remain on the surface, forming a lubricant between particles. This causes that during the pelletizing process, the center of the material that passes through the die extrudes more quickly than the one in contact with the channel walls, forming what is known as cone-shaped pellets, which reduces the durability of the pellet. A low percentage of humidity, in turn, is highly undesirable because if it is significantly lower than that of the environment, the pellet will begin to gain moisture from the medium. In the work carried out by *(Y. Li & Liu, 2000)*

reports the realization of pellets with 4% humidity that became brittle after a few days due to the aforementioned process.

Material temperature
During the pelleting process, an increase in the temperature of the biomass is generated due to the friction between the particles and the die walls. In some processes, in addition to the heat generated by friction, an external source is used to further increase the temperature. *(Serrano et al., 2011)* studied the temperature distribution by taking thermographic images of a pelletizing machine and found that the temperature of the die in stable operation was around 90 °C while the temperature of the pellet leaving the die was 70 °C. In the literature, most authors agree that an increase in pellet quality is observed when the process is carried out at temperatures greater than 60 °C, regardless of the type of biomass studied *(S. M. Lee et al., 2013; Stelte et al., 2011; Stelte, W. et al., 2012; van Dam et al., 2004)*. The effect of temperature on the quality of the pellet becomes significant when working above the glass transition temperature of the polymers that make up the biomass, such as hemicellulose, cellulose, and lignin, since it allows plastic deformation of the grains, facilitating the flow of biomass through the pelletizing channels and a better contact between particles that facilitates the formation of solid bridges between them *(Stelte, W. et al., 2012)*. Also, the increase in temperature helps the agglomeration of particles, especially in the presence of water, since the combination of the two induces a wide range of physical and chemical effects such as thermal softening of biomass, starch gelatinization, and solubilization and the subsequent recrystallization of sugars and salts *(Kaliyan & Morey, 2010; Thomas et al., 1998)*.

Particle size
Grain size is an essential factor for the durability of pellets. Generally, the larger the grain size, the greater the durability *(Kaliyan & Vance Morey, 2009)* since, the smaller its size, the greater the surface area of grain contact, which helps pelletization *(Tumuluru et al., 2010)*. In truth, when looking for the ideal grain size, what is done is to find a balance between the quality of the pellet and the cost of grinding the material since the smaller the grain size, the higher the cost of grinding *(Mani et al., 2004)*. According to *(Franke & Rey, 2006)*, particles with grain sizes greater than 1 mm will act as predetermined breakpoints in the pellet, so it is advisable to work with grain sizes smaller than 1 mm. Although laboratory equipment with closed dies fully complies with the that the smaller the grain size, the better the durability, in industrialized equipment with open dies, there is a point where if the grain is tiny, the material has difficulties flowing, creating clogging of the material in the die *(Tumuluru et al., 2010)*. Due to this, it is common when looking for information on the ideal grain size that the authors report a minimum and maximum grain size within which it is ideal for making pellets. For example, *(Franke & Rey, 2006)* report good pellets using a particle size between 0.5 and 0.7 mm, while *(Turner, 1995)* recommends a size between 0.6 and 0.8 mm. Other authors, such as *(Payne, 2006)*, are more detailed and recommend a grain size distribution, as shown in Table 2.2.

Table 2.2 Recommended grain sizes to produce good quality pellets, according to (Payne, 2006).

Sieve opening (mm)	Percentage retained on sieve (%)
3.0	Up to 1
2.0	Up to 5
1.0	Around 20
0.5	Around 30
0.25	Around 24

Die geometry

The die is a fixed part of a pelletizing machine, so it is generally one of the least manipulated parameters. Doing experiments with different die sizes, several authors have found that as the diameter of the pellet decreases, its durability increases. The same happens as the length/diameter (L/D) ratio increases *(Franke & Rey, 2006; Pfost, 1964; Tabil & Sokhansanj, 1996; Thomas et al., 1998)*.

Pelletizing pressure

Since one of the main objectives of pelleting is to increase the bulk density of the biomass, the pressure at which the pelletizing is carried out is one of the main parameters to be taken into consideration. The pelletizing pressure is directly in charge of compacting the biomass to agglomerate the particles and thus increase the density of the biomass. The higher the pelletizing pressure, the higher the density of the pellets, so it is sought to carry out the process at the highest possible pressure. The only physical limitation to take into account is, according to *(Ndiema et al., 2002)*, that for a given size of die and biomass, there is a maximum pressure after which no significant increase in pellet density is observed. In the densification process, what is done is to reduce the space between the particles and promote their agglomeration. The density of the individual particles is not modified because it is a mechanical process, so the maximum density that a pellet can reach is the density of the particles it is made up. In the literature, the pelletizing pressures required for good agglomeration vary widely depending on the biomass used, from 5 MPa for oak sawdust *(Y. Li & Liu, 2000)* to 800 MPa for waste paper *(Demirbas & Sahin, 2004)*.

2.6 Pellet properties

In this study, the CANplus certification was used to evaluate the physical and chemical properties of the manufactured lignin pellets. Table 2.3 summarizes these properties.

Table 2.3 Threshold values of the most important pellet parameters.

Property	CANplus certification			Testing standard
	A1	A2	B	
Diameter (mm)	6 ± 1 or 8 ± 1			ISO 17829
Length (mm)	$3.15 < L \leq 40$			ISO 17829
Moisture content (%)	≤ 10			ISO 18134
Ash content (%)	≤ 0.7	≤ 1.2	≤ 2.0	ISO 18122
Mechanical durability (%)	≥ 98.0	≥ 97.5		ISO 17831-1
Fines content (%)	≤ 1.0			ISO 18846
HHV (MJ/kg)	≥ 16.5			ISO 18125
Nitrogen	≤ 0.3	≤ 0.5	≤ 1.0	ISO 16948
Sulfur	≤ 0.04	≤ 0.05		ISO 16994

2.6.1 Moisture content

Moisture content (MC) was measured before and after granulation, as suggested by (ISO 18134-3:2015, n.d.). According to this procedure, samples are dried in an oven at a temperature of 105 °C to a constant mass. The mass loss induced from the drying process is then interpreted solely as a loss of humidity. Mass of water reported on dry matter mass was used to calculate the water content. This part of the testing was performed using an HT1000 industrial oven (The Grieve Corporation, Round Lake, IL, USA). Four initial moisture content were analyzed. The final moisture content of the pellets was shown to be highly dependent on the conditions of the granulation process, especially the initial moisture content of the lignin and die temperature, extrusion rate, and compression pressure.

2.6.2 Dimensions

The dimensions of the lignin pellets were measured using a digital electronic micrometer (iGaging 35-040-025-I; San Clemente, CA, USA) with an accuracy of 0.001 mm, and the results were reported for lignin pellets manufactured at different moisture content. The measurements for the diameter and length of the pellets were performed according to (ISO 17829:2015, n.d.) and are shown below:

i. For the length: each end of the micrometer was positioned at both ends of the pellets.
ii. For the diameter: three measures were gathered, the first one in the center as well as two more from each end of the pellets.

2.6.3 Impact resistance

The impact resistance was conducted following (ASTM D440-86, n.d.) guidelines and was applied to pellets made from the varying humidity content. Each sample contained approximately 48.0 g of lignin pellets. The bags to store the pellets were 170 mm x 129 mm sealable bags made from a 100% cotton canvas material and sold by Baotongle. Each bag was dropped 10 times, from a 2.0 m height. The mass of the bag before and after the experiments

was determined using a precision electronic scale (model Poker). Then, equation (1) was used to determine the percentage of weight loss for the resistance to impact experiments.

$$P = 100 \times \frac{W_1 - W_2}{W_1} \qquad (1)$$

where P is the percentage of weight loss, W_1 is the weight of lignin pellets before shattering and W_2 is the weight of lignin pellets after shattering and sieving.

2.6.4 Water resistance
The percentage of water adsorbed by the pellets was obtained through water resistance experiments that were performed for each value of the initial moisture content used to produce the pellets. Three samples of approximately 10.29 g (of lignin pellets) were used in this experiment. The samples were immersed in 0.52 liter of water for 2 minutes at 23.5 °C after which the mass gain percentage was calculated. The mass of the samples was determined using the same precision scale as described in the previous steps. The lignin pellets were then sieved to select the samples that were to be used for the impact as well as the water resistance experiments.

2.6.5 Fines content
Fines are here defined as the particles attached to the pellets of dimension less than 3.15 mm. To reduce the fines content, after production and cooling, the pellets are passed through sieves. The fines content in lignin pellets was determined using (ISO 18846:2016, n.d.).

2.6.6 Mechanical durability
Durability is an important parameter in the wood pellet industry, and tumbling is the most commonly employed method to determine the durability and quality of pellets. Low durability usually leads to a greater tendency towards rupture, hence producing fine particles. High content of the latter may suggest issues in storage and handling and may induce health and environmental challenges as well. In addition, to determine the durability of the pellets manufactured in this work, two samples of approximately 100 g each were used. These samples have been set to tumble for 2 min at 50 pm, after which the pellets were sieved on a 3.15 mm diameter sieve. The durability of the pellets produced was evaluated as described by (ISO 17831-1:2015, n.d.) then calculated using equation (2).

$$DU = 100 \times \frac{m_2}{m_1} \qquad (2)$$

where DU is the mechanical durability (in %), m_1 is the mass of the sieved pellets before the tumbling process (expressed in g), and m_2 is the mass of the sieved pellets after the tumbling process (also expressed in g).

2.6.7 Calorific value
The calorific value was obtained using a model 6400 calorimeter from the company Parr Instruments (Moline, IL, USA) already available at the BTL. The calorimeter was calibrated using benzoic acid (recommended as standard) and verified before each run. The method used

in this specific case was based on (ISO 18125:2017, n.d.). This method relies on the combustion of the product from the ignition caused by the electric current (through conductive cables) and oxygen. At first, water was added to the calorimetric pump to generate a saturated vapor phase before the combustion. All the water formed from the combustion of hydrogen as well as from the original moisture content was considered liquid water. For the analysis of the lignin pellets, the first step involved the preparation of the sample. This part included the sample mass measurement and its subsequent introduction into the equipment that was then closed and pressurized with oxygen.

2.6.8 Ash content

The determination of the ash content is based on the measurement of the residual mass recovered after subjecting the samples to combustion at 550 ± 10 °C, as described in (ISO 18122:2015, n.d.). The equipment that was used to determine the ash content in the lignin pellets was a Thermolyne F-A1730 industrial furnace (Sybron Corporation, Dubuque, IA, USA).

2.6.9 Carbon, hydrogen, and nitrogen

The nitrogen content in the lignin solid biofuel was obtained using (ISO 16948:2015, n.d.). A mass sample is burned in a mixture of oxygen and gas, under conditions such that it generates ash and gaseous combustion products. The mass fractions of carbon dioxide, nitrogen, and water vapor were then quantified.

2.6.10 Sulfur content

The sulfur content was determined by decomposition through a calorimetric bomb with an excess of oxygen followed by the absorption of the acidic combustion gases in water. The quantification of both elements was performed following (ISO 16994:2016, n.d.).

CHAPTER 3

METHODOLOGY

Although forest biomass has good characteristics as a fuel, it also has logistical drawbacks, particularly in the collection, handling, transportation, and storage. In addition, its use in domestic heating systems is not rapid due to its irregular and heterogeneous shape. For these reasons, a way of using this biofuel has been proposed, allowing, to a certain extent, to compete with fossil fuels used for heat production. In this context, the present work on the production of pellets began, which could eventually constitute the most advanced way of harnessing the energy potential of forest biomass, presenting a simple and practical format for storage, transport, and disposal of use, in addition to, focus on the part of the biomass that is difficult to use, such as lignin.

3.1 Initial consideration

Finding the optimal manufacturing conditions for the granulation process, such as pressure, temperature, and compression rate (processing parameters), usually requires extensive experiments. For this study, the CANplus certification was used to validate the properties of the manufactured pellets. For the first study, two scenarios were considered. In scenario 1, four values of initial moisture content in the raw material were randomly chosen and analyzed (% humidity): 8.01% (H1), 26.21% (H2), 30.07% (H3), and 38.83% (H4). Reference pellets were manufactured in the same pellet mill from softwood (mixture of balsam fir and spruce) with 6.57% of humidity. The physical properties were compared with pellets made from poplar wood lignin. To improve the physical properties of the pellets, four different types of additives were used in scenario 2. Also, pellets were stored inside the building for 30-days storage time at 22.3 °C (condition 1), and other samples of pellets were stored in a cold chamber for 8-days at 2.0 °C (condition 2) only for those manufactured using a laboratory-scale pellet mill. For another study, softwood and lignin from softwood were used to manufacture pellets through the laboratory-scale pellet mill. Finally, in the single pellet system, different temperature conditions, compression pressure, and time were used until the resulting pellets were within the values required [12]. Finally, in the single pellet system, different temperature conditions, compression pressure, and time were used until the resulting pellets were within the values required [12]. Different types of lignin, from poplar wood and corn stover, were used for this device. As additional work to the main objective of this research, softwood was used to perform steam explosion experiments. The residue obtained from this process was dried and subsequently used to manufacture pellets using the single pellet system. Finally, biomass from hemp was used for the manufacture of pellets.

3.2 Raw material

This study used poplar wood and softwood bark as forest residue to produce sugar and lignin at a pilot scale. RéSolve Énergie Inc. (Lac Mégantic, QC, Canada) provided the purified lignin

that was generated through their proprietary process. The latter is a "direct saccharification of lignocellulosic biomass," a non-enzymatic chemical process. Sugars were used to produce low carbon intensity (CI) ethanol. In contrast, the residual lignin was used as raw material to produce pellets through two devices, a single pellet system, and a laboratory-scale pellet mill. The lignin samples intended to produce pellets were mixed with hot water to obtain the different initial moisture contents. To find and homogenize the initial moisture content in samples, they were stored in plastic buckets and sealed for ten days before pelletization. In addition, thermogravimetric analysis (TGA) was used to characterize lignin degradation and evaluate its thermal stability and degradation kinetics. The material was tested on a range of temperatures to identify the maximum operating one, at which lignin should get softer while degrading as minimally as possible. This technique (TGA) allows measuring the mass variation of the sample as a function of temperature. This technique used the operating temperature range of 10.0 °C/min to 1000.0 °C using nitrogen gas with a 90.0 ml/min mass flow. The general block diagram of the ReSolve process is shown in figure 3.1.
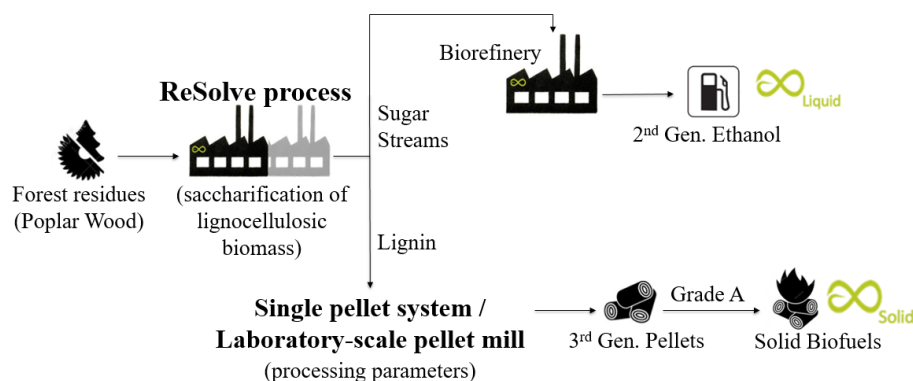
Figure 3.1 Block diagram of the ReSolve process, source of the lignin used in this work

3.3 Experimental setup

3.3.1 Single pellet system

Pellets were individually produced in a piston-cylinder type system that was designed and assembled at the Biomass Technology Laboratory (BTL) machine shop located at the Université de Sherbrooke (Sherbrooke, QC, Canada). The system, although strongly inspired by models used in the literature *(Frodeson, S. et al., 2018; Lam et al., 2011; Rudolfsson et al., 2015)* involved two modifications:

  i. A temperature control and heating system were implemented in the system and,
  ii. A sensor was added to the bench to monitor compression pressure during the process.

These modifications allowed for a better understanding of the pelletization procedure while providing more data on system behavior. The lignin compression system consisted of a classical metal piston-cylinder where the latter is 6.5 mm in diameter and is made of hardened steel, packed with heating elements and thermal insulation while the piston is 80 mm in length. The cylinder channel allowed the introduction of the lignin and a removable base to manage the pellets after pressing. A general three-dimensions (3D) overview of the design of the experimental bench is shown in figure 3.2A. Furthermore, the individual hydraulic press was

mounted on a Chicago Pneumatic CP86200 test machine (Chicago, IL, USA) make it possible to control the force of the piston inside the cylinder during the lignin compression process (see figure 3.2B).

(A)   (B)
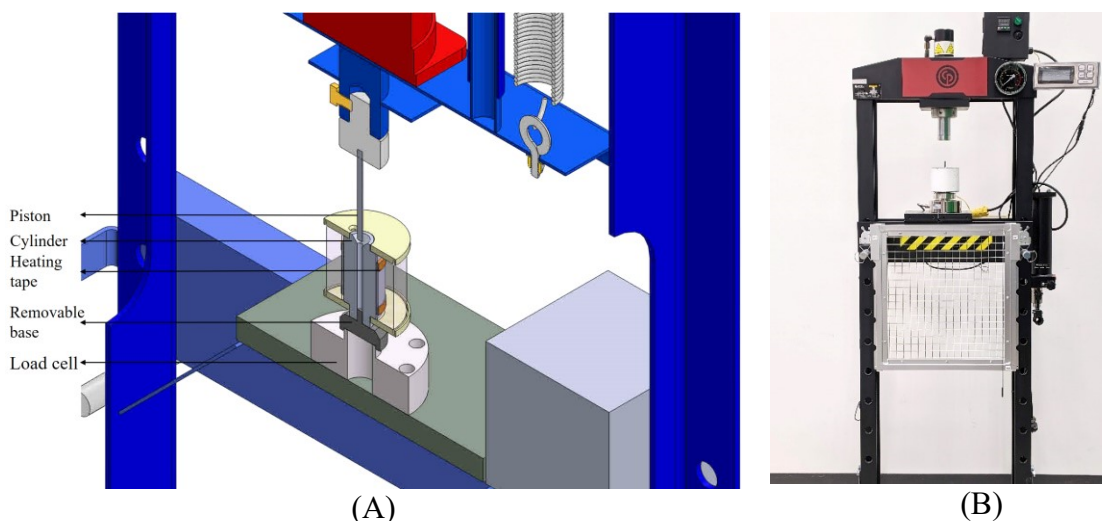
Figure 3.2 (A) 3D drawing of the experimental system used to make the pellets, and (B) picture of the actual experimental bench located at the Biomass Technology Laboratory

Heating was supplied to the cylinder by conduction using a heating tape that was wrapped around the compression chamber and the temperature was monitored directly using a thermocouple. During the manufacture of one pellet (as shown in figure 3.3), the system was preheated to reach the desired temperature (77 °C). It remained stable showing a temperature variation of ± 3 °C. The single pellet system was employed to determine the influence of the compression chamber temperature on the formation of a single lignin pellet. The compression chamber of the single pellet system was fed with sequential samples of 0.26 g of lignin per layer, producing pellets with three layers with a 0.78 g average mass. The lignin sample was compressed to a maximum pressure of 12 MPa, the value that was confirmed using a 50 kN load cell located at the base of the cylinder. The force supplied by the hydraulic press was 21.57 kN and the compaction pressure of the sample under this force was calculated considering the area of the cylinder-piston system and yielded a pressure of 650.17 MPa. The compression pressure was kept stable for 2 minutes, then, the base of the cylinder was removed, and the pellet was pressed out at the same compression velocity. This pelletizing procedure resulted in a product with a shiny structure, where each layer was exposed to the same pressure for the same time. The pellet was cooled down and stored in closed-in air-tight plastic bags at room temperature (22.3 °C) after which physical and chemical parameters measurements were performed. The reproducibility of the experimental conditions was facilitated by an exhaustive cleaning (involving brushing and air blowing the compression chamber) between samples.

Raw material

Single pellet system

Lignin pellets
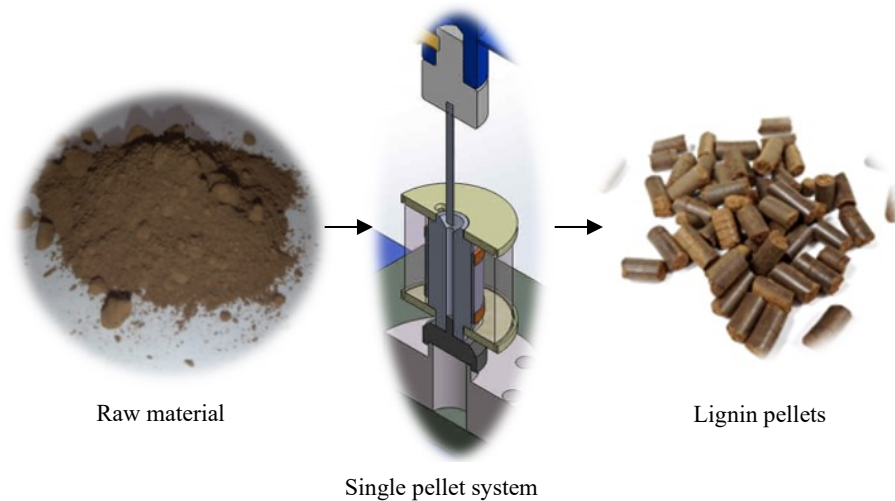
Figure 3.3 Pellets production process using the single pellet system employed at the
Biomass Technology Laboratory

3.3.2 Laboratory-scale pellet mill

This device involved a minor adaptation: a silicone rubber heating tape equipped with a time percentage dial control (BSAT) and a thermal insulation tape around the die. The previously mentioned heating tape system was a BSAT051006 model from BriskHeat (Columbus, OH, USA), and by adding it to the unit, it allowed supplying heat to the flat die during the pelletization thus providing more data on the thermal behavior of the manufacturing process. The pellet mill was a Buskirk Engineering laboratory-scale unit (Ossian, IN, USA) model PM605, and the pelletizer employed in this study is shown in figure 3.4. It was equipped with a variable-speed electric drive, although the extrusion rate used to manufacture lignin pellets was 1920 RPM. The flat die used in the present experiments had a hole diameter of 6.35 mm and a length of 38.1 mm, providing a compression ratio of 6.

Figure 3.4 The PM605 (Buskirk Engineering) laboratory-scale pellet mill used for the
production of lignin pellets

Before pelletization, the system was preheated for 1 hour, after which the pellet mill was fed with approximately 1 kg of raw material. The heat was supplied to the system by conduction using the previously mentioned silicone rubber heating tape positioned around the flat die. The temperature was set between 86.1 °C and 132.1 °C and led to an operating temperature ranging between 61.1 °C and 77.1 °C inside the roll-die system. A Fluke model PTi120 pocket thermal camera (Everett, WA, USA) was used to monitor the temperature inside the system. After pelletization, a sieve with round holes (3.15 mm diameter) was used to sieve the solid biofuel that was produced, according to (ISO 3310-2:2013, 2013). The lignin pellets were then cooled and stored in a closed plastic bag at room temperature (23.5 °C), after what physical and chemical parameters measurements were performed. Figure 3.5 shows the lignin pellets production procedure using the continuous laboratory-scale pellet mill.

Raw material

Lignin pellets

Laboratory-scale pellet mill
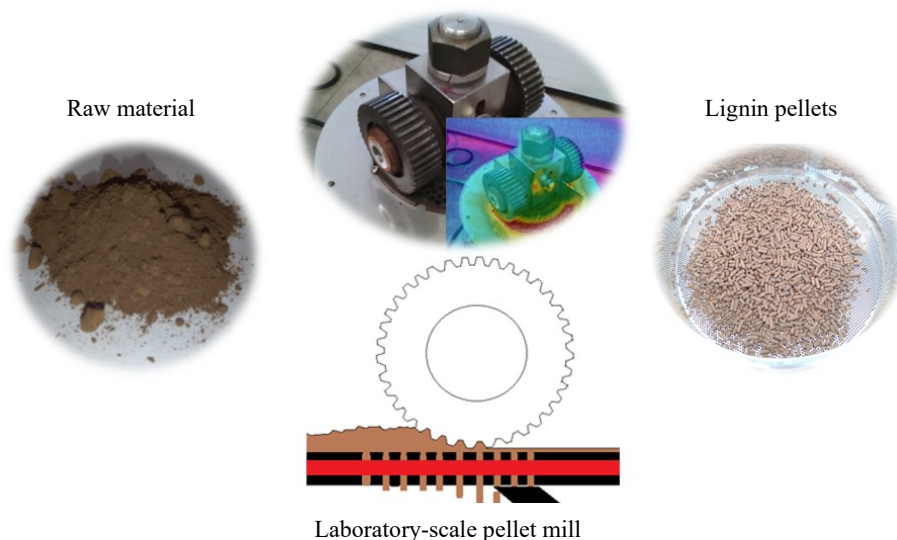
Figure 3.5 Pellets production process through the laboratory-scale pellet mill employed at the Biomass Technology Laboratory.

The reproducibility of the experimental conditions was facilitated by a thorough cleaning between samples (involving brushing and air blowing in the roll-die system). The temperature of the heating tape was selected considering the results from the Thermogravimetric Analysis (TGA) of the poplar wood lignin. For the latter, the operating temperature range was from 10.0 °C/min to 1000.0 °C/min, and the gas used was nitrogen with a mass flow of 90.0 ml/min. The TGA (TA Instruments Q500 - New Castle, DE, USA) experiments were performed at the Biomass Technology Laboratory (BTL). The different moisture content values were selected based on previous studies that were made for this type of biomass, as well as on work performed to manufacture pellets by (Berghel et al., 2013; Civitarese et al., 2019; Monedero et al., 2015; Peng et al., 2013; Stelte et al., 2012; Stelte, W. et al., 2012; J. Stevens & Gardner, 2010; Tarasov et al., 2013; Tumuluru, 2014, 2016; Zafari, A. & Kianmehr, M.H., 2012). Furthermore, the temperature value for the pelletization process was selected based on previous studies on lignin, such as those performed by (Antoniow et al., 2012; Back & Salmén, 1982; Baker, D.A. & Hosseinaei, O., n.d.; Goring, 1963; Goring, D., 2018; Hosseinaei et al., 2017; Kelley et al., 1987; J. Z. Lu et al., 2004; N. P. K. Nielsen et al., 2009, 2010; N. Nielsen & Vinterbäck, 2008; Sadatnezhad et al., 2017; Stelte et al., 2012).

Die geometry

The pellets were produced in a laboratory-scale pellet mill with a horizontal circular die from Buskirk Engineering with a production capacity of 68.03 kg/h. Three types of die compression channel dimensions were used.

    i. a hole diameter of 6.35 mm and a length of 38.1 mm, providing a compression ratio of 6.
    ii. a hole diameter of 6.35 mm and a length of 31.8 mm, providing a compression ratio of 5.
    iii. a hole diameter of 6.35 mm and a length of 25.4 mm, providing a compression ratio of 4.

3.4   Additives

In this part of the work, four additives were employed to see their impact on the downstream pellets, including (i) corn oil, (ii) citric acid, (iii) glycerol, and (iv) d-xylose. Corn oil is obtained from the germ of corn that has been previously separated from corn (maize). It can be used as a raw material to produce biodiesel and other industrial uses such as balsam, paint, nitroglycerin, etc. The pure vegetable glycerin that was used in this work was clear, odorless, lubricating, and emulsifying glycerin. This product is hypoallergenic and easily soluble in water, which makes it a good candidate to be used as an additive in the raw material. Citric acid powder ($C_6H_8O_7$) is one of the most common preservatives and flavoring additives. It can be found naturally in fruits and vegetables. It can also be obtained at an industrial level as a by-product of the metabolism of sucrose or glucose from the mold *Aspergillus niger*. Finally, d-xylose (wood sugar, $C_5H_{10}O_5$) is a fundamental component of hemicellulose in lignocellulosic biomass. Xylose can represent 20-30% of the weight of lignocellulosic biomass. (Zhang et al., 1995) suggested that xylose, along with glucose, can be converted into liquid biofuels (e.g., ethanol or butanol). In this study, a mixture of 60 grams of d-xylose in 100 ml of water were separately mixed with poplar wood lignin. Also, 330 ml of pure vegetable glycerin derived from non-GMO palm equivalent to 22% of the raw material used. Each additive used was blended for about 10 min to provide a uniform distribution in the raw material. The mixtures were stored in plastic buckets inside the laboratory at 22.3 °C. It is expected that these four products, used as bio-additives with the raw material, could act as co-binders and lubricants to reduce the energy required for the production of lignin pellet at a laboratory scale.

3.5   Steam explosion process

Softwood bark was used as raw material for this procedure. During the pretreatment by steam explosion, the biomass was subjected to 205, 215, and 225 °C through the direct injection of saturated steam (235, 291, and 355 psi) for 2, 3, and 4 min. After the treatment time, the material was subjected to rapid depressurization, which caused evaporation of the internal water, creating shear forces that produced the separation of the fibers, mainly from the weakest regions (amorphous cellulose). The experiments of pretreatment by the steam explosion of softwood bark were carried out using a pilot-scale reactor with a capacity of up to 1 kg of material, provided with sensors to monitor pressure and temperature, and valves for the entry and its subsequent steam decompression. For this additional work, 200 g of raw material was used in each test. The residence time counting was started after the pressure reached the values defined in the experimental design. The hydrolyzed material was filtered to separate the black liquor from the fiber and stored at -20°C. After filtration, the solid and liquid fractions were weighed, and their total solids and moisture contents were determined for mass balance evaluation. The

hydrolyzed fibrous materials obtained in these experiments were later used to manufacture pellets using the single pellet system.

CHAPTER 4

RESULTS

During the present work, four types of lignin were initially used for pellet production, namely poplar wood, corn stover, maple wood, and softwood bark. Lignin pellets were randomly selected to measure physical and chemical properties in each run. From the experimental tests carried out with two types of lignin (poplar wood and softwood bark) and two devices (as described in subchapter 3.3), an improvement was made in the pellet manufacturing process to deepen the concepts and inherent phenomena related to the physical and chemical properties of the lignin pellets. Scheme 4.1 shows the different types of pellets manufactured through both devices. For pellets made from steam-exploded softwood bark and hemp, the results can be found in annexes 1 and 2, respectively. The experimental work, related to the production of pellets and the analysis of the properties, was carried out at the Biomass Technology Laboratory (BTL) of the Université de Sherbrooke.
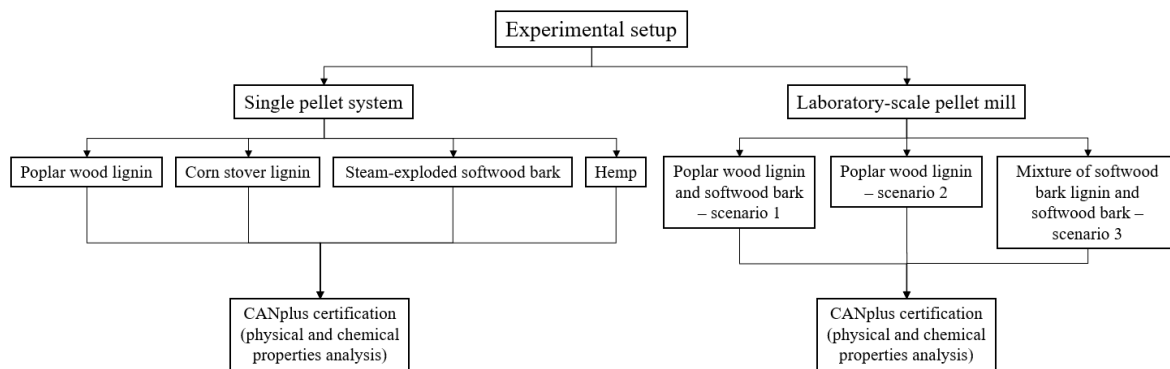
Figure 4.1 Devices used for the manufacture of pellets.

4.1 Sensibility analysis

The main objective of sensibility analysis is to study how a model and/or a process reacts to variations in parameter values. The analysis allows identifying the parameters that significantly influence the results. The prioritization of sensitive parameters during system calibration, on the other hand, lends itself to a better understanding of the process under study and a better estimation of its values, which allows reducing uncertainties, that is, when the sensitivity of the parameters is unknown, the time increases with those that are not sensitive, which takes more time to achieve the approximation of the measured data.

The experimental test carried out was based on the sensibility analysis performed so far. It is essential to point out that the parameters involved in the granulation process were varied in this analysis. Each parameter varied between its limit, maximum and minimum values, defined by the experimenter. In this way, the variation of a parameter is carried out, keeping the others constant. Thus, through the sensitivity analysis of each parameter, it is possible to identify and

understand which parameters most influence the granulation process. Table 4.1 below shows the parameters used in the process.

Table 4.1 Parameters employed in the manufacturing lignin pellets

Parameters	Minimum value	Value range	Maximum value
Compression pressure (MPa)	2.73	2.73	13.63
Temperature (ºC)	23.5	10.0	95.0
Moisture content (%)	10.40	10.0	79.12
time (s)	60.0	30.0	180.0

The sensibility analysis results can significantly direct resources to highly influential variables in the lignin pellet manufacturing process. Considering this, after experimental tests, the optimal process conditions that produce quality lignin pellets are compression pressure (650.0 MPa), temperature (between 61.1 °C and 77.1 °C), lignin moisture content (between 9% and 15%), and compression time (180s).

4.2   Properties of raw material

The thermogravimetric curve (green line) represents the mass loss in percentage, as a function of temperature. The derivate weight change curve (blue line) corresponds to the first derivative of the thermogravimetric curves and shows the variation in mass over time, recorded as a function of temperature. Figure 4.2 presents three evident stages of decomposition: the first, at temperatures around 100 °C can be attributed to the loss of water through desorption (considered a thermal event of physical origin, the mass loss is not significant). The second, at higher temperatures, is attributed to the decomposition of the lignin pellets. The third, at temperatures above 370 °C, is due to the decomposition of the remaining lignin, which started at lower temperatures and continues up to 500 °C. Also, according to the thermo-gravimetric analysis, poplar wood lignin showed a decrease in its thermal stability, exhibiting a glass transition temperature (Tg) at 90.68 °C.
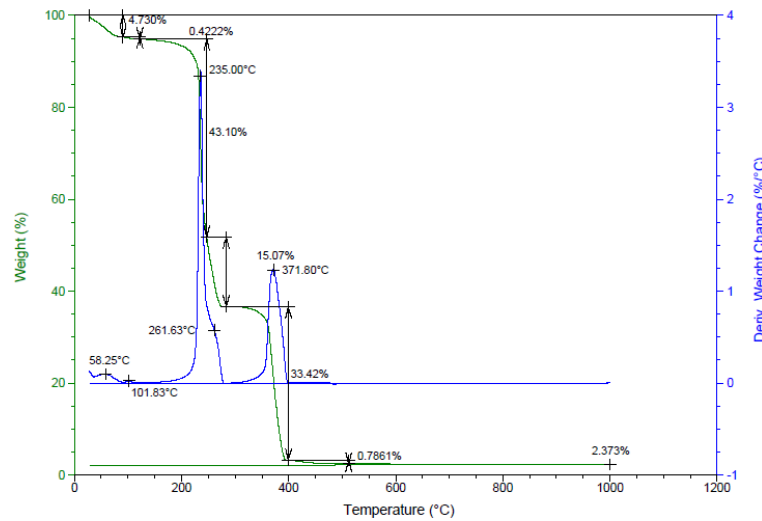
Figure 4.2 Thermogravimetric analysis of poplar wood lignin in an inert atmosphere.

4.3 Thermogravimetric image of the experimental setup

In light of the information gathered from the TGA, specific attention was given to the temperature inside the roll-die system employed for the production of the pellets. An overview of the temperature found inside the experimental setup was obtained using a pocket thermal camera as can be seen in figure 4.3.

(A)   (B)

Figure 4.3 Thermogravimetric image of the system used for the production of (A) lignin pellets, and (B) both lignin and softwood bark pellets.

4.4 Pellets from a single pellet system

4.4.1 Poplar wood lignin – case 1

Wood pellets are a compressed form of crushed biomass. According to (CANplus certification, 2016), the cylindrical pellet must have a diameter of 6 to 8 mm. The length can vary from 3.15 to 40 mm but usually averages around 10 mm. The moisture content of the pellets produced must be less than 10% (based on wet mass). The pellet manufacturing process consists of drying, size reduction, granulation, cooling, and packaging (Mani et al., 2004), and the traditional raw material for pellets is sawdust and chips. The high lignin content in the raw material provides a suitable bond to make durable pellets. Logging residue pellets are more durable than pellets from industry residues such as sawdust and chips (Lehtikangas, 2001). A less durable pellet tends to quickly disintegrate into fines during handling and storage. In addition to possible explosions, the inhalation of fines is an occupational health problem (Sebastian et al., 2006). In order to gather this information, a single pellet system was used in this work and enabled the rapid and inexpensive manufacture of pellets at a smaller scale. According to the (CANplus certification, 2016), the optimal lignin pellets were manufactured at 79.1 °C and 12 MPa, where the compression pressure was kept stable for 2 minutes. Figure 4.4 provides an example of the pellets that were produced from poplar wood lignin, while Table 4.2 shows reports on their physical and chemical properties.

Figure 4.4 Poplar wood lignin pellets produced with lignin originally having a 6.14% moisture content using a single pellet system.

The results showed that the properties of the pellets depended on the initial moisture content of the lignin. In addition, to obtain pellets that comply with the certification requirements, it is necessary to guarantee an initial moisture content between 9 and 12% in the original lignin feedstock. Table 4.2 shows that the physical properties are within the values required by the CANplus certification except for ash content.

Table 4.2 Presents the average values and standard deviation for the properties of 40 pellets from poplar wood lignin

Property	Poplar wood lignin	CANplus certification		
		A1	A2	B
Diameter (mm)	6.25 ± 0.04	6 ± 1 or 8 ± 1		
Length (mm)	20.01 ± 4.09	3.15 < L ≤ 40		
Moisture content (%)	6.14 ± 0.47	≤ 10		
Mechanical durability (%)	99.16 ± 0.03	≥ 98.0	≥ 97.5	
Fines content (%)	0.19 ± 0.14	≤ 1.0		
HHV (MJ/kg)	19.26	≥ 16.5		
Ash content (%)	1.97 ± 1.16	≤ 0.7	≤ 1.2	≤ 2.0

The conditions used in the single pellet system were then applied to a laboratory-scale pellet mill and the results are presented in the following section.

4.4.2 Corn stover lignin – case 2

Corn stover usually contains high levels of moisture, and for this reason, when it is sent for pellets production, it must often go through a drying process until moisture levels are below 15% (as often recommended by equipment manufacturers). This ensures pellet production with humidity levels below 10%, as standard (ISO 18134-3:2015, n.d.) requires. The moisture content influences the self-ignition capacity of the biomass and the calorific value because during combustion, part of the fuel energy is wasted in the evaporation of water and, consequently, is not available for other energy uses. This parameter also intervenes in decreasing pellet durability and increasing bulk density, fungi, and spore emissions. Lignin pellets were

randomly selected from each trial to measure physical and chemical properties. Figure 4.5 provides an example of the pellets that were produced from corn stover lignin, while the physical properties of lignin pellets produced at the laboratory scale were measured three times after extrusion, and the results are presented in Table 4.3. All values represent the average value of 20 samples of each type.

Figure 4.5 Corn stover lignin pellets produced with lignin originally having a 10.64% moisture content using a single pellet system.

Table 4.3 Presents the average values and standard deviation for the properties of 20 pellets from corn stover lignin manufactured at 85ºC

Property	Corn stover lignin	CANplus certification		
		A1	A2	B
Diameter (mm)	6.47 ± 0.53	6 ± 1 or 8 ± 1		
Length (mm)	14.45 ± 1.54	3.15 < L ≤ 40		
Moisture content (%)	4.83 ± 0.02	≤ 10		
Mechanical durability (%)	96.89 ± 0.05	≥ 98.0	≥ 97.5	
Fines content (%)	0.71 ± 0.19	≤ 1.0		
HHV (MJ/kg)	18.21	≥ 16.5		
Ash content (%)	12.64 ± 0.04	≤ 0.7	≤ 1.2	≤ 2.0

According to (Petridis et al., 2011), there is a transition between high and low temperatures between lignin molecules, moving from the mobile and extended state to a glassy and compact state. During the pelletization process, this phenomenon occurs. It positively influences the durability of the pellets when they are cooled because the lignin is re-associated and establishes bonds between its particles. These results show the importance of temperature in manufacturing lignin pellets for the recorded physical properties.

The results obtained from the analysis of the chemical properties were suitable for approximating the behavior of this type of feedstock (in this case, corn stover lignin) in the manufacture of pellets. Due to the polymeric behavior of lignin, during the manufacture of pellets, there is a thermal softening that promotes particle agglutination (Stelte, W. et al., 2012). Therefore, when the manufacture of pellets is performed at 85 °C, a better cohesion occurs between the lignin macromolecules, and a high calorific value is obtained. This is demonstrated in the present work and the results from (Demirbas, 2001, 2002). In contrast, the ash content of lignin pellets made from corn stover is essential when used as a solid biofuel. A high ash content (12.64% on a dry basis) could be detrimental if such feedstock is used in a scenario where combustion is involved, such as heating and generation of thermal energy. (Demirbas, 2004) reported that corn stover has a high natural ash content. Furthermore, (Samson & Mehdi-Schulz,

1998) claimed that this ash content value could change according to the hybrid variety used, fertilization practices, corn maturity, and soil contamination where the original feedstock was planted. These methods can be adjusted to reduce soil contamination before the corn stover crop is expanded for industrial-scale biofuel production.

However, the lignin pellets having low ash contents could be suitable for thermal conversion (including combustion) due to the potential low ash accumulation, slagging, or corrosion in the boilers; in this case, the lignin pellets manufactured from poplar wood - case 1.

4.5   Pellets from a laboratory-scale pellet mill
4.5.1 Poplar wood lignin and softwood bark – scenario 1

For scenario 1, four cases of initial moisture content were analyzed (% humidity): 8.01% (H1), 26.21% (H2), 30.07% (H3), and 38.83% (H4). Poplar wood lignin and softwood bark pellets manufactured through the laboratory-scale pellet mill are both shown in figure 4.6.

(A)   (B)

(C)   (D)   (E)
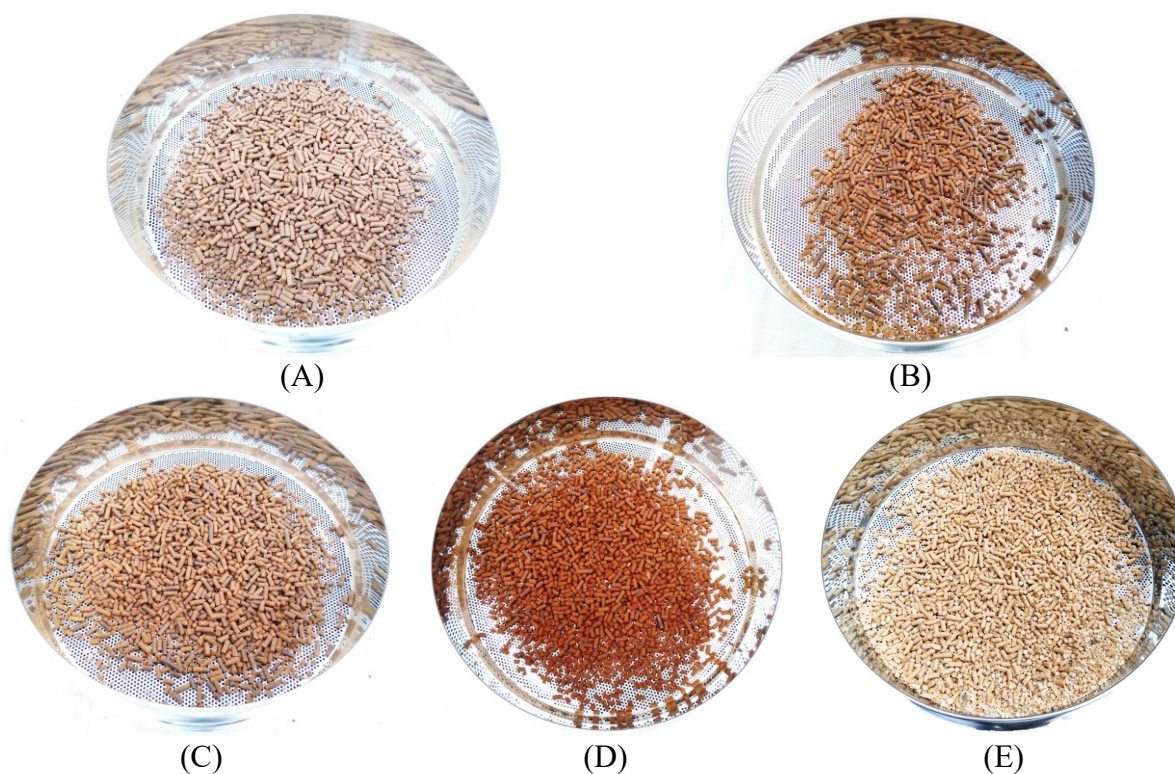
Figure 4.6 Scenario 1: poplar wood lignin pellets produced with an original feedstock having a moisture content of (A) 8.01 %, (B) 26.21 %, (C) 30.07 %, (D) 38.83 %, and softwood bark pellets (E) 6.57 %

Results for the physical properties, both for lignin and softwood bark pellets manufactured using the laboratory-scale pellet mill are depicted in Table 4.4.

Table 4.4 Physical properties of the poplar wood lignin and softwood bark pellets produced using the laboratory-scale pellet mill following this scenario 1

Property	Poplar wood lignin				Softwood bark
	H1	H2	H3	H4	
Moisture content (%)	8.01 ± 0.62	26.21 ± 1.80	30.07 ± 0.42	38.83 ± 0.37	6.57 ± 0.15
Diameter (mm)	6.39 ± 0.04	6.40 ± 0.05	6.40 ± 0.03	6.43 ± 0.28	6.52 ± 0.07
Length (mm)	12.47 ± 5.67	12.26 ± 5.67	13.84 ± 5.45	12.71 ± 6.01	16.22 ± 3.32
Mass (g)	0.41 ± 0.21	0.45 ± 0.59	0.46 ± 0.21	0.47 ± 0.27	0.55 ± 0.13
Mechanical durability (%)	94.80 ± 0.28	93.78 ± 0.90	91.46 ± 1.88	88.90 ± 2.01	99.48 ± 0.23
Fines content (%)	1.45 ± 0.11	2.90 ± 0.09	4.73 ± 1.36	9.87 ± 0.66	0.17 ± 0.04
HHV (MJ/kg)	23.17	19.57	18.87	16.06	18.34
Ash content (%)	1.11 ± 0.49	1.37 ± 0.11	2.55 ± 0.15	2.79 ± 0.29	1.01 ± 0.40

The diameter of the pellets is determined by the diameter of the compression channels of the pellet die. For scenarios 1 and 2, a compression ratio of 6 was used with a hole diameter of 6.35 mm and a length of 38.1 mm. The pellet dimensions, diameter, and length averaged 0.0029% and 1.39%, respectively (Table 4.4). According to (Mahapatra et al., 2010), the variation in the diameter of the pellets can be caused by the migration of water vapor from the center to the surface, which interrupts the bonds formed in the pelletization. However, no relationship was observed between the moisture of the raw material or pellets and the diameter. The length is given by knives installed below the die so that the length does not exceed a maximum defined by the knife's adjustment. Thus, a homogeneous solid biofuel is obtained in terms of shape and size, allowing automatic combustion equipment to be used (Obernberger, I. & Thek, G., 2010). According to (Liu et al., 2013), the diameter and length of the pellets affect combustion so that smaller diameters allow a more uniform combustion rate, and smaller sizes facilitate feeding into the firing system. Mechanical durability indicates the ability of pellets to withstand physical disintegration, which leads to dust formation due to mechanical impacts during storage and transport (Tumuluru, 2014). Therefore, pellets with low mechanical durability tend to disintegrate more quickly, which can cause problems in conveyor belts and the combustion chamber (Carroll & Finnan, 2012). (Kaliyan & Vance Morey, 2009) concluded that the size of the particles, the chemical composition, and especially the moisture of the raw material, in addition to the temperature and pelletizing pressure, influence the mechanical durability of the pellets.

Also, the results from Table 4.4 show that, as expected, the high moisture content in the initial feedstock usually induces low durability of the lignin pellets. Such condition also leads to the production of a high fines content, which, as mentioned earlier, can lead to different problems at a larger scale. Overall, the results showed that the moisture content is an essential parameter for the granulation process, both for the lignin and softwood bark pellets. The calorific value of the solid biofuels, corresponding to the amount of energy released during combustion per unit mass (expressed in MJ/kg) is known to vary for pellets according to the origin of the feed. According to the (CANplus certification, 2016), independently of the type of feedstock used to produce the solid fuel, the calorific potential must be equal or greater to 16 MJ/kg. Some research published in the literature (Ebeling, J.M & Jenkins, B.M., 1985; Klasnja et al., 2002)

reported the calorific potential between 18.56 and 19.38 MJ/kg for poplar wood. However, in contrast to these publications, this work focuses only on the lignin fraction of this biomass; hence, it should allow pinpointing the direct impact of the macromolecule on the calorific value of the biomass. Due to the polymeric behavior of lignin, the pelletization process induces a thermal softening that promotes particle agglutination (Demirbas, 2001, 2002; Stelte et al., 2012). Therefore, when the operation is performed at 61.6 °C, a better cohesion occurs between the lignin macromolecules, which overall leads to a solid biofuel with a higher calorific value (see Table 4.4). Ash content is also essential for boiler design (or selection) and cleaning operation. Hence, the combustion of solid biofuels with high ash contents would logically require a more regular and effective ash removal process. This parameter, of course, varies according to the different types of biomasses used to produce the pellets. In addition, ash is an abrasive material that, in the long term, can cause additional problems such as corrosion of the metallic components of the boilers. The inorganic components that contribute the most to the ash formation are Si, Ca, Mg, K, Na, P, S, Cl, Al, Fe, and Mn. Different authors (Demirbas, 2004; Ebeling, J.M & Jenkins, B.M., 1985; Klasnja et al., 2002; Klašnja et al., 2013; Melin, 2008) reported that poplar wood has a higher natural ash content, reported to be between 0.52 and 1.33% as compared to softwood bark, which was reported to contain between 0.3 and 0.7% of inorganics. In addition, they also claimed that this ash content could change according to the variety of the hybrid used, fertilization practices, poplar wood maturity, and soil contamination where the original feedstock was planted. However, according to (CANplus certification, 2016), the lignin pellets that had low ash contents (pellets produced from an 8.01 % humidity content – as shown in Table 4.4) could eventually be suitable for thermal conversion (including combustion) due to the potential low ash accumulation, slagging, or corrosion in the boilers. The impact resistance of lignin and softwood bark pellets is shown in Table 4.5. After being dropped, the softwood bark pellets showed a weight loss of 0.61 ± 0.17 %, while the lignin pellets produced from the samples with the lowest moisture content (8.01 %) had a weight loss of 3.71 %. The loss was still lower when compared to the lignin pellets that were produced from the material having the highest moisture content (38.83 %), for which the mass loss reached 21.65 %. Overall, results showed that softwood bark pellets had a higher impact resistance than lignin pellets.

Table 4.5 Average weight loss for pellets following the impact resistance test (pellets were dropped from a 2.0 m height onto a concrete floor) for scenario 1

Property	Poplar wood lignin				Softwood bark
	H1	H2	H3	H4	
Moisture content (%)	8.01 ± 0.62	26.21 ± 1.80	30.07 ± 0.42	38.83 ± 0.37	6.57 ± 0.15
Initial weight before dropped (g)	47.86 ± 0.06	47.27 ± 0.16	47.21 ± 0.11	47.15 ± 0.13	48.98 ± 0.03
Final weight after dropped (g)	46.08 ± 0.10	43.85 ± 0.26	41.97 ± 1.46	36.94 ± 0.76	48.68 ± 0.05
Weight loss (%)	3.71 ± 0.17	7.23 ± 0.38	11.11 ± 3.06	21.65 ± 1.40	0.61 ± 0.17

Overall, the lignin pellets with the 8.01 % humidity content produced the most robust samples compared to the one produced with the material having a higher water content. Table 4.4 reports

the fines content for the lignin and softwood bark pellets produced during this project. These results are presented as average values (over three repetitions) and indicate the fines generated after the impact resistance test (i.e., after ten drops). According to the (CANplus certification, 2016), this value can be equal to or less than 1.0 %. Results show that the lignin's high moisture content impacted the durability and the production of fines for the produced pellets. More specifically, pellets containing 38.83 ± 0.37 % humidity led to the production of 9.87 ± 0.66 % fines. However, for lignin pellets with an 8.01 ± 0.62 % humidity content, the production of the fine after the impact resistance experiments was 1.45 ± 0.11 %. For comparison purposes, when it comes to softwood bark pellets (to 6.57 ± 0.15 %), the percentage of fines after ten drops was 0.17 ± 0.04 %. The fines content is an essential parameter since high values could impact the storage and transport of the pellets. For larger quantities, the number of fines could be related to health hazards (due to the inhalation of dust), without forgetting the potential for explosion. During combustion, the fine content also influences the combustion behavior of the fuel, and it can induce plugging or even damage the ventilation system. Among the other parameters that could negatively affect the quality of the pellets is their short, medium, and long-term exposure to rain. Other aspects to consider would be the humidity conditions during shipping, handling, and storage. To address this concern, water resistance was tested for pellets made from lignin and softwood bark. Results showed that none of the softwood bark pellets maintained their integrity while submerged in water at room temperature for more than 2 minutes. The pellets swelled on contact with water then disintegrated after a few seconds. This shows that softwood bark pellets are brittle in contact with water, as shown in figure 4.7E. In contrast, lignin pellets (regardless of the moisture content) presented good resistance when submerged in water, as shown in figure 4.7(A-D). Table 4.6 shows the mass of the pellet before and after being submerged in water for 2 minutes, as well as the percentage of water absorbed.

(A)   (B)

(C)   (D)   (E)
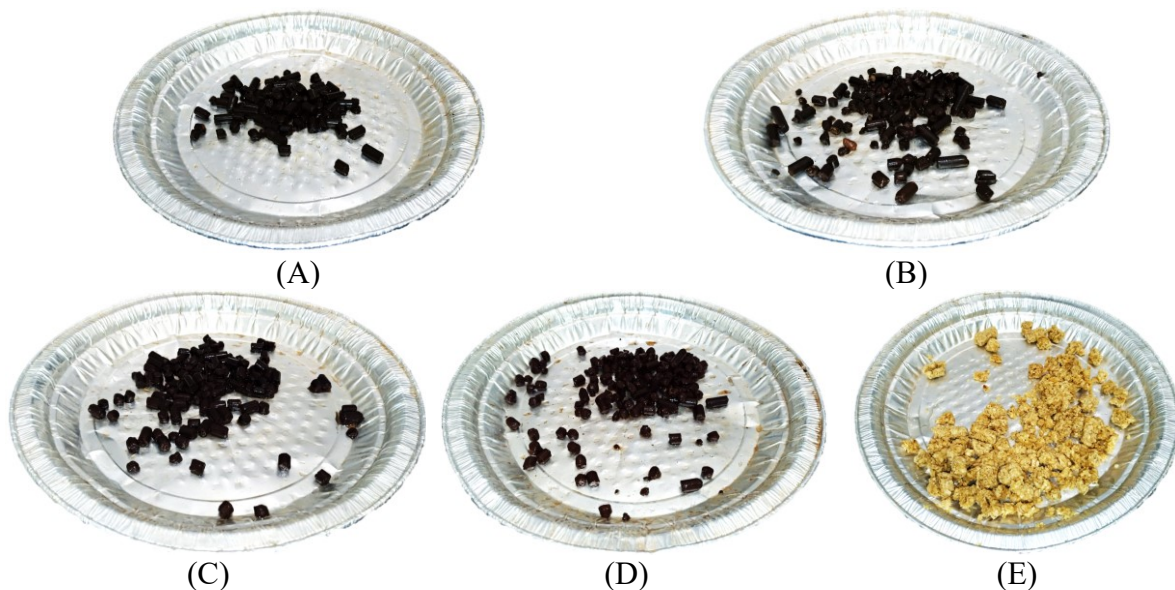
Figure 4.7 Picture of the poplar wood lignin pellets after 2 minutes submerged in water for pellets being having an original moisture content of (A) 8.01 %, (B) 26.21 %, (C) 30.07 %, (D) 38.83 %, as well as softwood bark pellets (E) 6.57 %.

Table 4.6 Scenario 1: mass of pellets before and after being immersed in water for 2 minutes as well as the percentage of water absorbed

Property	Poplar wood lignin				Softwood bark
	H1	H2	H3	H4	
Moisture content (%)	8.01 ± 0.62	26.21 ± 1.80	30.07 ± 0.42	38.83 ± 0.37	6.57 ± 0.15
Initial weight before immersion (g)	10.11 ± 0.03	10.23 ± 0.02	10.19 ± 0.02	10.63 ± 0.02	10.10 ± 0.03
Final weight after immersion (g)	12.30 ± 0.03	12.58 ± 0.02	12.84 ± 0.08	13.70 ± 0.02	30.63 ± 0.02
Water absorbed (%)	21.62 ± 0.15	23.05 ± 0.03	25.97 ± 0.58	28.87 ± 0.21	205.64 ± 0.04

After being immersed in water, the softwood bark pellets showed a 205.64 % mass increase over their original weight. In opposition, lignin pellets showed a 24.88 ± 3.22 % water absorption. This result indicates that lignin pellets manufactured in this study have a higher hydrophobic potential when compared to softwood bark pellets. Therefore, it is foreseeable that such pellets could be stored outdoor, which would significantly reduce the capital expenditure (CAPEX) of any pellet-based heating system relying on such solid biofuel.

4.5.2 Poplar wood lignin – scenario 2

The additives that were used had an impact on the physical and chemical characteristics of the pellets since they acted as binders for the raw material. To improve the properties of lignin pellets, four different bio-additives were employed in the feedstock including (i) corn oil, (ii) citric acid, (iii) glycerol, and (iv) d-xylose. For this scenario, the poplar wood lignin pellets manufactured through the laboratory-scale pellet mill are shown in figure 4.8.
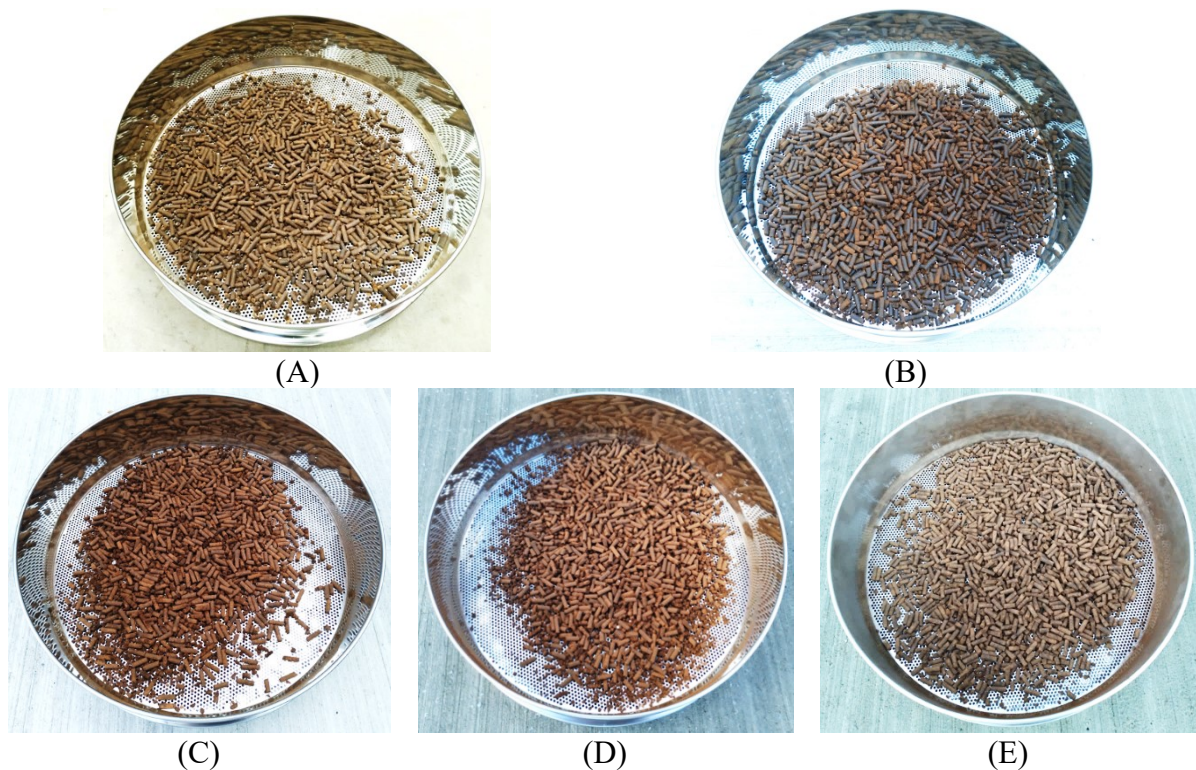
Figure 4.8 Poplar wood lignin pellets produced using a laboratory-scale pellet mill with (A) pure lignin, (B) corn oil, (C) citric acid, (D) glycerol, and (E) d-xylose.

Literature (Tarasov et al., 2013) carried out bibliographical research using lignosulfonate, dolomite, starches, flour, potato peel, and some motor oils to manufacture poplar wood pellets. They found that lignosulfonate and starch additives improved mechanical durability but tended to reduce the calorific value of poplar wood pellets. Moreover, vegetable and motor oil additives minimally increased heating value but significantly increased carbon monoxide emissions. Similarly, (Mediavilla et al., 2012) conducted a comparative study to analyze the impact of different additives (lignosulphonate, maize starch, and their different combinations) on the particle density and mechanical durability under similar initial conditions (same raw material, exact dosage of additive, and same compression rate). The addition of lignosulphonate resulted in higher mechanical durability as compared to the addition of maize starch. The mechanical durability varied between 93.2% and 98.8% for different additives and their combinations. For the results presented in this work, measurements were made immediately after the manufacturing process to obtain the physical and chemical properties of the pellets, and the results are depicted in Table 4.7. Compared with the results presented by Tarasov and Mediavilla, in this work, d-xylose improved the mechanical durability of the pellets by 0.5%, while the other three additives (corn oil, citric acid, and glycerol) impacted this parameter.

Furthermore, additives such as corn oil and glycerol improve the calorific value, while citric acid and d-xylose slightly impact this parameter. Also (Kuokkanen et al., 2011) found that when lignosulfonate was used at 1% and 2%, the ash content of wood pellets increased from 0.5% (native wood) to 0.6% and 0.8%, respectively. However, the 0.5% wheat starch additive significantly reduced ash formation two-fold. Instead, this work found that the additives used (corn oil, citric acid, glycerol, and d-xylose) improved the ash content in poplar wood pellets by an average value of 0.49%.

Finally, the ultimate analysis provided a fraction (by weight) of the elemental constituents of the biomass. The main elements analyzed were carbon and hydrogen, although nitrogen and sulfur concentrations were also analyzed. The used additives significantly increased the carbon fractions but reduced the sulfur fractions for the elemental analysis. The high sulfur content in pure lignin pellets could be associated with the high concentration of sulfuric acid used in the biomass pretreatment process. As for the fines content, the four additives used in this work significantly increased this value to a mean value of 0.61%.

Table 4.7 Physical and chemical properties for pellets manufactured from poplar wood lignin combined with additives (Scenario 2). The results show an average value for 91.0 grams of pellets approximately, expressed on a dry basis

Property	Poplar wood lignin	Corn oil	Citric acid	Glycerol	D-xylose
Diameter (mm)	6.33 ± 0.02	6.34 ± 0.03	6.32 ± 0.03	6.06 ± 0.09	6.18 ± 0.08
Length (mm)	16.82 ± 2.54	12.42 ± 3.67	19.22 ± 6.11	18.40 ± 2.76	17.1 ± 4.38
Moisture content (%)	13.17 ± 0.35	8.41 ± 0.14	7.09 ± 0.28	6.05 ± 0.46	9.12 ± 0.41
Mechanical durability (%)	93.81 ± 1.62	93.77 ± 0.97	91.20 ± 0.70	89.44 ± 1.84	94.31 ± 0.48
Fines content (%)	0.29 ± 0.02	0.62 ± 0.09	0.88 ± 0.35	1.56 ± 0.07	0.56 ± 0.06
HHV (MJ/kg)	22.62	27.40	22.11	23.17	22.59
Ash content (%)	1.58 ± 0.12	1.26 ± 0.15	1.13 ± 0.15	0.94 ± 0.16	1.06 ± 0.13
Ultimate analysis					
Carbon	53.56 ± 1.25	62.20 ± 0.25	54.66 ± 0.09	55.98 ± 0.43	54.24 ± 1.15
Hydrogen	5.53 ± 0.28	6.72 ± 0.09	5.25 ± 0.05	6.13 ± 0.13	5.18 ± 0.14
Nitrogen	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Sulfur	0.32 ± 0.06	0.00 ± 0.00	0.15 ± 0.03	0.15 ± 0.02	0.15 ± 0.02

In literature, some previous work reported on the ultimate analysis values for poplar wood; however, the actual work shows slightly higher values for carbon and sulfur content than those previously reported (Demirbas, 2002, 2004; Ebeling, J.M & Jenkins, B.M., 1985; Klašnja et al., 2013). Despite the difference, it is worth mentioning that previous studies in the literature have used biomass from poplar wood, while the present study uses only the extracted lignin from that feedstock. In the present work, the additives acted as lubricants and increased lignin pellet production. However, to further improve the physical properties of the lignin pellets, two different storage conditions were used. Pellets were stored inside the laboratory building at 22.3 °C for 30-days, and the second samples were stored for 8-days in a cold room (also located at the laboratory) at 2.0 °C. Once the storage period was completed, measurements were carried out to obtain the physical properties of the lignin pellets, such as their moisture content, mechanical durability, and fines content. All samples were stored in resealable plastic bags. For the first condition (see results in Table 4.8), the process led to an improvement of the properties of the pellets, namely on their mechanical durability and fines content. However, the use of citric acid, glycerol, and d-xylose increased the final moisture content more than for the pellets made with pure lignin or using corn oil as an additive. Nonetheless, all the pellets made using

additives in the feedstock are within the values required for moisture content by the (CANplus certification, 2016) except for d-xylose.

Table 4.8 Experimental results after 30-days of storage time at 22.3 °C (first condition) for pellets manufactured from poplar wood lignin and additives (Scenario 2).

Property	Poplar wood lignin	Corn oil	Citric acid	Glycerol	D-xylose
Moisture content (%)	3.90 ± 0.15	5.21 ± 0.08	7.48 ± 0.12	9.23 ± 0.09	14.90 ± 0.08
Mechanical durability (%)	95.70 ± 0.00	94.49 ± 0.11	91.97 ± 5.08	94.67 ± 0.72	95.79 ± 0.86
Fines content (%)	0.51 ± 0.00	0.30 ± 0.08	0.41 ± 0.25	0.44 ± 0.03	0.19 ± 0.05

For the second condition (storage at a lower temperature – see results in Table 4.9), the pellets made of pure lignin, corn oil, and citric acid maintained their moisture content within the values required by the CANplus certification (less than 10%). Results show that there was also a reduction in the fines content and a significant improvement in the pellet's mechanical durability. The addition of more citric acid hindered the pellet manufacture process by blocking the pellet mill, most probably due to poor lubrication. In addition, the final product seemed extremely dry, which affected the mechanical durability of the lignin pellets. On the other hand, corn oil acted as a good lubricant during the pelletizing process and produced the best lignin pellets in terms of moisture and durability values.

Table 4.9 Experimental results from an 8-days storage time at 2.0 °C (condition 2) for pellets manufactured from poplar wood lignin and additives (Scenario 2).

Property	Poplar wood lignin	Corn oil	Citric acid	Glycerol	D-xylose
Moisture content (%)	2.15 ± 0.04	9.78 ± 0.77	8.05 ± 0.41	10.11 ± 0.60	11.99 ± 0.17
Mechanical durability (%)	97.69 ± 0.09	97.07 ± 0.01	95.46 ± 1.85	96.89 ± 0.44	97.66 ± 0.25
Fines content (%)	0.16 ± 0.00	0.32 ± 0.05	0.24 ± 0.16	0.20 ± 0.00	0.13 ± 0.02

From these results, it was discovered that the storage process for scenario two and condition 2 (additives) caused an increase of the physical parameters of the pellets as compared to the first condition (without additives) immediately after the manufacturing process. Furthermore, results showed that the pellets made from pure lignin or additives in the lignin could potentially be stored indoors and outdoors. However, a temperature and time-controlled storage environment could be beneficial to increase solid biofuel performance. In addition, lignin, a dominant aromatic macromolecule in nature, is one of these components that could offer unique routes to produce different value-added products due to its structure and composition.

4.5.3 Mixture of softwood bark lignin and softwood bark – scenario 3

Using softwood as a raw material to manufacture pellets, (Kofman, 2007) found that adding 1% and 2% lignosulfonate and potato flour (as binding agents) increased the mechanical durability of wood pellets from about 96% to 98%. Also, (J. Stevens & Gardner, 2010) explored lignin as a wood additive to improve the value of pellet fuel. They examined two types of lignin in wood pellet production, Kraft black liquor and Indulin AT (IAT). The samples of wood pellets with IAT increased in calorific value as a function of the load level. However, black liquor pellets decreased in calorific value with higher load levels. This result was initially unexpected, but upon closer examination of the data, the fuel value reduction reflects the black liquor's composition. Also, (Takada et al., 2020; Whittaker & Shield, 2017) claim that softwood pellets have higher mechanical durability than pellets made from hardwood or herbaceous residues, the main reason being the higher lignin content of softwood pellets. Although various supplements, such as sugar, starch, and vegetable oils, have been added to improve pellet durability, lignin derivatives, such as lignosulfonate and Kraft lignin, have been added and shown to improve pellet durability of the pellets significantly. Similarly, (Takada & Saddler, 2020) concluded that when two commercial lignin's, a lignosulfonate and alkaline lignin derived from the Kraft process, were added to steam-treated softwood prior to pelleting, both lignin's improved pellet durability by doubling the lignin addition, from 1% to 2%, which conferred more excellent durability. As both lignin's have a relatively high molecular weight, they are likely to plasticize under pelletizing conditions, thus acting as glue and improving mechanical durability.

Using lignin as an additive to the raw material for pellet production is promising. However, few works are related to this type of research. As mentioned above, lignin is a macromolecule that forms part of the chemical constitution of wood and acts on the adhesion of the particles to form pellets. The properties of the lignin are specific to the extraction process and will positively or negatively affect the properties of the pellets (Berghel et al., 2013). The raw material used to produce pellets was softwood bark donated by the RéSolve Énergie Inc. Furthermore, the lignin was extracted by the direct saccharification of lignocellulosic biomass and was donated by the same company RéSolve Énergie Inc. The lignin from the same raw material was used as an additive for the production of pellets. Disregarding the highest and lowest values (0% and 100% lignin), the remaining ones (25%, 50%, and 75% lignin) were added concerning the dry mass of the raw material. The pellets were produced in the laboratory-scale pellet mill with a horizontal circular die, a hole diameter of 6.35 mm, and a length of 25.4 mm, providing a compression ratio of 4. On the other hand, the pelletizing temperature ranged between 52.5 ºC and 89.60 ºC. The manufactured pellets are shown in figure 4.9. Also, the following properties of the pellets were evaluated: diameter, length, moisture content, mechanical durability, fines content, HHV, and ash content. The lignin had an essential role in the properties of the pellets since it acted as a lubricant and binder for the raw material. However, a different storage condition was used to improve further the properties of the pellets manufactured in the laboratory-scale pellet mill. The pellets were stored for 8-days in a cold room (located in the laboratory) at 2.0 °C.
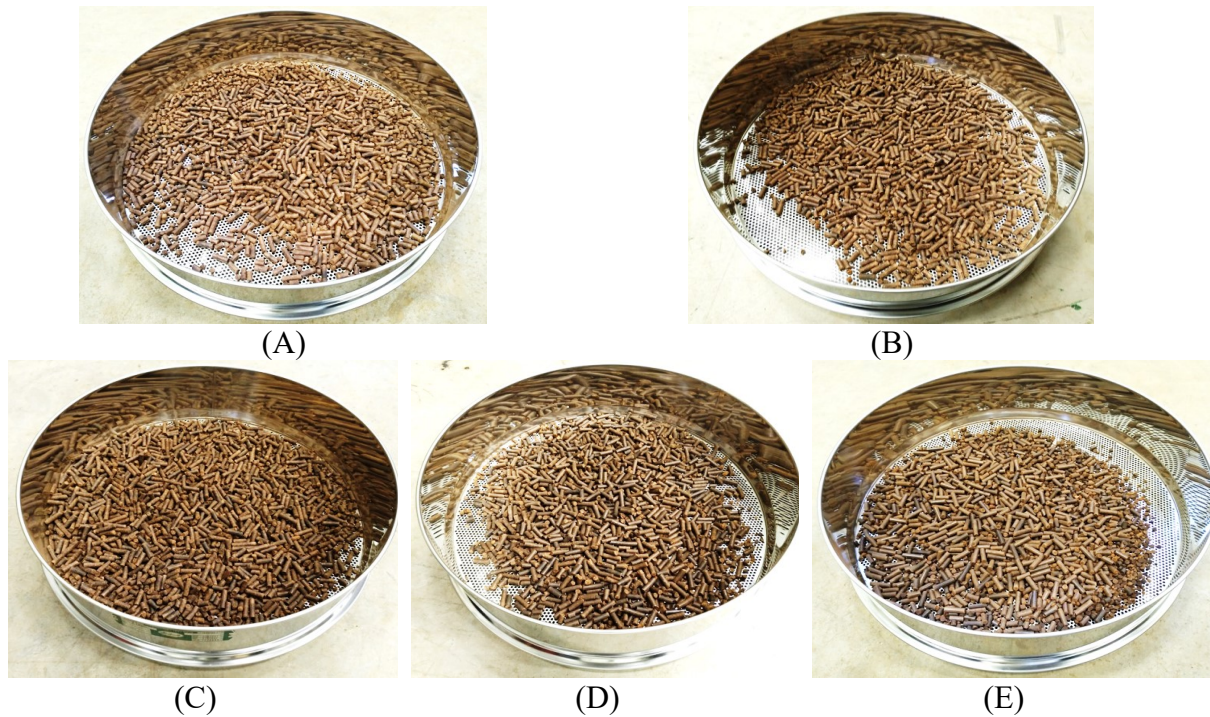
Figure 4.9 Pellets produced with an original feedstock softwood bark and different concentrations of softwood bark lignin (A) Pure feedstock, (B) 75% feedstock and 25% lignin, (C) 50% feedstock and 50% lignin, (D) 25% feedstock and 75% lignin, and (E) softwood bark lignin.

Immediately after the manufacturing process, measurements were made to obtain the properties of the pellets, and the results are shown in Table 4.10. It was observed that the moisture content of the pellets was lower than that of the raw material, and the higher the percentage of added lignin, the greater the moisture content of the pellets, probably due to the higher moisture content of lignin to raw material. However, these values are within the parameters required by CANplus certification. In this study, the raw material had an initial moisture content of 11.79% and lignin of 14.53%. The variation in the moisture content of the pellets, considering those produced with 0 and 100%, was on average equal to 9.40%. In Table 4.10, it was found that lignin in high concentrations (samples B, C and 100% lignin) decreased the ash content compared to pellets made with 100% and 75% raw material (samples pure and A). In addition, the lignin added in high concentration (samples B and C) increased the mechanical durability compared to the pellets made with 25% lignin (sample A). Also, the fines content was similar for all treatments, maintaining an average value of 0.18%. In (J. Stevens & Gardner, 2010) work, IAT preparations produced better quality pellets lower than those found in this study. Also, to improve the properties of mechanical durability and fines content in the pellets manufactured in Figure 4.9, it was necessary to store them in a cold room at 2ºC for 8-days, (results are shown in Table 4.11).

Table 4.10 Properties (after the manufacturing process) of the pellets produced with an original feedstock softwood bark and different concentrations of softwood bark lignin using the laboratory-scale pellet mill, where: (A) is 75% raw material and 25% lignin; (B) is 50% raw material and 50% lignin; and (C) is 25% raw material and 75% lignin

Property	Condition					CANplus certification
	Softwood bark	A	B	C	Softwood bark lignin	
Diameter (mm)	6,45	6,38	6,42	6,39	6,38	6 ± 1 ou 8 ± 1
Length (mm)	22,12	22,48	22,35	22,20	22,32	3,15 < L ≤ 40
Moisture content (%)	5,75	9,40	9,82	9,48	7,68	≤ 10
Mechanical durability (%)	98,42	96,93	97,16	97,68	95,58	≥ 98,0 (A1) ou ≥ 97,5 (B)
Fines content (%)	0,11	0,12	0,24	0,21	0,24	≤ 1,0
HHV (MJ/kg)	19,32	20,14	21,45	23,76	25,01	≥ 16,5
Ash content (%)	2,96	4,33	2,68	1,99	1,34	≤ 0,7 (A1) ou ≤ 2,0 (B)

Table 4.11 Properties (after 8-days storage time at 2ºC) of the pellets produced with an original feedstock softwood bark and different concentrations of softwood bark lignin using the laboratory-scale pellet mill.

Property	Condition					CANplus certification
	Softwood bark	A	B	C	Softwood bark lignin	
Moisture content (%)	3,96	8,26	9,77	7,76	6,67	≤ 10
Mechanical durability (%)	99,34	97,40	97,58	98,78	97,99	≥ 98,0 (A1) ou ≥ 97,5 (B)
Fines content (%)	0,12	0,15	0,10	0,16	0,19	≤ 1,0

For this storage condition, the results show a reduction in the moisture content and a significant improvement in the mechanical durability of the pellet. For this study, the results obtained are similar to those found in literature. According to (Demirbas, 2002), higher levels of lignin contribute to an increase in the calorific value of the solid biofuel because this calorific value of lignin is greater than that of the other primary components of wood (cellulose and hemicellulose). (J. Stevens & Gardner, 2010) found that the addition of lignin also increased the calorific value of the pellets. Furthermore, the addition of lignin can increase or decrease the quality of the pellets (Berghel et al., 2013), which mainly depends on the method used to extract and purify them. High ash contents are undesirable for pellets due to numerous factors, including the inversely proportional relationship to the calorific value and combustion residue. Also, depending on the chemical composition of the ash, scaling can form on equipment of combustion (Obernberger, I. & Thek, G., 2010). The particles rearrange to fill the compression channel and remove the air between them during the pelletizing process. Additionally, there are weak bonds in the close particles through van der Waals forces and electrostatic forces, which promote their union (Stelte, W. et al., 2012). Due to the high temperatures reached during pelletizing process, around 90 °C, the lignin plasticizes and functions as a binder between the particles (Carroll & Finnan, 2012; Kaliyan & Morey, 2010). According to (Narra et al., 2010), lignin forms a thin layer on the particles, improving the union between them, and this is because there is interdiffusion and molecular entanglement between adjacent chains, a phenomenon described as a "solid bridge" by (Kaliyan & Morey, 2010), that is, a network of macromolecules is formed that merges and subsequently solidifies (Stelte, W. et al., 2012). Therefore, the higher the percentage of lignin added, the more useful were the links between the particles, improving the densification of the material. Finally, the addition of lignin did not influence the length and diameter of the pellets because such dimensions are predetermined. Pellet's diameter is determined by the diameter of the compression channels of the pellet mill die and the length by knives located below the die so that the length does not exceed a maximum defined by the height of the knives. According to (Narra et al., 2010), the dimensions and shape of the pellets must be homogeneous for the best operation of small-scale furnaces and automatic heating equipment. For results obtained in table 4.10, the pellets diameter and length meet the (CANplus certification, 2016) requirements.

Otherwise, using Eucalyptus as raw material to manufacture pellets, (Clavijo et al., 2020) found that pellets with added lignin met all the requirements of the European standards for certification except for ash content. Also, they found that when lignin was added at 2.0% and 3.0%, the durability was acceptable for pellet commercialization and fulfilled the requirements for European Pellets certification. In addition, (Pereira et al., 2016) used Kraft lignin as an additive to the Eucalyptus raw material to manufacture pellets. Adding kraft lignin to the raw material improved the physical and mechanical properties of mechanical durability, fines content, and hardness. The addition of lignin caused an increase in the ash and moisture content of the granules. The heating power of two manufactured pellets was around 19.76 MJ/kg. Adding 5% Kraft lignin promoted a 5.5% increase in mechanical durability, going from 93.98% (without lignin) to 99.18%. Similarly, in this research project, the addition of lignin in high concentrations improved the calorific value, with a minimum value of 19.32 MJ/kg for pellets made with 100% raw material to 25.01 MJ/kg for pellets made with 100% lignin. This property (calorific value) represents an improvement and an alternative to be considered in manufacturing 100% lignin pellets and their subsequent possible commercial and industrial use.

4.6   Storage under different conditions

At different times of the year, the pellets are stored in different places without heating or are transported by trucks for long periods. As a result, the pellets are exposed to external climatic factors, including the different temperatures during the seasons of the year, and this can have a positive or negative impact on the quality parameters of the solid biofuel. In addition to transportation, the storage of pellets is another factor that can reduce their quality since they can be stored in plastic or paper bags for domestic use or in silos, in this case, for industrial use. Hence, all the activities involved in the process until reaching the final user can affect the mechanical properties and, as a consequence, the generation of fines and even, in some cases, the disintegration of the pellets can occur, which can cause loss of material and even increase the risk of fire. The main detrimental factor for pellets is moisture since the pellets will burn properly when dry and will be a more efficient product if they are in good condition. This work proposes different storage conditions for the pellets made from poplar wood lignin and softwood bark lignin, and the mechanical durability measurements were made after the storage time. The pellets used for these storage conditions are shown in figure 4.10. The proposed storage conditions are described below.

i.   22-days storage time indoor.
ii.   8-days storage time at 2ºC.
iii.   6-days storage-time outdoor.
iv.   12-days storage-time outdoor.
v.   18-days storage-time outdoor

(A)   (B)

Figure 4.10 Pellets produced with an original feedstock (A) poplar wood lignin, and (B) softwood bark lignin

The results presented in figure 4.11 revealed that freezing and subsequent thawing of the softwood bark lignin pellets only caused a slight drop in their mechanical durability as compared to the poplar wood lignin pellets and standard storage conditions. The highest mechanical durability was obtained for an 18-days storage time (outside the laboratory). For softwood bark lignin pellets, the most significant changes in pellet durability were observed after 22-days of storage inside the building and after the thawing process, with values ranging between 1.33% and 1.23%, respectively. Furthermore, for poplar wood lignin pellets, the most significant change in durability was observed in the freezing process at 2ºC and storage for 8-days, with a variation of 2.26%.
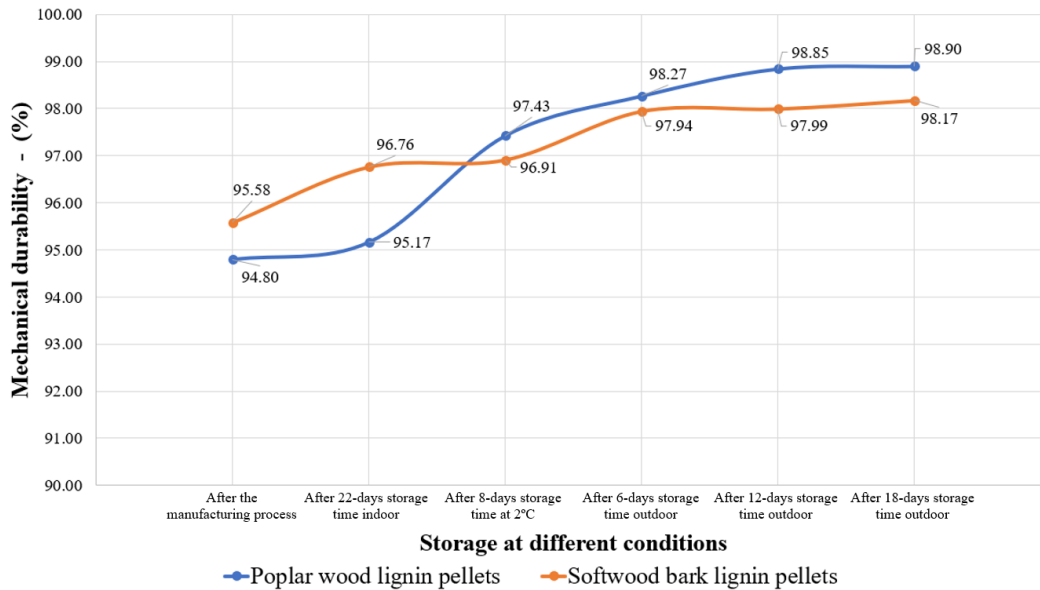
Figure 4.11 Mechanical durability of lignin pellets stored at different time and temperature conditions

Based on the results obtained, it was concluded that the storage of the pellets at different temperature and time conditions does not significantly affect their mechanical durability. On the contrary, all storage conditions improve the mechanical durability as compared to the one obtained immediately after manufacturing. However, if the mechanical durability of the pellets decreases, this result could be related to lignin pellets with low initial mechanical durability.

4.7 Ash content reduction process

The ash content in the pellets is one of the leading indicators in heat production since a high content of it causes problems in the combustion process. Furthermore, lignocellulosic biomass, such as lignin from corn stover and softwood bark (with initial ash content of 12.64% and 2.20%, respectively), contains a significant number of ashes acting as an inhibitor in subsequent conversion processes, in this case, into solid biofuels. In this subsection, the effectiveness of three ash reduction procedures was evaluated in lignin's from corn stover and softwood bark (as shown in figure 4.12), with limited success, as follows:

  i.   Chelation process in corn stover lignin: organic acid (oxalic) was used.
 ii.   Pre-washed with nonionic surfactant (Triton X100) and hot water in softwood bark lignin.
iii.   Pre-washed with only hot water (H_2O) in softwood bark lignin.

<div align="center">(A)   (B)</div>

Figure 4.12 Lignin used for the ash reduction process from (A) corn stover, and (B) softwood bark

There is a series of chemical compounds (the so-called chelating or chelating agents) capable of fixing or retaining, within their molecule, diverse chemical elements, forming very stable compounds called chelates. When a metal ion combines with an electron donor, the substance formed is said to be a complex or a coordination compound. If the substance that combines with the metal contains two or more donor groups, forming one or more bonds, then the resulting structure is a chelate compound, and the donor is called a chelating agent. The electron-pair bonds between the metal and the donor agent that forms the complex, or the chelate, can be "essentially ionic" or "essentially covalent," depending on the atoms involved. According to (Reza et al., 2015), chelating agents are commonly used to remove metal ions in soil research and other industries. Chelation has many typical industrial applications, including metal quenching, corrosion inhibition, solubilization, and cancer therapy. Scheme 4.13 shows the experimental chelation procedure using chelating agents. The effective removal of inorganic compounds was first removed by washing the sample with 100 ml of boiling water. Then 35 ml of acetone was used for the removal of non-polar extractives. This treatment prepared biomass without dirt and extractives, allowing greater consistency when studying the effects of chelation on structural ashes. The solid residue was subjected to chelation and mild hydrothermal treatment in a reactor with 100 ml of water at a temperature between 38.5 and 70.0 °C for 1.2 hours. After chelation, the solid residue was filtered and washed with 100 ml of boiling water for one hour. Subsequently, it was filtered, and the solid residue was placed in the drying oven at 105ºC to measure the moisture content. Finally, the samples were taken to the calcination furnace, after which the ash content was quantified using the (ISO 18122:2015, n.d.) procedure of the (CANplus certification, 2016).
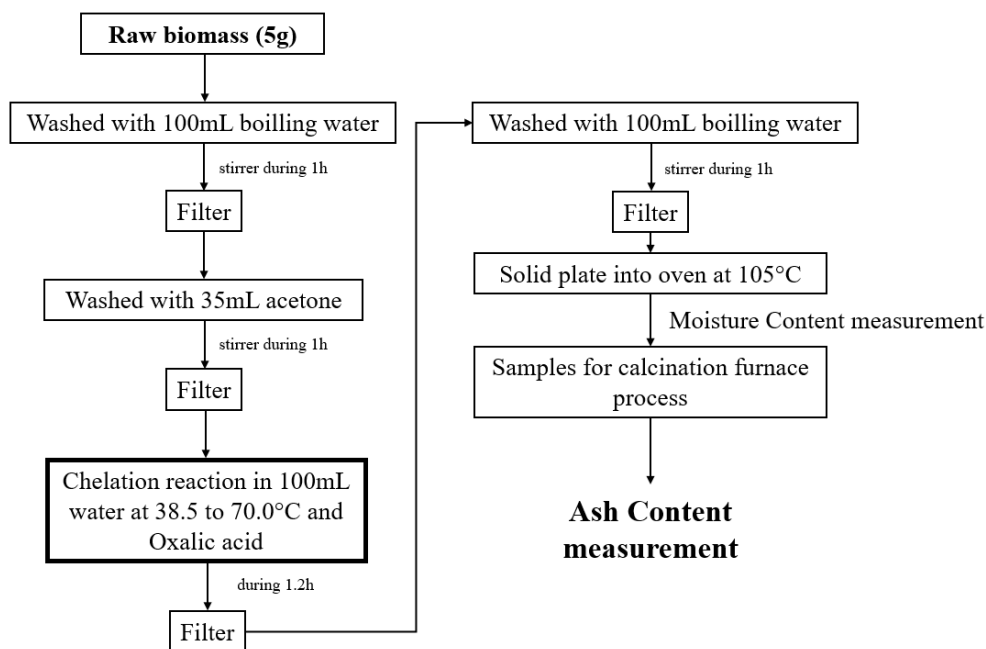
Figure 4.13 Oxidation process for lignin from corn stover.

The results presented in Table 4.12 show a reduction of 24.7% for the chelation process using oxalic acid and lignin from corn stover. The best condition was for sample 4, obtaining a reduction of 31.7%. The use of other citrates can further reduce the ash content of lignin. If an economical process for chelator recovery and regeneration is identified, this pre-process could play an essential role in supplying commercial grade biomass for a commercial biorefinery industry.

Table 4.12 Experimental results obtained for oxidation process in corn stover lignin

Sample	time (h)	Oxalic acid (g)	Water (ml)	Lignin (g)	Stirrer (rpm)	T (ºC)	Ash content (%)
1	1.0	2.5081	50.0	4.0125	700.0	38.5	9.70
2	1.0	2.5084	50.0	4.0162	700.0	38.5	9.61
3	1.0	5.0033	50.0	4.0166	700.0	38.5	8.76
4	1.0	5.0174	50.0	4.0109	700.0	38.5	8.63
5	1.0	2.5032	60.0	5.0022	800.0	40.5	10.09
6	1.0	2.5042	60.0	5.0063	800.0	40.5	10.05
7	1.0	5.0124	60.0	5.0138	800.0	40.5	9.61
8	1.0	5.0223	60.0	5.0104	800.0	40.5	9.39
9	1.0	5.01	60.0	5.01	800.0	40.5	9.16
10	1.0	5.02	60.0	5.01	800.0	40.5	9.94
11	1.0	15.0	50.0	5.04	600.0	70.0	9.37
12	1.0	20.0	50.0	5.05	600.0	70.0	9.85

Due to the high ash content found and possible deposition on boiler tube surfaces, heat transfer efficiency may decrease. Also, ash deposits, especially those with high chlorine content, can

lead to corrosion of boiler tubes. On the other hand, biomass ashes can contain appropriate amounts of nutrients for plants, such as Potassium, Magnesium, and Phosphorus (K, Mg, P). Corn stover is an agricultural residue used on farms for heating and drying crops. It was used to manufacture pellets, and the ash content was measured. Stubble ash in corn averaged 9.61% after the chelation process. However, (Lizotte et al., 2015) found that ash content for corn stubble averaged 4.8% in a cold crop heat unit zone and 7.3% for warmer zones. Also, it was found in the fall, the ash content of the stubble varied between 5.5% and 11.7%. According to (Biedermann & Obernberger, 2005), the ashes can also contain heavy metals, so possibilities for sustainable utilization of the ashes (recycling in agricultural fields or forests) must be found.. However, it was necessary to implement another procedure for ash reduction. For this study, lignin prewashed was used. Scheme 4.14 shows the procedure used to reduce ash content in softwood bark lignin (different from the previous procedure that was used chelation process in corn stover lignin). Triton X100 as a surfactant and hot water were used in this process. Inorganic compounds were removed by initially washing the lignin with surfactant and hot water. Furthermore, it was filtered, the liquid residue was stored, and the solid residue was placed in the drying oven at 105ºC to measure the moisture content. Subsequently, the samples were used to manufacture lignin pellets through the laboratory-scale pellet mill, and finally, the physical and chemical properties measurements were carried out using (CANplus certification, 2016).
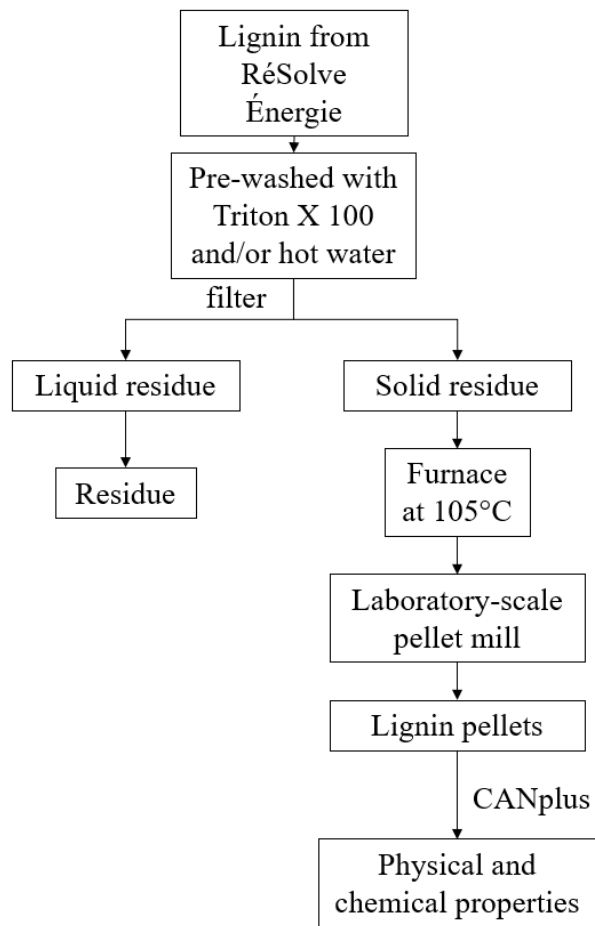
Figure 4.14 Pre-washed process for lignin from softwood bark

The results presented in Table 4.13 show a reduction of 65.45% for the pre-wash process using Triton X10 as a surfactant and subsequently hot water in the lignin of softwood bark. On the other hand, when the pre-wash was performed using hot water in large quantities (10 liters), a reduction of 75.91% was found. This pre-washing process was beneficial and could provide advantages in manufacturing lignin pellets at an industrial and commercial level.

Table 4.13 Pre-washed results using surfactant and hot water for softwood bark lignin

Sample	Lignin (g)	Surfactant (ml)	Water (ml)	Ash content (%)
1	50.20	103.54	0	1.61
2	50.74	100.00	500	1.59
3	50.49	104.00	2500	0.95
4	50.44	102.00	5000	0.76
1	50.20	---	500	1.97
2	50.74	---	1500	1.65
3	50.49	---	2500	1.21
4	50.44	---	10000	0.53

According to (Tu et al., 2019), solid biofuel has been used to supply heat or raw materials in the industry to replace traditional fossil fuels, which could be one of the leading causes of global warming. However, the large-scale use of solid biofuels may be restricted due to the high hydrophilicity of biomass, which may cause transport and storage problems. Therefore, biomass pelleting was used to improve its fuel density. In this study, pre-washing with a surfactant or hot water played a role in permeation, adsorption, and wetness in the solution, which was expected to improve the biomass properties and the effectiveness of corn stover pelletization.

Of the three procedures presented for reducing ashes in lignin (before its use in the pellet manufacturing process), the most effective was pre-washing with hot water. The raw material used was lignin softwood bark. The results obtained in this procedure are within the values required by the CANplus A1 certification for all properties, including ash content. The results of the pellets manufactured with this biomass are presented in Table 4.14 and suggest that there could be opportunities to produce lignin pellets as a sidestream from a sugar-oriented biorefinery. Also, these results show that the procedures used to reduce the properties such as ash, sulfur, and fines and improve the mechanical durability were satisfactory. These results show that the manufactured lignin pellets in this research project were of excellent quality compared to commercial wood pellets and the lignin pellets manufactured in work proposed by (Rueda et al., 2022).

Table 4.14 Properties of the softwood bark lignin pellets produced through the laboratory-scale pellet mill.

Property	Softwood bark lignin pellets	CANplus certification A1
Diameter (mm)	6.47	6 ± 1 or 8 ± 1
Length (mm)	15.05	$3.15 < L \leq 40$
Moisture content (%)	10.03	≤ 10
Mechanical durability (%)	98.20	≥ 98.0
Fines content (%)	0.18	≤ 1.0
Calorific value (MJ/kg)	24.85	≥ 16.5
Hardness (kgf)	24.50	---
Ash content (%)	0.53	≤ 0.7
Ultimate analysis		
Carbon	60.44	---
Hydrogen	5.76	---
Nitrogen	0.27	≤ 0.3
Sulfur	0.00	≤ 0.04

CHAPTER 5

CONCLUSION (Français)

Après avoir rappelé la problématique et les objectifs établis dans la thèse, ce chapitre résume les principales conclusions, réitère les contributions originales, et propose des recommandations pour les travaux futurs.

Rappel des problèmes et des objectifs

Les granulés sont utilisés pour la production d'électricité, le chauffage et la climatisation de locaux résidentiels et commerciaux. Grâce aux études menées ces dernières années, des recherches théoriques et expérimentales ont été menées pour améliorer la connaissance de ce type de biocombustible solide. La production de granulés nécessite des matières premières avec des paramètres préétablis, tels qu'une faible teneur en cendres, en azote, en soufre et en chlore. De plus, il est nécessaire d'assurer une faible teneur en humidité, une faible teneur en fines et un pouvoir calorifique élevé. La procédure de production de granulés dépend essentiellement des propriétés physiques et chimiques et des variables de processus, telles que la pression et la température atteintes pendant la granulation. Selon le contexte présenté, le projet de thèse se proposait de répondre aux objectifs suivants.

1. Tirer parti de la lignine des résidus agricoles et forestiers pour fabriquer des biocarburants solides.
2. Déterminer les propriétés physiques et chimiques des granulés de lignine selon la certification CANplus.
3. Concevoir une stratégie de contrôle pour réduire le temps de fabrication et garantir la qualité du produit final.
4. Réduire la teneur en cendres de la lignine par différentes stratégies et son utilisation ultérieure dans la fabrication de granulés.

Résumé des conclusions

L'objectif de ce projet était d'étudier l'utilisation potentielle de la lignine obtenue à partir de résidus forestiers pour la production de granulés énergétiques. Différents aspects du processus de granulation, y compris la nouvelle matière première, l'optimisation des paramètres et le développement de granulés de haute qualité, ont été étudiés pour développer une compréhension plus approfondie de la fabrication de granulés de lignine. De plus, la fabrication de granulés de lignine fabriqués à partir de la macromolécule de lignine extraite de la biomasse de bois de peuplier et d'écorce de résineux a été rapportée à l'aide d'un procédé d'hydrolyse acide concentrée et d'une évaluation de leurs propriétés. Deux scénarios ont été étudiés. Dans le premier, différentes teneurs en humidité initiales pour la matière première de lignine ont été utilisées pour produire des granulés afin de déterminer les propriétés physiques et chimiques du produit en aval. Ces résultats ont été comparés à des granulés d'écorce de résineux fabriqués

avec le même appareil à l'échelle du laboratoire et avec des références bibliographiques. Les résultats ont montré que la teneur en humidité est cruciale dans la production de granulés de lignine de haute qualité car elle influence directement leur durabilité mécanique, leur teneur en fines, leur teneur en cendres et leur pouvoir calorifique. Pour ce premier scénario, les granulés de lignine fabriqués avec 8,01 % d'humidité présentaient une valeur de durabilité mécanique de 94,80 %. Les granulés de lignine pure avaient une durabilité mécanique inférieure à celle des granulés de bois résineux produits à 6,57 % d'humidité, ce qui a conduit à une valeur de durabilité mécanique de 99,48 %. De plus, cette propriété a été améliorée avec les conditions de stockage. Cependant, pour les granulés de lignine (à 8,01 % d'humidité), la propriété de pouvoir calorifique a présenté le meilleur résultat de 23,27 MJ/kg par rapport aux granulés de bois résineux (à 6,57 % d'humidité) de 18,24 MJ/kg. Le deuxième scénario portait sur l'utilisation de quatre types de bio-additifs dans la matière première de lignine, ce qui s'est traduit par des avantages mineurs pour les propriétés physiques des granulés.

De plus, lorsque la production de biocombustible solide à partir de lignine est envisagée, la faible teneur en humidité et en cendres de la matière première est requise. Ces résultats impliquent que l'amélioration la plus significative de l'humidité, de la durabilité et de la teneur en fines a pu être observée après le stockage. Ces résultats ont montré que la teneur élevée en minéraux de la lignine pouvait être réduite en préparant la charge avec un lavage neutre après le prétraitement de la biomasse. De même, et pour le second cas, l'influence de la lignine dans la fabrication de granulés de bois a été étudiée. Pour ce cas, différentes concentrations de lignine ont été utilisées. Les résultats ont montré que les meilleures conditions étaient lorsqu'une concentration de 75% de lignine et 25% de bois était utilisée, obtenant des résultats exceptionnels de pouvoir calorifique avec une valeur de 25,01 MJ/kg. Cependant, la durabilité mécanique obtenue après le processus de fabrication pour cette condition était de 95,58%, étant améliorée avec des conditions de stockage de 18 jours et à l'extérieur et obtenant finalement 98,17%. Enfin, deux procédés différents ont été mis en œuvre pour réduire la teneur en cendres de la lignine : procédé de chélation et prélavage avec tensioactif et eau chaude. Les meilleurs résultats ont été obtenus lorsque le prélavage à l'eau chaude uniquement a été utilisé avec une réduction de 75,91 % de la teneur en cendres de lignine. Cependant, lorsque le prélavage avec tensioactif et eau chaude a été utilisé, une réduction de 65,45% de la teneur en cendres de la lignine a été obtenue.

Dans l'ensemble, ce projet de thèse a utilisé deux appareils pour fabriquer des granulés de lignine, le système à un seul granulé et le moulin à granulés à l'échelle du laboratoire. Pour mieux comprendre le processus de granulation, il était nécessaire de réaliser une analyse de sensibilité du système et de caractériser la matière première. Une fois cet objectif atteint, les granulés de lignine ont été fabriqués à partir de deux matières premières, la lignine de bois de peuplier et la lignine d'écorce de résineux. De plus, des granulés de chanvre ont également été fabriqués à l'aide du système de granulés uniques. De plus, des expériences de prétraitement (explosion à la vapeur) ont été réalisées sur la biomasse d'écorce de résineux et son utilisation ultérieure dans la fabrication de granulés. Quatre types d'additifs naturels (huile de maïs, acide citrique, glycérol et d-xylose) ont été utilisés pour améliorer les propriétés physiques des granulés de lignine.

D'autre part, différentes concentrations de lignine ont été utilisées pour déterminer l'influence de la lignine dans les granulés de bois. De plus, une étude a été réalisée pour déterminer l'influence du temps et des conditions de stockage sur les pastilles de lignine fabriquées. Enfin, un procédé de réduction de matière inorganique dans la matière première et son utilisation ultérieure dans la fabrication de granulés a été mis en place. Cette étude se veut un premier pas

ver la production industrielle de granulés de lignine, que l'on pourrait qualifier à terme de "granulés de troisième-génération".

Rappelant les contributions originales

La liste suivante rassemble les contributions originales de cette recherche.

1. Ce travail propose et développe une étude pour la production industrielle de biocarburant solide utilisant la lignine comme matière première.
2. Ce projet de recherche développe un procédé de fabrication de granulés de lignine qui fournit une recette de fabrication optimale basée sur les paramètres du procédé de granulation tels que la température, la pression et la vitesse d'extrusion.
3. Fournir et garantir les paramètres de qualité physique et chimique requis par la norme CANplus.
4. Développer une méthodologie pour l'élimination des substances inorganiques de la lignine et son utilisation ultérieure dans la fabrication de pellets.

Recommandations et travaux futurs

Sur la base de la revue de la littérature effectuée et des résultats obtenus dans cette étude doctorale, on peut constater, bien que superficiellement, l'intérêt croissant pour l'utilisation des granulés de lignine, issus de la biomasse agricole et forestière, comme source d'énergie alternative et durable, ainsi que le positionnement et le comportement des principaux acteurs du marché international des granulés de bois, dans lequel le Canada a une participation importante. Le Canada compte 46 usines industrielles qui produisent environ 5130300 tonnes métriques/an (décembre 2021). La province de Québec possède une usine de Lac-au-Saumon qui produira 100000 tonnes de granulés annuellement (juin 2022). Par conséquent, le pays a un fort potentiel pour se démarquer sur le marché mondial. Néanmoins, il a besoin de plus d'attention et de soutien de la part des agents de l'État et de détermination de la part des entrepreneurs du secteur pour développer des produits répondant aux spécifications requises par le marché international. Contrairement à ce qui est affirmé dans la littérature, ce travail de recherche doctorale se veut un premier pas vers la production industrielle de granules de lignine, qui pourraient être qualifiées à terme de granules de "troisième génération". Il est recommandé de considérer les questions suivantes dans les études futures. Il est recommandé de tenir compte des questions suivantes dans les études futures.

1. Utilisez des additifs basés sur différentes compositions chimiques et leur effet possible pour réduire les problèmes liés aux cendres lors de la combustion des granulés.
2. Analyser l'efficacité thermique des granulés de lignine à l'aide d'un brûleur industriel et son utilisation ultérieure dans le processus de gazéification.
3. Mettre en œuvre un système de fabrication de granulés de lignine à l'échelle de la production à usage résidentiel et/ou industriel.

CHAPTER 6

CONCLUSIONS (English)

After recalling the problems and objectives established in the thesis, this chapter summarizes the main conclusions, reiterates the original contributions, and provides recommendations for future work.

Recalling the problems and objectives

Pellets are used for the production of electricity, heating, and air conditioning of residential and commercial premises. Due to the studies carried out in recent years, theoretical and experimental research has been carried out to improve the knowledge of this type of solid biofuel. The production of pellets requires raw materials with pre-established parameters, such as low ash, nitrogen, sulfur, and chlorine content. In addition, it is necessary to ensure low moisture content, low fines content, and high calorific value. The pellet production procedure is critically dependent on the physical and chemical properties and process variables, such as the pressure and temperature reached during pelletizing. According to the context presented, the thesis project proposed to address the following objectives.

1. To take advantage of lignin from agricultural and forest residues to manufacture solid biofuels.
2. To determine the physical and chemical properties of lignin pellets according to CANplus certification.
3. To design a control strategy to reduce manufacturing time and guarantee the quality of the final product.
4. To reduce the ash content in lignin through different strategies and its subsequent use in the manufacture of pellets.

Summary of conclusions

The objective of this project was to study the potential use of lignin obtained from forest residues for the production of energy pellets. Different aspects of the pelleting process, including new raw material, optimization of parameters, and development of high-quality pellets, were studied to develop a deeper understanding of lignin pellet manufacturing. Furthermore, the manufacture of lignin pellets made from the lignin macromolecule extracted from poplar wood and softwood bark biomass was reported using a concentrated acid hydrolysis process and an assessment of their properties. Two scenarios were investigated. In the first one, different initial moisture contents for the lignin feedstock were used to produce pellets to determine the physical and chemical properties of the downstream product. These results were compared to softwood bark pellets manufactured with the same apparatus at a laboratory-scale and with literature references. Results showed that moisture content is crucial in producing high-quality lignin pellets since it directly influences their mechanical durability, fines content, ash content, and

calorific value. For this first scenario, lignin pellets manufactured with 8.01% moisture presented a 94.80% value in mechanical durability. Pure lignin pellets had inferior mechanical durability than softwood pellets produced at 6.57% humidity, leading to a 99.48% mechanical durability value. In addition, this property was improved with storage conditions. However, for lignin pellets (at 8.01% moisture content), the calorific value property presented the best result of 23.27 MJ/kg compared to softwood pellets (at 6.57% moisture content) of 18.24 MJ/kg. The second scenario addressed the use of four types of bio-additives in the lignin feedstock, which translated into minor benefits for the physical properties of the pellets.

Furthermore, when solid biofuel production from lignin is intended, the raw material's low moisture and ash content are required. These results imply that the most significant improvement in moisture, durability, and fines content could be observed after storage. These results showed that the high mineral content of lignin could be reduced by preparing the feedstock with a neutral wash after the biomass pretreatment. Likewise, and for the second case, the influence of lignin in the manufacture of wood pellets was studied. For this case, different concentrations of lignin were used. The results showed that the best condition was when a concentration of 75% lignin and 25% wood was used, obtaining outstanding results of calorific power with a value of 25.01 MJ/kg. However, the mechanical durability obtained after the manufacturing process for this condition was 95.58%, being improved with storage conditions of 18-days and outdoor and finally obtaining 98.17%. Finally, two different processes were implemented to reduce the ash content in lignin: chelation process and pre-washed with surfactant and hot water. The best results were obtained when hot water only pre-wash was used with a 75.91% reduction in lignin ash content. However, when the pre-wash with surfactant and hot water was used, a reduction of 65.45% of the ash content in the lignin was obtained.

Overall, this thesis project used two apparatus to manufacture lignin pellets, the single pellet system and the laboratory-scale pellet mill. To better understand the granulation process, it was necessary to perform a sensitivity analysis of the system and characterize the raw material. Once this was achieved, lignin pellets were manufactured using two raw materials, poplar wood lignin, and softwood bark lignin. In addition, hemp pellets were also manufactured using the single pellet system. Furthermore, pretreatment experiments (steam explosion) were carried out on the softwood bark biomass and its subsequent use in the manufacture of pellets. Four types of natural additives (corn oil, citric acid, glycerol, and d-xylose) were used to improve the physical properties of the lignin pellets.

On the other hand, different concentrations of lignin were used to determine the influence of lignin in wood pellets. In addition, a study was carried out to determine the influence of time and storage conditions on the manufactured lignin pellets. Finally, a process for reducing inorganic material in the raw material and its subsequent use in the manufacture of pellets was implemented. This study aims to be a first step towards the industrial production of lignin pellets, which could eventually be referred to as "third-generation" pellets.

Recalling the original contributions

The following list gathers the original contributions of this research.

1. This work proposes and develops a study for the industrial production of solid biofuel using lignin as raw material.

2. This research project develops a lignin pellet manufacturing process that provides an optimal manufacturing recipe based on the granulation process parameters such as temperature, pressure, and extrusion speed.
3. To provide and guarantee the physical and chemical quality parameters required by the CANplus standard.
4. To develop a methodology for the elimination of inorganic substances from lignin and its subsequent use in the manufacture of pellets.

Recommendations and future work

Based on the literature review carried out and the results obtained in this doctoral study, it can be seen, albeit superficially, the growing interest in the use of lignin pellets, from agricultural and forestry biomass, as an alternative and sustainable energy source. as well as the positioning and behavior of the leading players in the international wood pellet market, in which Canada has significant participation. Canada has 46 industrial plants that produce around 5.130.300 metric tons/year (December 2021). The province of Quebec has a Lac-au-Saumon plant that will produce 100.000 tons of pellets annually (June 2022). Hence, the country has a high potential to stand out in the global market. Nonetheless, it needs more attention and support from government agents and determination on the part of entrepreneurs in the sector to develop products that meet the specifications required by the international market. Contrary to what is stated in the literature, this doctoral research work aims to be a first step towards the industrial production of lignin granules, which could be described in the long term as "third generation granules". The following issues are recommended to be considered in future studies.

1. Use of additives based on different chemical compositions and their possible effect to reduce ash-related inconveniences during pellet combustion.
2. Analyze the thermal efficiency of lignin pellets using an industrial boiler and its subsequent use in the gasification process.
3. Implement a production-scale lignin pellet manufacturing system for residential and or industrial use.

ANNEXES 1

Steam-exploded softwood bark

In this study, softwood bark was used as raw material. Samples were steam-treated using a 50-liter reactor in the Biomass Technology Laboratory (BTL) machine shop located at the Université de Sherbrooke (Sherbrooke, QC, Canada). Figure 4.4 shows the steam explosion procedure used. The raw material used was previously dried and crushed. Water Impregnation of the raw material was carried out at room temperature and for 24h before the experiments. It was then pressed and filtered to separate liquid and solid residues. The solid residue was subjected to the steam explosion process at different severity factor conditions. The raw material exploited with steam was again pressed and filtered to separate the residues. The liquid obtained was collected in buckets, sealed, and stored in the cold room at -20 ºC. The solid residue was placed in the furnace at 105 ºC and then was used as raw material to manufacture steam-exploded softwood bark pellets through the single pellet system.

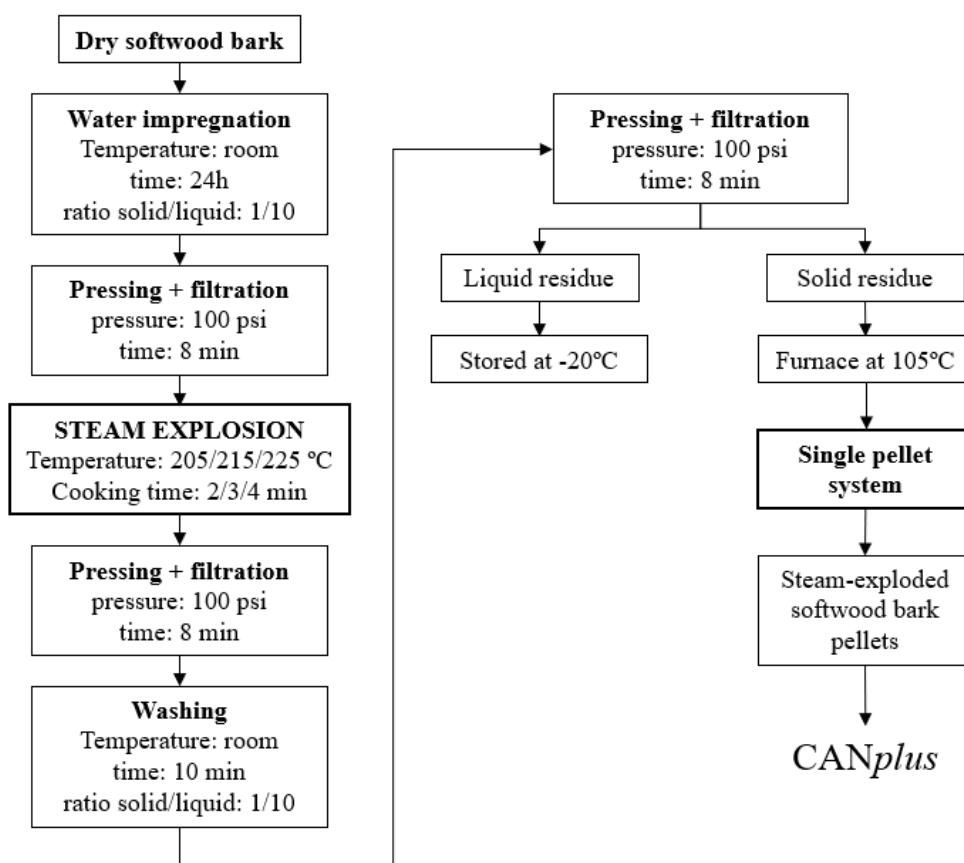Figure A.1 Flow diagram for dry softwood bark and steam explosion process, added to the operational conditions used in each step.

The conditions used to obtain each substrate and the code associated with each of them are indicated in Table A. This same table tabulates the degree of severity for each pretreatment condition, whose determination was made using equation 1 (Overend & Chornet, 1987).

Table A Experiment conditions for steam-exploded softwood bark.

Condition	Temperature (ºC)	Pressure (psi)	time (min)	Severity factor	Mass loss (%)
1	205	235	2	3,39	48,28
2	205	235	3	3,57	34,12
3	205	235	4	3,69	35,82
4	215	291	2	3,69	60,23
5	215	291	3	3,86	36,64
6	215	291	4	3,99	38,42
7	225	355	2	3,98	61,97
8	225	355	3	4,16	41,71
9	225	355	4	4,28	37,82

The physical and chemical properties of pellets made from softwood bark milled and steam-exploded and untreated were investigated. Pellets made from steam-exploded samples required a compression pressure of 650.17 MPa. The results obtained are presented in table B. The color (darkness) of the samples increased with the severity of the treatment. The untreated pellet was light in color, and the rest of the pellets made from steam-treated softwood bark turned brown. (Sehlstedt-Persson, 2003) suggested that the darkening of the color of treated wood at higher steam temperature and longer residence time due to degradation of hemicelluloses could be due to hydrolysis by a reaction similar to the reaction of Maillard. According to (Lam et al., 2011), the Maillard reaction is a non-enzymatic reaction between an amino acid and reducing sugar in the presence of heat. In this reaction, the carbonyl group of the sugar reacts with the amino acid to form complex chemical compounds that can produce unpleasant odors and colors.

The moisture content of the samples after the steam explosion pretreatment ranged between 0.87% and 8.71%, with an average value of 4.99% (see Table 4.4), while the moisture content of the untreated sample was 8.88%. Another result found in these experiments was the high nitrogen concentration for all steamed pellets samples, except samples 2 and 4. For this property, the pellets (samples 2 and 4) are within the required values by CANplus A1 certification. In addition, the best ash content obtained was for sample 1, with a value of 1.27%. However, samples 1 and 2 are within the values required by the CANplus B certification for wood pellets. According to the values obtained, it is possible to conclude that there is a directly proportional relationship between the high severity factor (in this case, sample 9) and the properties of mechanical durability, heating power, carbon content, and ash content. Finally, it was challenging to relate the loss of volatiles and the solid yield of the biomass treated with steam. Most of the original wood extracts were probably lost as volatile compounds, and according to (Esteves, Marques, et al., 2008), new extracts could appear as degradation products of structural polymers of carbohydrates and lignin. Wood pellets tend to absorb moisture from the moist air around them. Also, wet pellets tend to disintegrate and provide an ideal environment for microbial and biochemical activities. This was confirmed in the works of (Lehtikangas, 2001; Rupar & Sanati, 2005). Work published in the literature has (Anglès et al., 2001; Esteves, Graça, et al., 2008) shown that wood products made from groundwood are more stable and less hygroscopic after steam treatment . Also, (Anglès et al., 2001) showed that the strength of panels made from steam-exploded wood increased as the pretreatment severity factor increased, but up to a certain point beyond which no gain in strength was observed.

Table B Properties of the pellets produced with softwood bark and different severity factor conditions using the single pellet system.

Property	Condition										CANplus certification
	Without	1	2	3	4	5	6	7	8	9	
Diameter (mm)	6,81	6,79	6,77	6,76	6,74	6,74	6,79	6,77	6,78	6,77	6 ± 1 ou 8 ± 1
Length (mm)	16,90	21,49	22,58	22,27	22,11	22,83	22,56	22,28	22,00	23,72	$3{,}15 < L \leq 40$
Moisture content (%)	8,88	1,65	2,55	0,87	7,88	8,02	6,21	8,71	2,53	6,51	≤ 10
Mechanical durability (%)	99,59	99,89	99,90	99,90	99,90	99,91	99,92	99,92	99,93	99,94	$\geq 98{,}0$ (A1) ou $\geq 97{,}5$ (B)
Fines content (%)	0,27	0,11	0,52	0,18	0,29	0,18	0,23	0,18	0,19	0,18	$\leq 1{,}0$
HHV (MJ/kg)	19,32	20,64	20,86	21,35	20,62	19,44	21,64	20,82	20,86	21,91	$\geq 16{,}5$
Ash content (%)	3,08	1,27	1,65	2,42	2,48	2,55	2,73	2,77	2,81	2,85	$\leq 0{,}7$ (A1) ou $\leq 2{,}0$ (B)
Ultimate analysis											
Carbon	--	51,29	51,94	52,04	36,85	53,90	53,86	52,51	53,28	53,63	---
Hydrogen	--	5,85	5,86	5,72	4,02	5,70	5,64	5,70	5,80	5,75	---
Nitrogen	--	0,32	0,28	0,32	0,26	0,37	0,37	0,34	0,36	0,37	$\leq 0{,}3$ (A1) ou $\leq 1{,}0$ (B)
Sulfur	--	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	$\leq 0{,}04$ (A1) ou $\leq 0{,}05$ (B)

ANNEXES 2

Hemp pellets

While wood pellets are currently the market for fuel pellets, hemp (*Cannabis sativa L.*) pellets could hold a significant market share. As the use of industrial hemp increases, more hemp powder will be produced. The raw material is a by-product. Making fuel pellets from hemp could be the most efficient/sustainable biofuel pellet process. However, hemp pellets can be more corrosive when burned than wood pellets, generate more ash, and always have the same high quality found in premium wood pellets. This product comes from the spike of hemp cane and does not have the possibility of including any additional material that could lead to a lower quality grade. According to (Prade et al., 2011), solid biofuel production from hemp is best achieved when hemp is harvested between February and April when the biomass moisture content is low. Also, (Parvez et al., 2021) state that solid hemp biofuel has the highest energy yield compared to other hemp biofuels, such as biogas and liquid biofuels, as it is not separated. (Parvez et al., 2021) assure that hemp is a crop that has many potentials uses but faces stiff competition from many other crops. Despite this, hemp remains an excellent opportunity, achieving high biomass and biofuel yields compared to other primary energy crops (Das et al., 2017). The low requirements for growing hemp allow it to be competitive with higher-yielding crops, and hemp's versatility opens up many opportunities for co-production. Pellets were manufactured from hemp using the single pellet system, shown in figure 4.5.

Figure A.2 Hemp pellets produced through the single pellet system

Figure 4.6 presents two evident stages of decomposition: the first, at temperatures around 100 °C, can be attributed to the loss of water by desorption. The second, at higher temperatures, is attributed to the decomposition of the hemp pellets. Then at temperatures above 270°C, it is due to the decomposition of the remaining hemp, which started at lower temperatures and continues up to 430°C. Likewise, according to the thermogravimetric analysis, it is possible to affirm that the hemp showed a decrease in its thermal stability, exhibiting a glass transition temperature (Tg) between 60.84 °C and 90.0 ºC.
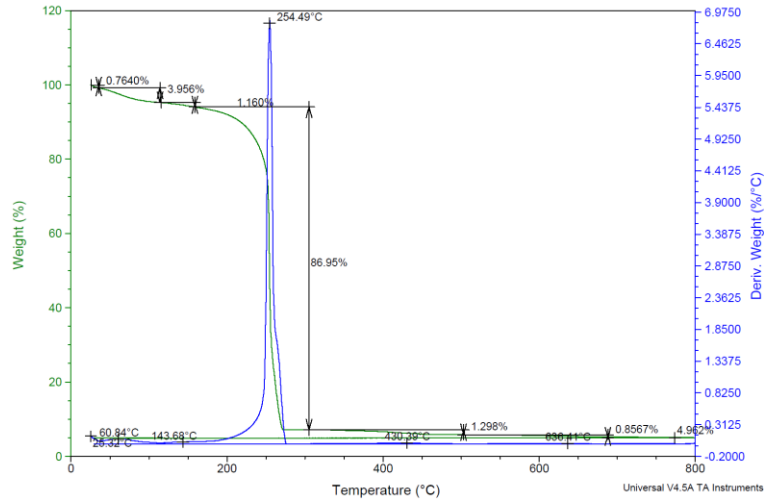
Figure A.3 Thermogravimetric analysis of hemp in an inert atmosphere.

According to the results shown in table C, the hemp pellets produced approximately 3.97% ash, and their high nitrogen and sulfur content (in this case, 1.69 and 0.07, respectively) probably make them unusable in the wide range pellet burners currently on the market. However, pellets made from hemp have very similar physical properties to pellets made from poplar wood lignin at 6.14%.

Table C Properties of hemp pellets produced through the single pellet system

Property	Hemp	CANplus certification		
		A1	A2	B
Diameter (mm)	6.34 ± 0.07	6 ± 1 or 8 ± 1		
Length (mm)	21.15 ± 2.23	3.15 < L ≤ 40		
Moisture content (%)	4.38 ± 0.29	≤ 10		
Mechanical durability (%)	99.36 ± 0.05	≥ 98.0	≥ 97.5	
Fines content (%)	0.23 ± 0.17	≤ 1.0		
HHV (MJ/kg)	17.27	≥ 16.5		
Ash content (%)	3.97± 0.28	≤ 0.7	≤ 1.2	≤ 2.0
Ultimate analysis				
Carbon	43.95	---		
Hydrogen	6.02	---		
Nitrogen	1.69	≤ 0.3	≤ 0.5	≤ 1.0
Sulfur	0.07	≤ 0.04	≤ 0.05	
Oxygen	42.78	---		

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