AUTONOMOUS UNIVERSITY OF SAN LUIS POTOSÍ

FACULTY OF CHEMICAL SCIENCES

CHEMICAL AND FOOD PROCESS SIMULATION LABORATORY

EXPERIMENTAL AND SIMULATION STUDY OF THE HYDROTHERMAL CARBONIZATION OF BIOMASSES FOR THE PRODUCTION OF SYNTHETIC FUELS

A thesis submitted in fulfillment of the requirements for the degree of doctor of philosophy in chemical engineering sciences

by

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FACULTAD DE
CIENCIAS QUÍMICAS

SAN LUIS POTOSI, JULY 2021

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ESTUDIO EXPERIMENTAL Y SIMULACIÓN DE LA CARBONIZACIÓN HIDROTÉRMICA DE BIOMASAS PARA LA PRODUCCIÓN DE COMBUSTIBLES SINTÉTICOS

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Presente:

Por medio de la presente comunicamos que la tesis llevada a cabo por el alumno de doctorado de PCIQ. Diakaridia Sangaré, titulada “Experimental and Simulation Study of the Hydrothermal Carbonization of Biomasses for the Production of Synthetic Fuels”, ha sido concluida y aprobada por el comité tutorial para dar inicio a los tramites correspondientes para su titulación, la cual tendrá lugar el próximo día 16 de julio a las 10:00 hrs. en CICBI (Centro de Información en Ciencias Biomédicas).

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Abstract:

Renewable energies allow us to reduce our dependence on fossil fuels and greenhouse gas emissions. In this study, a suitable methodology for the conversion of wet biomass into fuels was established by using the hydrothermal carbonization process (HTC). The hydrocarbons obtained in the HTC process show better fuel properties compared to those of the raw biomasses during gasification. The use of modeling and process simulations allowed us to determine the optimum conditions for converting biomass moisture into energy. Furthermore, the simulation results show that the HTC process is economically feasible for producing hydrocarbons as pellets and could compete with bulk pine pellets.

Keyword: *Biomass, hydrothermal carbonization, synthetic fuels, gasification, hydrochar, modeling, simulation.*

Resumen:

Las energías renovables nos permiten reducir nuestra dependencia de los combustibles fósiles y las emisiones de gases de efecto invernadero. En este trabajo, se estableció una metodología adecuada para la conversión de biomasas húmedas en combustibles, utilizando el proceso de la carbonización hidrotermal (HTC). Los hidrocarbones obtenidos en el proceso de HTC mostraron mejores propiedades como combustibles en comparación con las biomasas brutas durante la gasificación. La utilización de modelado y simulaciones de proceso nos permitió encontrar las mejores condiciones de conversión de biomasa humedad en energía. Además, el resultado de la simulación mostro que el proceso de HTC es económicamente factible para producir hidrocarbones como pellet y podría competir con el pellet de pino a granel.

Palabra clave: *Biomasa, carbonización hidrotermal, combustibles sintéticos, gasificación, hidrocarbon, modelado, simulación.*

Résumé :

Les énergies renouvelables nous permettent de réduire notre dépendance vis-à-vis des combustibles fossiles et les émissions de gaz à effet de serre. Dans ce travail, une méthodologie appropriée pour la conversion de biomasses humides en carburants a été établie en utilisant le procédé de carbonisation hydrothermale (HTC). Les hydrochar obtenus dans le procédé de l'HTC ont montré de meilleures propriétés en tant que combustibles par rapport aux biomasses brutes pendant la gazéification. L'utilisation de la modélisation et des simulations de procédés nous a permis de trouver les meilleures conditions pour la conversion de la biomasse humide en énergie. En outre, le résultat de la simulation a montré que le procédé HTC est économiquement réalisable pour produire des hydrochar sous forme de pellets et qu'il pourrait concurrencer les pellets de pin en vrac.

Mot clé : *Biomasse, carbonisation hydrothermale, carburants synthétiques, gazéification, hydrochar, modélisation, simulation.*

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INTRODUCTION

The current socio-economic growth would not have occurred if fossil fuels had not been exploited. Coal, oil, natural gas, and other alternative energy sources have been the global economic engine. Energy consumption is one of the outstanding gauges of a society's progress and well-being as well as a fundamental factor for economic development. An economic model, such as the present one, whose functioning depends on continuous growth, also requires an equally increasing demand for energy. The productions of clean and sustainable fuels are the main challenge facing the impending energy crises and global warming. These clean and sustainable fuels are called renewable energy and represent the fourth largest energy source globally, behind oil, coal, and natural gas, accounting for about 19% of global primary energy production (Mujtaba et al., 2017). Renewable energy sources will constitute a major part of the future energy on the planet if sustainable development is promoted. In many countries, there are appropriate conditions to the use of some of these sources, which can contribute not only to partially solve part of the energy demand but also to the environment protection. Fossil fuels have been the primary source of energy so far. These fuel resources are not sustainable and cause Green House Gas emissions (GHGs) responsible for global warming (Deng et al., 2020). The immediate consequence is the increase in global temperature and extreme climatic events, which are increasingly frequent and harm health and agriculture. According to World Bank data (2019), there is a growing accumulation of emissions of polluting gases globally. Therefore, it is essential to utilize renewable energy resources that provide low GHGs emissions, which contributes to limiting the greenhouse effect. Many researchers in the world have been looking for alternative energy resources and fuels, including wind power, Hydropower, Solar energy, Geothermal energy, and Bioenergy (Dunn, 1986; Mohtasham, 2015).

Among these forms of renewable energy resources, bioenergy is expected to be one of the predominant forms of renewable energy sources in the future due to its abundance, manageability, and accessibility. Unlike other renewable energies, bioenergy is the only renewable energy utilized and stored in different forms, such as solid, liquid, or gas. For this versatility, bioenergy is gaining special attention among all renewable energy sources as a potential alternative for energy independence from fossil fuels. The use of bioenergy continues to grow, both in industrialized and developing countries. Today, bioenergy is set to play an increasingly important role in energy supply, both in the industrialized world and in developing countries, as concern about the state of the global environment grows. Bioenergy is energy produced from biomass or biofuel. Biomass can be converted into liquid, solid, or gaseous fuels; through a series of conversion processes to enhance its energy content. The ability to convert biomass materials through physical, chemical, or biological processes allows transforming solid carbonaceous materials that can be difficult to handle due to their bulkiness and low energy density, fuel with enriched physicochemical characteristics, high energy density, and ease to store and transport (Welfle, 2015). The least expensive biomass resources are agricultural waste products, municipal waste residues, but their supply is limited. To overcome this limitation, many countries worldwide are considering biomass crops for energy purposes and have begun to develop technologies to use biomass more efficiently (Baum et al., 2013; Börjesson et al., 2017; Cosentino et al., 2008). To contribute to a larger extent to the world's energy supply, the cultivation of dedicated biomass crops for energy purposes will be required, using uncultivated land and marginal land (McKendry, 2002). Recently, many researchers have studied the economic and environmental impact of energy obtained from biomass (Basu, 2010; Damartzis and Zabaniotou, 2011; Goldemberg and Coelho, 2004; López González, 2013; McKendry, 2002). However, biomass conversion efficiency and production costs with current biomass conversion technologies remain the two biggest challenges (Mafakheri and Nasiri, 2014). One of the main obstacles to constructing large biomass plants is the transportation of large quantities of biomass fuels from forest sources to the point of use.

Compared to fossil fuels, biomass has a low energy density and a high moisture content (Acharjee et al., 2011; Medic et al., 2010). These properties make biomass relatively expensive to transport, and thus higher transport levels are a barrier to large-scale plants. In contrast, small-scale biomass electricity generation plants can be fuelled by local resources from small adjacent catchment areas, such as agricultural waste that can be turned into electricity. Even though biomass fuels are dried, they can rehydrate and rot during storage. In general, moisture plays a fundamental role in any biologically derived material (Vasquez and Coronella, 2009). Dry biomass is much more stable and exhibits reduced rates of biological deterioration. Furthermore, increasing the energy density is recommended because, in applications like combustion and gasification, a significant biomass volume is needed to substitute an equal amount of coal. To solve this moisture problem and increase the energy content, one of the alternatives can be hydrothermal carbonization or wet roasting, which results in high energy density and low moisture.

Thermochemical conversion, including pyrolysis, liquefaction, combustion, gasification, and other processes, is one of the most common biomass-to-energy conversion pathways (Liu et al., 2017; Nsaful et al., 2013). Pyrolysis, liquefaction, and gasification turn biomass into more practical, flexible fuels and high-value-added chemical products that can be used in various applications, while combustion is mainly limited to the generation of thermal energy from biomass. Furthermore, combustion, which entails the oxidation of carbonaceous materials into biomass to release steam, creates polluting and undesirable gaseous compounds with no energy, such as CO2, NOx, and SOx (Okoro et al., 2020). One of the most promising routes for generating green energy is biomass gasification due to its high energy efficiency, lower impact on the environment, and flexibility for the producer gas to be utilized considering its availability. Therefore, in this project, wet biomass is used to convert it into energy; for them, it is necessary to know its conversion's best process and technologies.

THESIS CONTENT AND STRUCTURE

This doctoral thesis deals with an Experimental and Simulation Study of the Hydrothermal Carbonization of Biomasses for the Production of Synthetic Fuels. The experimental and simulations results obtained and their discussion are presented in eight chapters.

Chapter 1 consists of a literature review of the essential elements of the importance of energy consumption on economic development. The main problem is linked to fossil fuels and the need to use alternative renewable energy sources. Among these renewable sources, the advantages of the use of biomass as an energy source are explained. Different technologies or ways of converting biomass into energy are presented. The thermochemical conversion process (hydrothermal carbonization, pyrolysis, gasification, and combustion) is explained. It was explained the thermochemical conversion process (hydrothermal carbonization, pyrolysis, gasification, and combustion). It is also discussed with converting the gasification products to synthetic fuels by Fischer-Tropsch synthesis. Finally, the importance of modeling and simulation to carry out these processes is explained.

Chapter 2 explains the problem statement, the justification, the hypotheses, the objectives, and a global approach of how the project will be carried out, both in the experimental part and in the simulations.

Chapter 3 is dedicated to the development and characterization of the raw biomasses used. This chapter presents the different analytical approaches to biomass characterization during the biomass pretreatment and conversion process. The main methods used to characterize these biomasses were: Analysis of the thermochemical properties such as compositional analysis of biomass (extractible, hemicellulose, cellulose, and lignin), thermogravimetric analysis (TGA/DTG), Heating value analysis (HHV and LHV), proximate and ultimate analysis. Analysis of the microstructure and chemical composition of the biomass was carried out as Fourier transform infrared (FTIR) and Scanning Electron microscopy (SEM). In addition, the thermophysical properties of biomasses such as heat capacity, thermal conductivity, and density are determined.

Chapter 4 presents the experimental setup and the principle of the hydrothermal carbonization (HTC) process to produce hydrochar. An in-depth study of the effect of operating conditions on the HTC process of biomasses is presented, with a particular interest in the properties and yields of hydrochar. This chapter aims to understand better and qualitatively analyze the effect of operating conditions on the HTC process and properties of hydrochar yields.

Chapter 5 explains the experimental studies of pyrolysis and gasification of biomasses and the corresponding hydrochars produced using TGA. The TGA was coupled with an online Micro Gas Chromatograph (TG/μ-GC) to analyze the gas product. In addition, this chapter focuses on the effects of biomass types, operating conditions, emphasizing the air-to-biomass ratio (ABR), temperature, and heating rate during the pyrolysis and gasification process on product distribution. A parametric study of the effect of operation conditions on gas product properties such as cold gas efficiency or process efficiency, gas yield, and heating value was carried out. The quantification of gas evolution as a function of the temperature was performed. Also, the kinetics of the pyrolysis reaction and the gasification of these biomasses were studied.

Chapter 6 focuses on modeling and numerical simulation in CFD. The main objectives of this study were to use the CFD technique to produce a 3D simulation of the HTC stirred reactor for an open-loop control system using COMSOL Multiphysics software: (a) to study hydrodynamics and to determine the biomass distribution inside the reactor, the mixing intensity, and stagnation zones. (b) to determine the heat of the reaction and the type of chemical reaction. c) to combine the kinetics, temperature, mass, and velocity fields to predict the biomass conversion inside the reactor, considering the thermal properties of the AS and the heat of reaction, and the effect of the biomass/water ratio on the heat transfer. These results were compared with the experimental data of the AS HTC. In addition, the design of experiments was studied to present a mathematical model describing the effects of the HTC operation parameters on the final product.

Chapter 7 simulated the hydrothermal carbonization process and the pyrolysis and gasification process of the biomass in Aspen Plus®. The results obtained were validated with experimental data. These results propose a plant for the production of hydrochar combined with pyrolysis and gasification of a continuous system, which can be designed on an industrial scale. In addition, this chapter provided a theoretical study of the production of synthetic fuels from synthesis gas obtained experimentally in Aspen HYSYS® to show the potential of using biomass to produce liquid fuels.

Chapter 8 groups the steps and equations to estimate the energy balance of the HTC process in a global way to identify the most influential parameters in this process. The HTC process is broken down into unit operations with a detailed presentation of the equations used in the energy balance calculations. The results of the energy balance calculations at the laboratory level are presented. Based on these results, a simulation was performed in Aspen plus® a continuous industrial-scale process considering the integration of energy in the HTC process.

The result of the simulation allowed an economic study of the use of hydrochar as an energy source. In general, the HTC process is economically feasible and competitive price of pelletized hydrochar compared to palletized bulk pine wood. This study could encourage the development of HTC plants, therefore, the hydrochar pellet market.

At the end of this manuscript, we present the most salient conclusions of this work and some perspectives regarding future research on biomass conversion into an energy source.

Some of the results of the research work carried out during the development of this thesis are collected in the following papers:

1. **Sangare, D.,** Bostyn, S., Moscosa-Santillan, M., Gökalp, I. (2021). Hydrodynamics, heat transfer and kinetics reaction of CFD modeling of a batch stirred reactor under hydrothermal carbonization conditions. *Energy*, 219, 119635.

2. **Sangare, D.,** Missaoui, A., Bostyn, S., Belandria, V., Moscosa-Santillan, M., Gökalp, I. (2020). Modeling of Agave Salmiana bagasse conversion by hydrothermal carbonization (HTC) for solid fuel combustion using surface response methodology. *aimspress energy*, 8(4), 538-562.

3. **Sangare, D.,** Bostyn, S., Moscosa-Santillan, M., Belandria, V., Gökalp, I. (2021). Quantification and Kinetic Study of the Main Compounds in Biocrude Produced by Hydrothermal Carbonization of Lignocellulosic Biomass. *Bioresource Technology Reports*, xxx

4. **Sangare, D.,** Chartier, A., Bostyn, S., Moscosa-Santillan, M., Gökalp, I. (2021). Kinetic Studies of Hydrothermal Carbonization of Avocado Stone and Analysis of the Polycyclic Aromatic Hydrocarbon Contents in the Hydrochars Produced. (Submitted for publication)

5. **Sangare, D.,** Bostyn, S., Moscosa-Santillan, M., Belandria, V., Gökalp, I. (xxx). Pyro-gasification of Biomass: Use of TGA Coupled to µ-GC for Analysis and Quantification of Gas Evolution (Ready to submit for publication).

6. **Sangare, D.,** Bostyn, S., Moscosa-Santillan, V., Gökalp, I., Belandria, V….., (xxx). Hydrothermal Carbonization of biomass: Laboratory Trials, Energy balance, Process Simulation, Design and Cost Analysis (Ready to submit for publication).

Chapter1 BACKGROUND

1.1. Current energy situation

Energy consumption has increased since the industrial revolution. Global energy demand is increasing rapidly because of population and economic growth, especially in emerging market economies. While accompanied by greater prosperity, rising demand creates new challenges. Global energy consumption has increased by more than 50% (Looney, 2020). **Figure 1-1** shows the increase in primary energy consumption in recent years, and it can be seen that most consumption comes from fossil fuels (oil, coal, and natural gas).

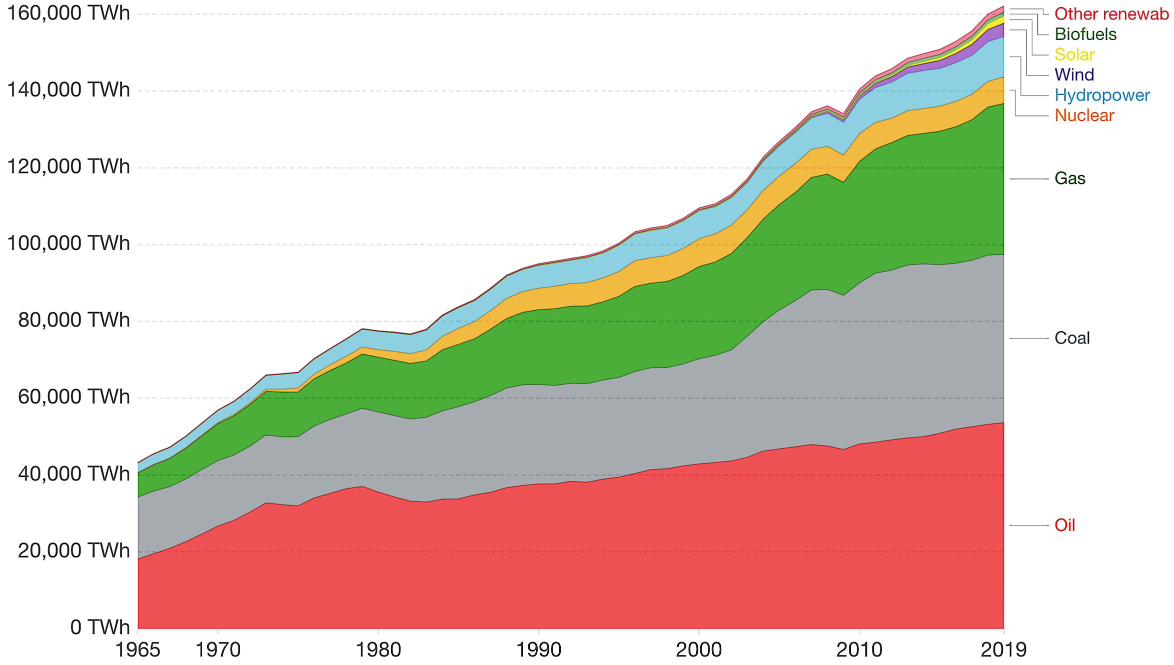

Figure 1-1: Global primary energy consumption by different sources (Looney, 2020)

The majority of consumption comes from fossil fuels (oil, coal, and natural gas). Today, fossil fuels satisfy more than 80% of the world's primary energy consumption (Looney, 2020). However, the percentage of renewable energy contribution to global demand has remained almost constant over the past 20 years.

1.1.1. Fossil fuel

Most of the world's energy comes from fossil fuels (oil, coal, and natural gas). In the nineteenth century, crude oil was chemically transformed into a financially viable fuel supply, resulting in a massive economic boost. The oil industry's advancement paved the way for the growth of other sectors such as shipping, electricity, telephones, and even pharmaceuticals. This impulse also impacted the generation of jobs, helped in the industrialization of the world, raising the quality of life of millions of people. Although fossil fuels were the engine of the world economy, they have caused numerous environmental problems. Their use is directly linked to global warming. As fossil fuels are burned, they release large amounts of gases, known as Greenhouse Gases (GHGs), mainly carbon dioxide. Recent years have seen a significant increase in the levels of GHGs in the atmosphere, mainly carbon dioxide (CO_2), sulfur oxides (SOx), and nitrogen oxides (NOx). These compounds are largely the problem of environmental pollution (Akimoto and Narita, 1994). In fact, in 2019, the CO_2 concentration was about 75 % higher than it was in the mid-1980s (Braun, 2020). **Figure 1-2** shows the main countries that increase GHGs through CO_2 emissions.

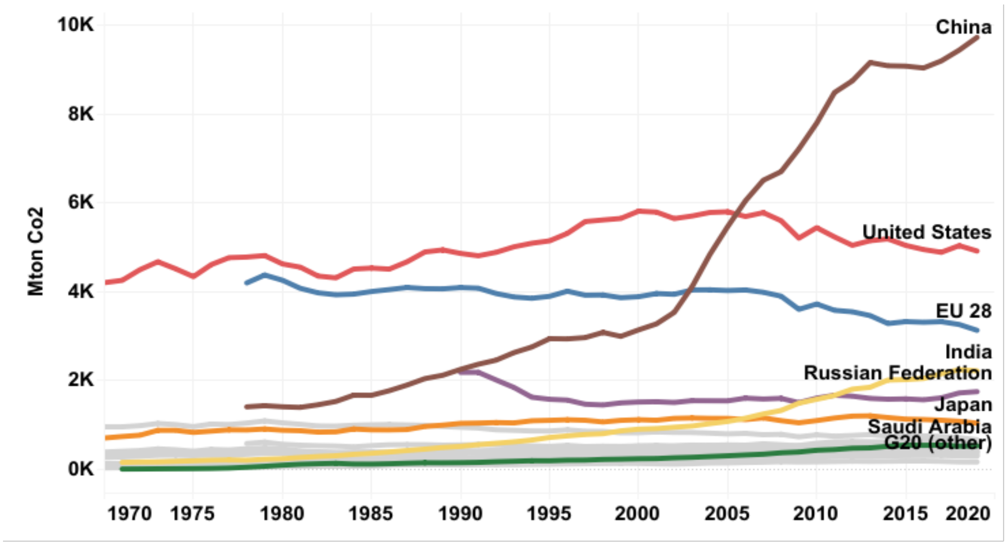

Figure 1-2: CO_2 Emissions from fuel combustion 1970-2019 (Braun, 2020).

The CO_2 emissions are strongly linked to the greenhouse effect. As a result, the United Nations proposed reducing GHGs by the Kyoto Protocol in 1992 and the COP21 in Paris in 2015, an international negotiation to reduce greenhouse gas emissions that affect global warming. The proposed emissions reduction for the period 2008-2012 was 5.2% compared to those reported in 1990. This agreement has been ratified by 166 nations, including Mexico. Human operations are responsible for various greenhouse gas emissions (land use, livestock, transportation, so forth). About 90% of GHGs emissions come from the electricity industry due to fossil fuel combustion (Agency, 2015). The need to reduce CO_2 emissions derived from the use of fossil fuels is imperative, not only because of the future extinction of oil reserves but also because of the irreparable environmental damage that is increasing day by day on our planet. This situation has given rise to a growing interest in the study and development of new technologies for energy production that are sustainable from an environmental, economic, and social point of view. In this sense, renewable energy sources are expected to play a significant role in the future.

1.1.2. Renewable energies

Renewable energies are all those forms of energy obtained or generated from the use of natural and renewable resources. There are many forms of renewable energy. Most of these renewable energies depend in one way or another on sunlight. Wind and hydroelectric powers are the direct results of differential heating of the earth's surface, which leads to air moving about (wind) and precipitation forming as the air is lifted. Biomass energy is stored sunlight contained in plants. Other renewable energies that do not depend on sunlight are geothermal energy, which results from radioactive decay in the crust, combined with the original heat of accreting earth, and tidal energy, which is a conversion of gravitational energy. The energy obtained from these sources can be classified differently, such as solar energy, wind energy, hydropower, geothermal energy, biomass energy, and so forth (Goldemberg and Coelho, 2004). Based on REN21's 2017 report, renewables contributed 19.3% to human beings' global energy consumption. This energy consumption is divided up into 8.9% from traditional biomass, 4.2% as heat energy (modern biomass, geothermal and solar power), 3.9% hydropower and 2.3% is electricity from wind, solar, geothermal, and biomass (REN21, 2017).

The advantages and disadvantages of some common renewable energies are explained below: hydropower, wind power, solar power, geothermal power and biomass.

1.1.2.1. *Hydropower*

Hydropower or water power is based on a simple process, taking advantage of the kinetic energy freed by falling water. It is a process that transforms the kinetic energy of falling or flowing water into electrical or mechanical energy (Egré and Milewski, 2002). Hydropower is a sustainable and environmentally friendly energy source. Most countries favor hydropower production because of its fiscal, technological, and environmental benefits. China, for example, has the world's richest hydropower resources, with a gross theoretical hydropower output of 694GW(Huang and Yan, 2009). Hydropower development is critical for alleviating the energy shortage and emissions caused by China's and other countries' rapid economic growth in the twenty-first century. Hydropower has many benefits over most other forms of renewable or sustainable energy. High reliability, proven technologies, high performance, relatively low operation, and maintenance costs, and the ability to easily respond to load changes are only a few of them. Many hydropower plants are built next to reservoirs, which provide the city with electricity, flood protection, and recreational opportunities. Furthermore, hydropower does not generate waste materials that contribute to acid rain and greenhouse gas emissions (Salame et al., 2015). However, the high initial facility costs; reliance on precipitation (no control over the volume of water available); changes in stream regimens can impact fish, vegetation, and biodiversity by altering stream flows, flow patterns, and temperature; inundation of land and wildlife habitat; and relocation of people living in the reservoir area are only a few of the disadvantages of hydropower (Liu et al., 2013a).

1.1.2.2. *Wind power*

Wind power, also known as wind energy, is a relatively simple technique. Wind power systems convert the kinetic energy of the wind into other forms of energy such as electricity (Bull, 2001). The electricity is pumped into a generator, converted to electrical energy a second time, and then fed into the grid to be transmitted to a power plant. One of the fastest-growing clean energy technology is wind power. Globally, use is increasing, partly due to lower prices (Salame et al., 2015). Wind energy, like all alternative energy sources, has several advantages. It reduces greenhouse gas emissions and lowers power prices by using wind turbines, which provide energy and electricity when moved by the wind (Jacobson and Delucchi, 2011). All required for the turbines to operate is wind, which is simply air in motion, and the air is found everywhere. Wind represents a cheap, abundant, and renewable energy source that would not depreciate if we use it. It can make the most of this opportunity, and it will only serve to make our planet a safer and healthier environment (Salame et al., 2015). Wind power has been used for thousands of years, but it has only recently been a major industrial electricity source. Many of the world's windiest regions, such as northern Canada and Russia, are situated far from urban centres, where transmission and repair costs will be extremely expensive. Wind power's erratic and unreliable existence would restrict its contribution to any area unless large-scale energy storage or intercontinental transmission were possible. Environmental limits, such as forests and conservation areas, and general approval, restrict the placement of wind turbines. Wind turbines are not desirable, and they've caused concerns about pollution, radio and TV signal interference, and the killing or messing with migratory birds (Khatoniar, 2020; Salame et al., 2015).

1.1.2.3. *Solar power*

Solar power or solar energy is the most abundant renewable resource on our planet. Despite its abundance, only 0.04% of primary human energy comes directly from solar sources. The cost of using a photovoltaic (PV) panel is the main reason for the non-use of this energy source. Recently, organic materials have been intensively studied for photovoltaic applications to generate energy from organic photovoltaic (OPV) materials. The use of OPVs can considerably decrease the cost of photovoltaic technologies (Moulé, 2010). Solar energy is a true renewable resource. Most of planet earth has the ability to collect some amount of solar power. Solar energy is non-polluting, does not create greenhouse gases, such as oil-based energy does, nor does it create waste that must be stored, such as nuclear energy. It is also far quieter to create and harness, drastically reducing the noise pollution required converting energy to a useful form. Residential size solar energy systems also have very little impact on the surrounding environment, in contrast with other renewable energy sources such as wind power and hydropower (Pogson et al., 2013). Solar panels have no moving parts and need only routine cleaning for repair. Maintenance and replacement costs are very low after the initial costs of assembling the panels, so there are no moving components to crack and restore. It's also worth noting that photovoltaic solar panels are the only option that can meet current demand (Pogson et al., 2013; Salame et al., 2015). The main disadvantage of solar energy is its high cost. Despite technological advances, solar panels continue to be expensive. Even if the panels' expense is not taken into account, the device used to store and use the energy can be very expensive (Fitzgerald et al., 2015).

1.1.2.4. *Geothermal power*

Geothermal power is an energy used to produce electricity. Dry steam power plants, flash steam power plants and binary cycle power plants are operating technologies. Geothermal power generation is currently used in 26 countries (El Bassam et al., 2013). Geothermal energy is produced by storing heat underground and releasing energy as heat rises to the surface. This heat is harnessed and used to transform a steam engine to generate electricity as it spontaneously produces hot water or steam. Geothermal energy, or energy derived from heat from inside the Earth, has many different uses. These uses can be grouped into three categories: heating systems (and direct use), electricity generation, and use in geothermal heat pumps. In addition to these practical uses of geothermal energy, many other things make geothermal energy a valuable energy resource. Since the Earth's core continuously produces heat with the radioactive decay of potassium and uranium, geothermal energy becomes a renewable, abundant, and reliable energy source. A geothermal power plant uses no fuel, making it sustainable and environmentally safe. Geothermal power operations produce few emissions. These operations do not pollute the air or contribute to global warming (Edenhofer et al., 2011). The disadvantages of geothermal energy power plants are their location since it is difficult to locate suitable sites for these power plants. The number of places where geothermal power plants can be built is extremely small. The site must have hot rocks that can be drilled quickly. There is also the question of sustainability and the scarcity of appropriate geothermal power plant locations. Geothermal energy is typically localized along plate margins, where volcanoes are concentrated, and earthquakes are most common (Salame et al., 2015). Geothermal power plants occasionally run out of steam for a few months, which prevents the plant from producing electricity. Compared to other energy sources, geothermal energy produces a smaller amount of electricity. It is difficult to transport geothermal energy. Therefore, geothermal power plants can only supply electricity to the regions in their immediate vicinity. Although the steam itself may be clean and pure, it may contain toxic materials such as hydrogen sulfide, mercury, ammonia, and arsenic that have been released from underground. Finally, geothermal energy can cause earthquakes (Gupta and Roy, 2006).

1.1.2.5. *Bioenergy*

Bioenergy is energy obtained from biomass. Any organic matter that has absorbed sunlight and retained it as chemical energy is known as biomass. Wood, agricultural, and poultry residues; short-rotation forest plantations; energy crops; the renewable components of urban solid waste; and other organic waste sources will all be used to produce bioenergy. This material may be used to generate electricity or heat directly via a variety of processes. They can also be used to make liquid, gaseous, or solid fuels. Bioenergy systems come in a wide variety of forms, with varying degrees of technological sophistication. In both centralized and decentralized environments, bioenergy technologies are being used. The most popular existing applications in developed countries are conventional biomass uses (primarily for cooking and heating). Bioenergy projects are typically dependent on the availability of local and regional fuel supplies, but recent trends indicate that solid biomass and liquid biofuels are rapidly traded globally (Edenhofer et al., 2011). Bioenergy can minimize greenhouse gas emissions, reduce reliance on oil, and benefit local agriculture and forest product sectors. Agro-industrial wastes, urban wastes, and other biomass feedstocks are the most common biomass feedstocks for energy production. Corn grain (for ethanol) and soybeans are now the most widely used feedstocks for biomass fuels (biodiesel). The planting and use of specific energy crops, such as fast-growing trees and grasses, as well as algae, are among the long-term plans. These feedstocks can be grown sustainably on land that does not support intensive food crops. Another advantage of biomass is its ability to be converted into a range of valuable fuels in solid, liquid, and gaseous forms and chemical products (Demirbas, 2001a; Kumari and Singh, 2018; Salame et al., 2015).

- **Biofuel:** Converting biomass into liquid fuels for transportation.
- **Biopower**: Burning biomass directly (combustion), or converting it into gaseous or liquid fuels that burn more efficiently, to generate electricity.
- **Bioproducts**: Converting biomass into chemicals for making plastics and other products that typically are made from petroleum.

Despite its many advantages, biomass can be harmful to the environment if it is not used for biomass energy production from the following sources:

- Energy crops that do not compete for land with food crops.
- Agro-industrial waste, sustainably grown timber, and tree residues
- Dispose of urban and agricultural wastes in a safe and environmentally friendly manner.

Aside from all the advantages of bioenergy, there are several disadvantages. Biomass energy, for example, has lower energy content than fossil fuels. Growing and processing the biomass feedstock, transporting the feedstock to the power plant, and burning or gasifying the feedstock can contribute significantly to global warming emissions, even if less than fossil fuels. For all forms of biomass, emissions from transport and combustion are about equal. Therefore, it is important to distinguish between biomass resources that are beneficial in reducing net carbon emissions, those that have an ambiguous impact, and those that increase net emissions (Spath and Mann, 2004). Another environmental impact of bioenergy is associated with land erosion due to the removal of green vegetation (Pimentel et al., 1995).

1.2. Biomass, characteristics and their relationship with energy production

What is biomass? The answer depends on who is asking the question.

- From an ecological perspective, the amount of living matter in a given habitat is expressed either as the weight of organisms per unit area or the volume of organisms per unit volume of habitat (Dayton and Foust, 2019).
- From an energy perspective, biomass can be defined as "any organic substance of plant or animal can be converted into energy (McKendry, 2002)."

If we consider biomass as an energy source, it can be defined as organic matter that captures sunlight to convert CO_2 and water through photosynthesis into stored chemical energy (carbohydrates) for plant growth. The CO_2 converted to fixed carbon in biomass is indiscriminate of renewable or fossil-derived sources, but biomass is considered a renewable resource because it is grown, used, and regrown on a comparatively short time scale in large quantities. Biomass also includes plant or animal matter that can be converted into fibers or other industrial chemicals, including biofuels (McKendry, 2002). Energy in biomass is one of the energies very commonly used throughout the world. Unfortunately, the most popular is the burning of trees for cooking and warmth. This process releases significant amounts of carbon dioxide gases into the atmosphere and is a significant contributor to unhealthy air in many areas. The energy available in biomass by combustion is around 8-20 MJ/kg, a relatively low value compared to coal which is 23-30 MJ/kg(Demirbas, 1997). Biomass can be used directly (e.g. in the combustion of wood for heating and cooking); or indirectly, by converting it into a liquid or gaseous fuel (e.g. bioethanol from alcoholic fermentation, synthesis gas from thermochemical conversion) etc. (Gropelli and Giampaoli, 2001). According to the International Energy Agency (IEA), In 2017, biomass contributes to about 10% of global energy demand (IEA, 2018), especially in Africa. Solid biomass is the largest renewable energy source globally, owing to the existence of traditional biomass in developing countries. One of the reasons why biomass has become so important is its high availability; it is estimated at approximately 220 billion tons of dry biomass per year (López González, 2013).

1.2.1. Biomass structure and composition

Bioenergy or biofuels are usually classified as follows:

- First-generation: First-generation bioenergy include ethanol and biodiesel and are directly related to a biomass that is more than often edible.
- Second-generation: Second-generation bioenergy are defined as fuels produced from a wide array of different feedstocks, especially but not limited to non-edible lignocellulosic biomass.

- Third-generation: The most accepted definition for third-generation biofuels is fuels that would be produced from algal biomass, which has a very distinctive growth yield as compared with classical lignocellulosic biomass (Brennan and Owende, 2010).

The second-generation bioenergy is sourced from lignocellulosic biomass. Biomass used for the production of second-generation bioenergy is usually separated into three categories: homogeneous, such as white wood chips with a price value; quasi-homogeneous, such as agricultural and forest residues; and non-homogeneous, including low-value feedstock as municipal solid wastes as reported by Lavoie et al.(Lavoie et al., 2011). Lignocellulosic biomass is a significant component of biomass. Cellulose, hemicellulose, and lignin are the main constituents of lignocellulosic biomass, with small amounts of acetyl groups, minerals, and phenolic substituents. The proportions are as follows: 20-55% cellulose, 16-85% hemicellulose, 10-40% lignin, and 1-3% of others (Howard et al., 2004). Depending on the type of lignocellulosic biomass, these polymers are organized in complex non-uniform three-dimensional structures to different degrees and varying relative compositions. Unlike carbohydrates or starch, lignocellulose is not easily digestible by humans. For example, we can eat rice, which is a carbohydrate, but we cannot digest straw, which is lignocellulose. The structure of lignocellulosic material is shown in **Figure 1-3.**

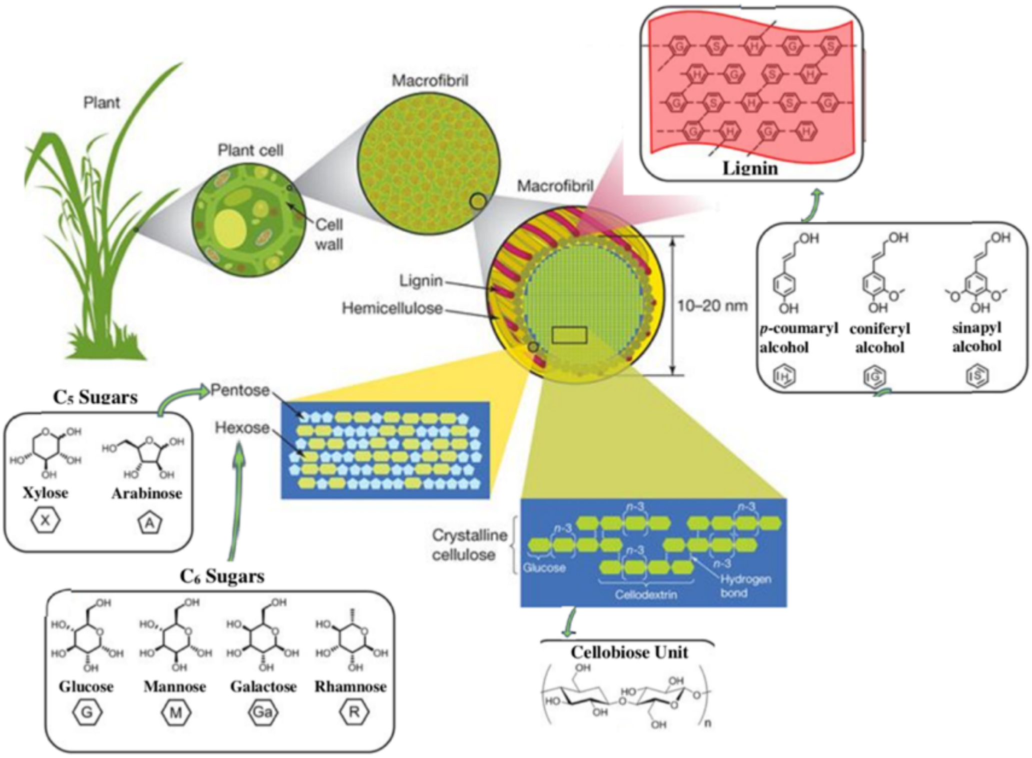

Figure 1-3: The main components and structure of lignocellulose (*Isikgor and Becer, 2015*; *Rubin, 2008*)

The main structural components of biomass are three polymers: cellulose, hemicellulose, and lignin. Cellulose and hemicellulose are linked to the lignin component through covalent bonds and hydrogen bridges, making the structure robust and resistant to any treatment. The major component of lignocellulosic biomass is cellulose. Unlike glucose in other glucan polymers, the repeating unit of the cellulose chain is the disaccharide cellobiose. Its structure consists of extensive intramolecular and intermolecular hydrogen bonding networks, which tightly bind the glucose units. The conversion of cellulose into fuels and high added value chemical products is of paramount importance (Somerville et al., 2010; Zhou et al., 2011). Hemicellulose is the second most abundant polymer.

The heteropolymers of hemicellulose are composed of sugar of 5- and 6-carbon monosaccharide units; pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and acetylated sugars. Unlike cellulose, hemicellulose has a random and amorphous structure, which is composed of several heteropolymers, including xylan, galactomannan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan (**Figure 1-3**) (Knauf and Moniruzzaman, 2004; Scheller and Ulvskov, 2010a). Lignin is an aromatic polymer with a rather complex, highly branched, and amorphous three-dimensional phenylpropanoid unit structure, a cross-linked polymer with molecular masses above 10,000 u. It is relatively hydrophobic and rich in aromatic subunits. The degree of polymerization is difficult to measure since the material is heterogeneous. It functions as the cellular glue, which provides compressive strength to the plant tissue and the individual fibers, stiffness to the cell wall, and resistance against insects and pathogens. The oxidative coupling of three different phenylpropane building blocks, that is, monolignols: p-coumarin alcohol, coniferyl alcohol, and sinapyl alcohol, forms the structure of lignin. The corresponding phenylpropanoid monomeric units in the lignin polymer are identified as p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively (**Figure 1-3) (**Abdel-Hamid et al., 2013**;** López González, 2013**;** Rubin, 2008**).**

1.2.1.1. *Cellulose*

The cellulose is a polysaccharide composed exclusively of glucose molecules; it is therefore a homopolysaccharide (composed of a single type of monosaccharide β-glucose from hundreds to several thousand units). **Figure 1-4** shows the primary structure of cellulose.

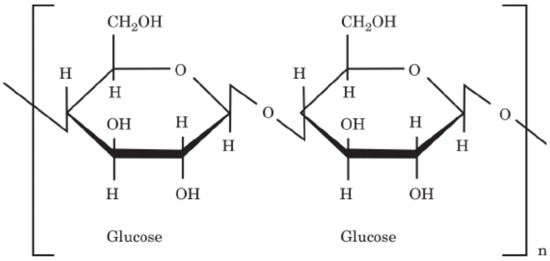

Figure 1-4: The primary structure of cellulose.

1.2.1.2. *Hemicellulose*

Hemicelluloses are heteropolysaccharides (polysaccharides composed of more than one type of monomer). Among these monosaccharides, the following stand out glucose, pentose, hexose. They form branched chains with a lower degree of polymerization than cellulose. Besides, hydrogen bonds are less effective, making hemicelluloses polysaccharides more accessible to attack by chemical reagents. Xylan is used as a representative compound for hemicellulose because it is one of the main components of hemicellulose and has been shown to have similar thermal behavior (Yang et al., 2006c).

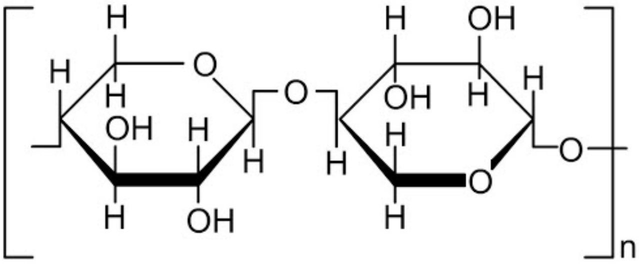

Figure 1-5: The structure of xylan (Hemicellulose).

1.2.1.3. *Lignin*

Lignin is an insoluble aromatic polymer of high molecular weight, which has complex and variable three-dimensional structures. For this reason, it is difficult to describe a definite structure of lignin. However, lignin is essentially composed of many methoxylated benzene derivatives (phenylpropanoid alcohols, also called monolignols), especially the coniferyl, sinapyl, and coumaryl alcohols (López González, 2013). **Figure 1-6** shows the structure of the three lignin constituents. The proportions of these three differ among different plants. The way in which lignin are synthesized in the plant is still unresolved, despite many decades of research

(David Moore et al., 2011). For several years, the theory that monolignols are randomly assembled to create a complex polymer that is strongly cross-linked in three dimensions reigned supreme, but it is now giving way to the idea that lignin has unique sequences of monolignols that fit the lignin to various roles in the plant cell wall, and that only a few native lignin primary structures exist. These three polymers make up the lignocellulosic materials. The main sources of lignocellulosic biomass are agro-industrial waste such as agave bagasse, avocado stone, cacao shell, and so forth.

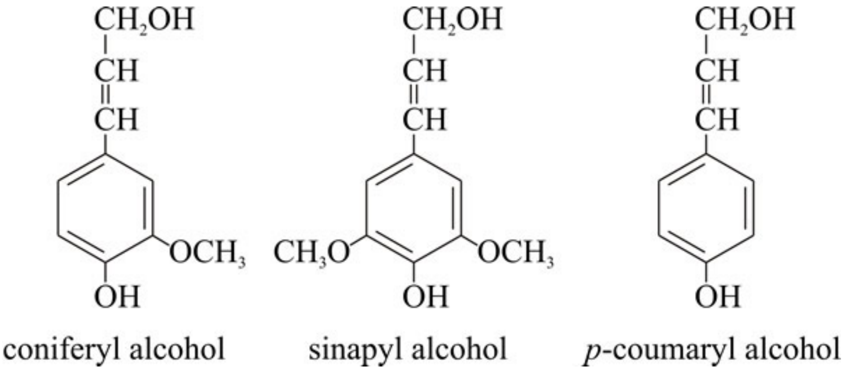

Figure 1-6: Chemical structures used to construct the lignin polymer.

1.2.2. Sources of biomass

Biomass is a key renewable energy resource that includes plant and animal material, such as wood from forests, material left over from agricultural and forestry processes, and organic industrial, human, and animal wastes. The major biomass sources currently used are sugarcane and corn to produce bioethanol and rapeseed for biodiesel production. Other sources are also used, such as sunflower seeds, jatropha curcas, soybean, peanuts, coconut, and palm oil for biodiesel production, wheat, sugar beet, sweet sorghum, and cassava for bioethanol. In Mexico, the major biomass source is agave bagasse, cacao shell, avocado stone, and so forth.

1.2.2.1. *Agave bagasse*

Agave bagasse is the main solid waste generated by the tequila and mezcal industries in Mexico. The production of distilled alcoholic beverages using agave has been a tradition since the XVII century (Marín et al., 2007). Depending on the production region, these beverages have different names, the most popular being tequila and mezcal. This last one is made from over 30 agave species, but the commonly used ones are *Agave angustifolia, karwinskii, Rodacantha, Potatorum, and Agave salmiana*. The production of mezcal begins with the harvesting of agave plants that are more than six years old. After removing the leaves and roots, agave heads "piñas" are obtained. These piñas rich in fructans are cooked in traditional broilers or autoclaves to hydrolyze the fructans and release fermentable sugars, mainly fructose. Once the heat treatment is completed, a syrup consisting mainly of fructose, glucose, xylose, and maltose is obtained. This syrup is transformed into mezcal, a large amount of waste is generated. **Figure 3** shows the agave harvesting stage until bagasse is generated.

Figure 1-7: *Agave salmiana* plant, piñas and bagasse

San Luis Potosi's state produces about 720 000 liters/year of mezcal (Baena González, 2005) from *Agave salmiana* bagasse. To produce 1 liter of mezcal, 15 kg of wet bagasse (moisture content equal to 70%) are produced (Chávez-Guerrero and Hinojosa, 2010). It is estimated that this mezcal industry generates more than 141 tons of bagasse monthly (Martinez Gutierrez et al., 2013), which is an environmental concern due to its considerable production volume.

Agave salmiana bagasse is lignocellulosic biomass that has been considered a potential feedstock for different industrial uses in the lignocellulosic biorefinery concept framework.

The *Agave salmiana* bagasse is a lignocellulosic material composed of three main fractions, cellulose (40.7% w/w), hemicellulose (43.8% w/w), lignin insoluble (14.2% w/w), and extractible (1.4% w/w). In many of the mezcal-producing states, such as San Luis Potosi, this bagasse has no benefit for the mezcal producers. These wastes are given to the community for fodder. Sometimes the air dries it and burns it.

There are different studies on the valorization of bagasse. For example, Iñiguez-Covarrubias et al. (Iñiguez-Covarrubias et al., 2001) studied the use of bagasse as feed for ruminants, however this application was limited by the presence of lignin, the difficulty of animals to digest bagasse. The bagasse has been used to produce paper, the authors claim that this application is feasible, however a low mechanical resistance paper is found (Idarraga et al., 1999). *Agave salmiana* bagasse was also studied as biosorbents precursor by Velazquez-Jimenez et al.

(Velazquez-Jimenez et al., 2013)The authors show that this application is efficient to remove Cd (II), Pb (II) and Zn (II) from water. However, these studies were not carried out in the practice; this waste has no practical application today. There are also studies on the use of bagasse as a renewable energy source, through the combustion of bagasse (Chávez-Guerrero and Hinojosa, 2010), this application is limited by the high moisture content (70%) of bagasse. Due to a large amount of waste generated monthly and the lack of utilization, it can be used as an energy source.

1.2.2.2. *Cacao shell*

Cocoa or Cacao, a native to the Americas, was a valuable crop in the earliest South American cultures. The term cocoa originated from the Nahuatl word “cacahuatl”. Many believe that the plant first grew in the Amazon and upper Orinoco basins, but the Mayans and the Aztecs eventually developed techniques to cultivate cocoa successfully. For these cultures, the plant was regarded as a token of prosperity, and its beans were used as currency. Cacao beans are the primary component of chocolate production. Cacao beans are grown in tropical areas along the Equator, where the climate is ideal for growing cocoa trees. Côte d'Ivoire, Ghana, Indonesia, Nigeria, Ecuador, Cameroon, and Brazil are the world's top cocoa bean producers, accounting for nearly 90% of global production as shown in **Figure 1-8**.

The four West African countries of Cote d'Ivoire, Ghana, Nigeria, and Cameroon produce roughly 70% of the world's cocoa beans (Shahbandeh, 2021). The cacao shell is removed together with the germ before or after roasting and the broken fragments of cotyledon, called nibs, free of the shell, are used in chocolate production (Wood, 2008). Cacao shells are considered an agro-industrial waste during the production of chocolate. This waste is of low commercial value (González-Alejo et al., 2019). The fruit of the cocoa tree is known as cocoa (Theobroma cacao L.). Its seeds, also known as cacao beans, are made up of an outer layer called a testa surrounding two cotyledons and a small germ (**Figure 1-9**) (Okiyama et al., 2017). It is estimated that cocoa shell production is very significant, since it represents 12–20% (w/w) of the cocoa seed (Okiyama et al., 2017). Considering the world production of cocoa beans, the world generation of this waste can be calculated at approximately 1000 thousand tons, which is a substantial amount. However, as we consider the shelling waste, this amount may be much higher if we consider that the germ and perhaps a portion of the nibs that are attached to the shell are extracted along with the shell (Okiyama et al., 2017). Owing to the lack of natural resources and significant environmental issues, the importance of agricultural by-products such as cocoa shells has recently gained increased interest.

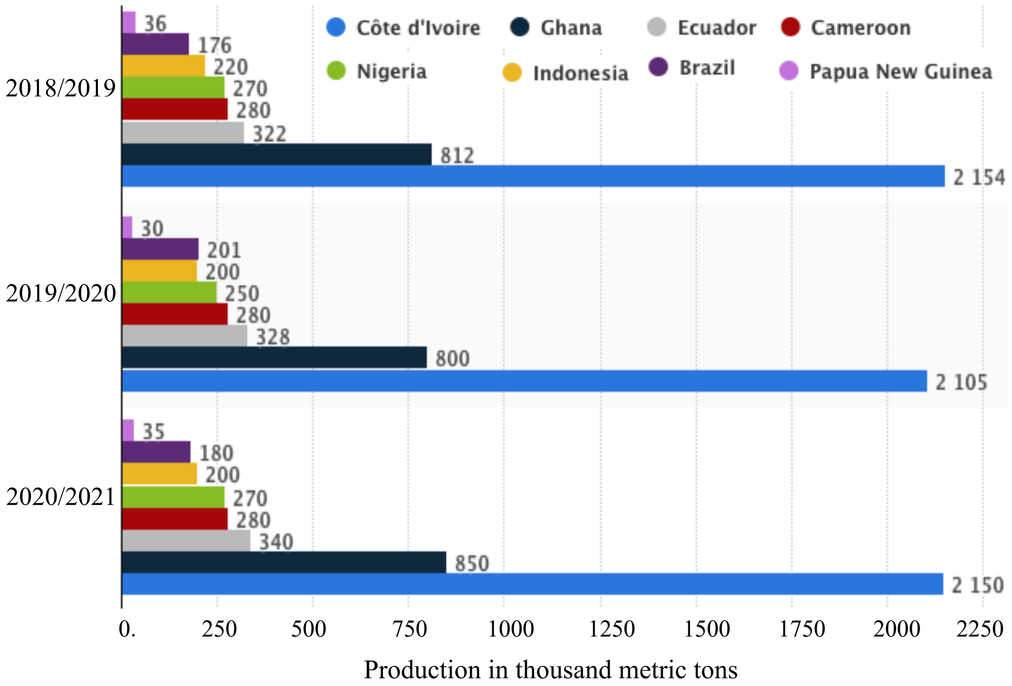

Figure 1-8: Global cacao bean production in 2018/19 to 2020/21 (Shahbandeh, 2021).

Many researchers recommend that these by-products be used in applications such as agricultural additives or other high-value-added products (Jahurul et al., 2013; Yusof et al., 2016). As a result, further research into using these ingredients as additives in high-nutrient foods or supplements is gaining traction, owing to their nutritional properties and, secondarily, that their recovery can be cost-effective (Murthy and Naidu, 2012).

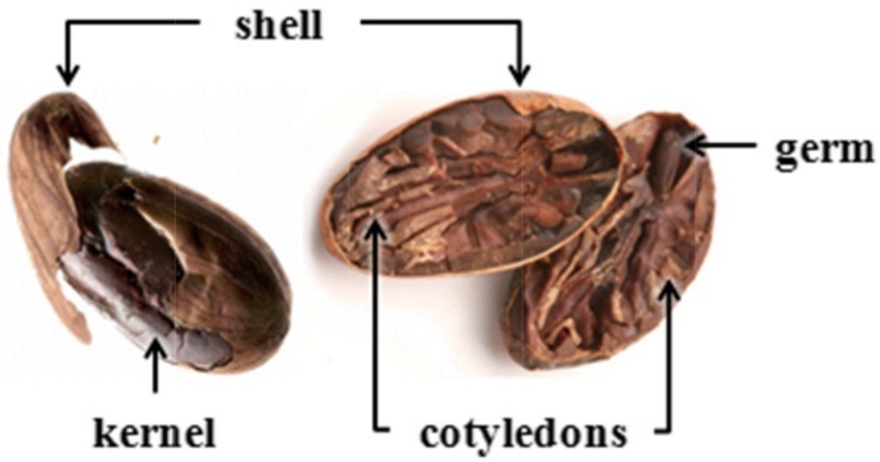

Figure 1-9: Parts of cocoa beans (*Okiyama et al., 2017*)) .

Since it is a green substance that contains fascinating compounds from a nutritional standpoint, such as phenolic compounds, fibers, and an actual fat content with a very attractive lipid profile, very close to that of cocoa butter, several studies and patents have recently been established that suggest alternative uses for this material. However, certain substances, such as mycotoxins and theobromine, should be closely analyzed since they are potentially harmful (Adamafio, 2013; Copetti et al., 2010; Okiyama et al., 2017).

1.2.2.3. *Avocado stone*

Mexico is the top avocado-producing country globally, producing 45% (1.89 million tons) of the total production in 2016 (FAO, 2017). Avocado in Mexico is not just a relationship between a fruit and its original place, but it is connected to its history and culture; it is connected to how Mexicans understand the lifestyle. Michoacán is Mexico's leader in avocado production and accounts for 80% of total Mexican avocado production (SAGARPA, 2018). There are different varieties of avocado in Mexico (*Hass, Criollo, Bacon, Fuerte, Pinkerton, Gwen*, so forth). The Hass variety is the most popular and most produced in Michoacán, with more than 85% of the total production annually (Oviedo and López). Avocados are often consumed fresh, but the processing industry for this product is increasing because of the increase in the product's production and seasonality. Products derived from avocados include ice cream, drinks, and, guacamole being the most marketed product (Perea-Moreno et al., 2016; Ramtahal et al., 2007). There are also examples of the production of avocado oil, which is of similar quality to olive oil (Salgado et al., 2008). Avocado processing generates a large amount of waste, particularly the skin and seed or stone. The stone represents 15.0–16.0% of the fruit weight (García-Fajardo et al., 1999; Rodríguez-Sánchez et al., 2013). In Mexico, the top producing country, 5% of fruit produced in 2008 was destined for processing (mostly for guacamole), producing 20,000 tons of waste (Perea-Moreno et al., 2016). Some pharmacological properties are attributed to avocado stone because of the presence of fatty acids (Werman and Neeman, 1987), steroids (Lozano et al., 1993), and polyphenols, which showed that it has high polyphenol content (Segovia Gómez et al., 2013). Although these subproducts may draw commercial interest in the cosmetic industry, they are discarded because they bring pollution issues in landfills (Schaffer et al., 2013) and, to date, have been valued for use as compost (González-Fernández et al., 2015).

It can be observed that there are several studies on these biomasses in the literature. However, many of these studies are limited. Also, there is no scientific study available to evaluate the technical feasibility of using these biomasses as a bioenergy source. The present research consists of studying the conversion of these biomasses into fuels and chemical products with high added value.

1.3. Biomass conversion technologies

Bioenergy development requires multidisciplinary competencies, from chemistry and biology to process development, agriculture, policymaking, and more. Due to the pervasiveness of energy issues in the world today, policymakers must be actively involved in the decision-making process to select strategies for the development of the next generation of bioenergy (Pandey et al., 2015). The conversion technologies for bioenergy production are divided into physicochemical, thermochemical, and biochemical treatment. The physicochemical approach serves mainly as pretreatment and does not involve any chemical transformation of the matter. The thermochemical and biochemical conversion of biomass changes its chemical structure by treating heat, chemicals, catalysts, or combinations (Basu, 2010; Zinoviev et al., 2010). The most appropriate technology for converting biomass depends fundamentally on its compositions, moisture content, and of course, on the desired final product (Martínez, 2014). The bioenergy obtained from the biochemical process can be liquid fuels or gases, while the bioenergy obtained from the thermochemical process can be solids, liquids, or gases. The fuel liquid obtained can be used directly or mixed with existing liquid fuels. Solid and gaseous fuels can be used to produce electrical power from purpose-designed direct or indirect power plants.

1.3.1. Biochemical conversion process

The biochemical conversion process includes biological and chemical conversion. The biological conversion of biomass involves bacteria, microorganisms, and enzymes to break down biomass into gaseous or liquid fuels, such as biogas or bioethanol. The most popular biological technologies are anaerobic digestion and fermentation (Ortega, 2014). Anaerobic digestion is a series of chemical reactions during which organic material is decomposed through the metabolic pathways of naturally occurring microorganisms in an oxygen-depleted environment to produce biogas. Biomass wastes can also yield liquid fuels, such as cellulosic ethanol for alcoholic fermentation, which can be used to replace petroleum-based fuels.

Chemical conversion involves the use of chemical agents to convert biomass into liquid fuels. Transesterification is the most common form of chemical-based conversion (Boz et al., 2009). Transesterification is a chemical reaction through which fatty acids from oils (triglycerides) are bonded to alcohol. This process reduces the viscosity of the fatty acids and makes them combustible. Biodiesel is a typical product of transesterification, as are glycerin and soaps. Almost any bio-oil (such as soybean oil), animal fat or tallow, or tree oil can be converted into biodiesel.

1.3.2. Thermochemical conversion process

Thermochemical conversion involves the use of heat as the primary mechanism for converting biomass into another form. This method encompasses everything from biomass combustion, one of the most basic forms of human energy production, to experimental methods for producing liquid transportation fuels and chemicals. Pyrolysis, torrefaction, combustion, gasification, and hydrothermal carbonization are examples of thermochemical conversion technologies (Panwar et al., 2012). The different thermochemical routes of conversion of biomass and their products are shown in **Figure 1-10**.

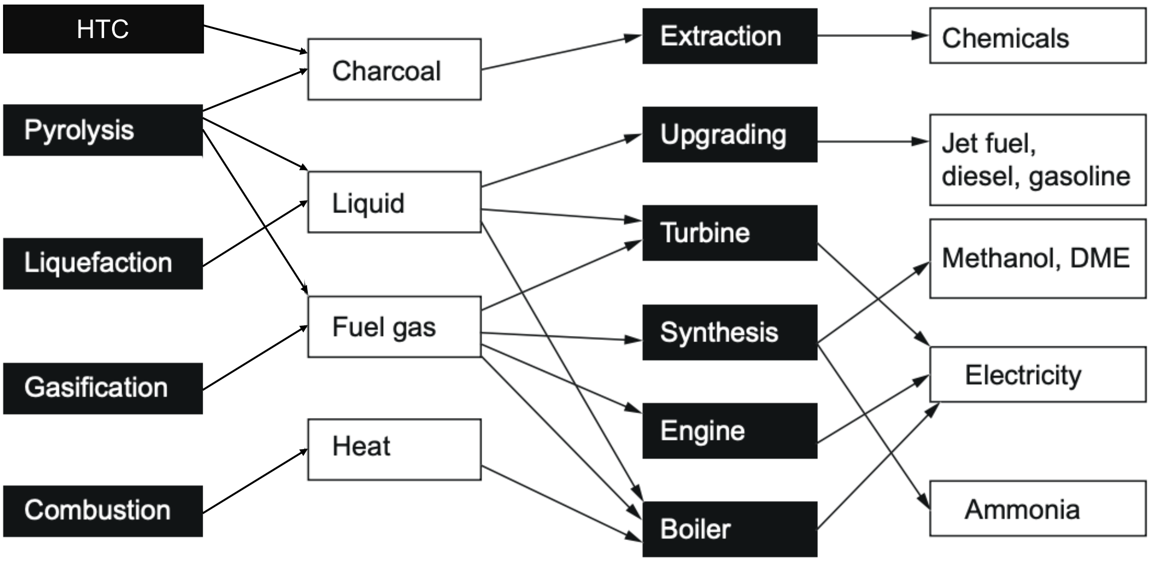

Figure 1-10: Thermochemical conversion processes and end products (Pandey et al., 2015).

Direct combustion of biomass produces heat for steam generation, and thus electricity can be produced, as seen in **Figure 1-10**. Gasification also provides a fuel gas that can be combusted to generate heat or used in an engine or turbine for electricity generation. The pyrolysis and liquefaction produce a liquid fuel used to replace fuel oil in any static heating or electricity generation application. Pyrolysis and hydrothermal carbonization (HTC) produce charcoal, which can be used as a feedstock for combustion or all of the above processes. Charcoal also has other uses.

1.3.2.1. *Pyrolysis*

Pyrolysis is the thermochemical process that converts biomass by the action of heat and in the absence of oxygen (Balat et al., 2009). The pyrolysis of biomass is produced through complex chemical reactions as well as mass and heat transfer processes, which make it difficult to predict the course of pyrolysis, because many variables, such as operating conditions or the type of biomass, are influenced (Melgar et al., 2008; Titirici and Antonietti, 2010). Pyrolysis of the three components of lignocellulosic biomass (cellulose, hemicellulose, and lignin) occurs as follows: Up to 200°C, moisture loss, and some volatile compounds occur. The hemicellulose pyrolysis starts at 220°C, and its maximum temperature value is 260 °C. In this range, the less stable biomass constituents decompose with the release of water and carbon oxides, forming alcohols and acids. Cellulose pyrolysis focuses on a temperature range of 315 to 390 °C and forms high molecular weight carbonaceous products (tars and coke). Pyrolysis itself begins at 275°C and is almost complete at 450°C, although some molecules of the formed products may rupture (cracking) at higher temperatures. From the ambient temperature to 700 °C, only ~40 %(w/w) of lignin is lost at a considerably slow rate (<0.15 %/°C). It might be attributed to the slow carbonization of lignin, and carbon could be the main product; lignin is mainly responsible for char production (Demirbas, 2010; Yang et al., 2006c). The main products of pyrolysis are liquid, solid, and gases, depending on the operating condition. The liquid product (bio-oil) is a heterogeneous mixture characterized by high oxygen content and alkalinity, which can be upgraded to fuels or chemicals. The solid product (biochar) can be used as a fuel or soil repairer. The pyrolysis mechanism is essential in all thermochemical biomass conversion processes because it determines the kinetics of the chemical reaction and, as a result, the reactor configuration and product structure, and properties (Balat et al., 2009; Sensöz and Can, 2002).

Pyrolysis is differentiated between fast and slow pyrolyzes. Fast pyrolysis, with residence times on the order of seconds to minutes, is optimized for pyrolysis bio-oil production, whereas slow pyrolysis, with residence times ranging from minutes to days, is optimized for the production of biochar (Babu, 2008; Tanger et al., 2013). The challenge of current research in engineering is to optimize process variables (temperature, heating rate, particle size, organic and inorganic matter, oxidation environment, residence time, son on) and product upgrading via catalytic and thermal processes to produce infrastructure-compatible liquid transportation fuels (Balat et al., 2009; Demirbas, 2007; Sensöz and Can, 2002).

1.3.2.1.1. *Pyrolysis mechanism*

Biomass pyrolysis starts with drying; once this stage is completed, the biomass undergoes devolatilization by breaking organic chemical bonds and vaporizing light gases and tars and char formation. During primary pyrolysis, weaker linkages are broken, producing molecular fragments during depolymerization (Solomon et al., 1993). These fragments abstract hydrogen from the hydrocarbon aromatic and aliphatic components and are subsequently released tar to the gas phase if they are small enough to vaporize and be transported out of the char particle (Solomon et al., 1992). In addition, permanent gases (CO_2, H_2, CO, CH_4, among others) are released during char condensation due to the decomposition of the functional groups. Tar species may be converted to char, light gas, and soot through secondary actions (Migliavacca et al., 2005). The depolymerization reactions compete with condensation and cross-linking reactions, responsible for tar formation with more significant aromatic sites. Condensation is assumed to act on species that are still connected to the fuel matrix, whereas cross-linking disconnects the bonds with the biomass matrix. During condensation and cross-linking reactions, aliphatic chains form light gases and aliphatic compounds. Char is formed from the unreleased or recondensed fragments (Trubetskaya, 2016).

1.3.2.1.2. *Effect of operating conditions on biomass pyrolysis*

Biomass pyrolysis operating conditions, such as temperature, heating rate, and residence time, affect yield and product composition. High heating rates, up to 10 °C/s, at temperatures of 650 °C and rapid cooling, favor the formation of liquid products and minimize char and gas formation; these process conditions are often referred to as "flash pyrolysis." High heating rates at temperatures of 650 °C tend to favor the formation of gaseous products at the expense of liquids. Slow heating rates coupled with low maximum temperatures maximize char yield (Horne and Williams, 1996; Onay and Kockar, 2003). Slow heating over long periods leads to maximum char yields with moderate amounts of tar (liquid), whereas high yields of liquids can be obtained with high heating rates and short reaction times (Onay and Kockar, 2003).

Heat treatment temperature

Figure 1-11 shows the mass loss of the main components in lignocellulosic biomass as a function of pyrolysis temperature. The decomposition temperature of all biomasses is in the range of the decomposition temperature of these three constituents. As can be seen in **Figure**

1-11, the TGA curve of rice husks lies in the TGA curves of the three biomass constituents. In this case, rice husk was mainly composed of hemicellulose, cellulose, and lignin. Lignin is challenging to break down compared to cellulose and hemicellulose. Therefore, its decomposition occurs slowly over the entire temperature range, as shown in **Figure 1-11**..

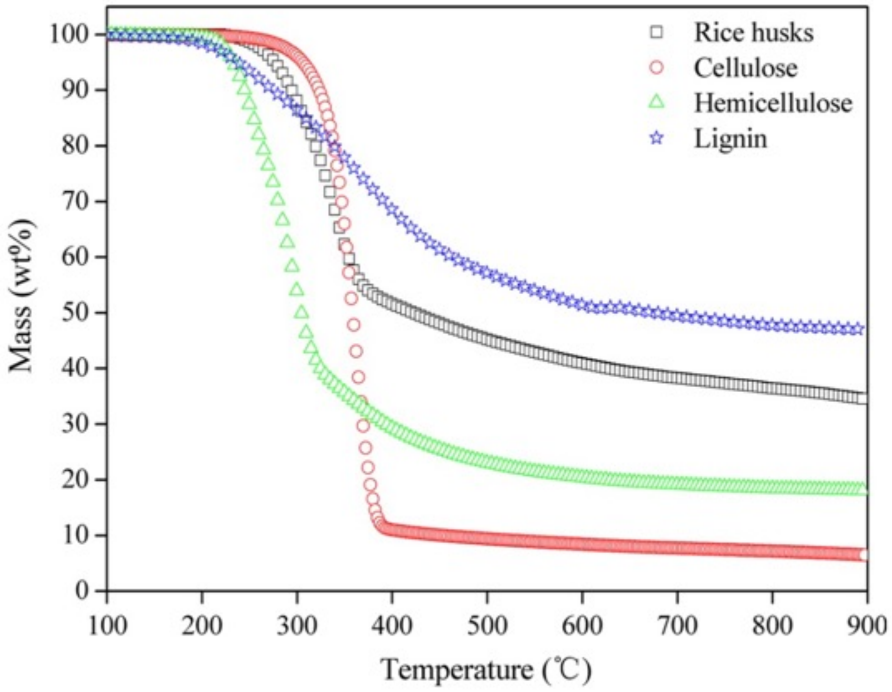

Figure 1-11: TGA curves of rice husks, cellulose, hemicellulose and lignin (Cheng et al., 2018)

For pyrolysis temperatures below 260 °C, the weight loss of rice husk is low, as shown in **Figure 1-11**. This phenomenon is mainly caused by dehydration and the low degree of decomposition of hemicellulose. For the temperature range of 260-300 ºC, the cellulose shows a minimal mass loss and hardly decomposes at all. At this temperature, the pyrolysis reactions of cellulose are mostly intramolecular dehydration. Therefore, the changes in the cellulose structure are relatively slight, and its crystalline form is maintained (Cheng et al., 2018; Xin et al., 2015). The significant changes in rice husk mass loss are observed at the temperature between 280 and 300 °C, resulting mainly from the decomposition of hemicellulose. A large amount of hemicellulose decomposes in this temperature range, as shown in the hemicellulose mass loss in **Figure 1-11**. Shafizadeh (1984) has shown for cellulose that at lower temperatures, below 300 ºC, the dominant reaction mechanism produces water, CO, CO_2, and char. At higher temperatures, cellulose is decomposed by an alternative pathway, and the primary evolved product is tar, which contains levoglucosan as the significant component with aldehydes, ketones and organics acids, and CO, CO_2, H_2, and char. The hemicellulose (xylan main component in hemicellulose) at 500 ºC produced mostly tar together with CO_2, water, char, and other hydrocarbons. The lignin decomposition involves lower-temperature releases of CO, CO_2, water, methanol, and tar and temperature above 500 ºC, the H_2 and CO are released.

Heating rate

The heating rate during pyrolysis has a significant effect on the distribution of the products. Pyrolysis is classified depending on the heating rate. There are three types of pyrolysis: 1) conventional/slow pyrolysis, 2) fast pyrolysis, and 3) flash pyrolysis (Onay and Kockar, 2003). The slow pyrolysis is typically used to modify the solid material, minimizing the liquid produced. Fast pyrolysis and flash pyrolysis maximize the gases and liquid produced.

In slow pyrolysis, the reactions that occur are always in equilibrium. The heating period is slow enough to permit equilibrium during the pyrolysis process. In this case, the final yield and the distribution of the products are limited by the heating rate. The residence time of the products in the reactor is also necessary because their presence can influence the primary and secondary reactions. **Table 1-1** summarize how each method differs in temperature, residence time, heating rate, and products distribution.

Table 1-1: Summary of the different pyrolysis modes with their process conditions and product distribution.

Process conditions	Slow pyrolysis	Fast pyrolysis	Flash pyrolysis
Temperature (°C)	400–900	450–850	600–1200
Heating rate (°C/s)	0.1–10	10–200	> 1000
Process time (min)	> 5	10–25	< 1
Vapor residence time (s)	≤550	0.5–10	< 0.5
Char yield (wt.%	25–50	15–25	5–15
Bio-oil yield (wt.%)	20–40	60–75	25–40
Gas yield (wt.%)	10–25	10–20	50–60

In fast pyrolysis, there are a negligible number of reactions during the heat-up period. Whatever pyrolysis reactions occur take place isothermally at the final temperature. Volatile residence time is a significant factor affecting the yields of gaseous and liquid products in a biomass sample. Fast pyrolysis is the most common of the methods, both in research and in practical use. Flash pyrolysis is a highly rapid thermal decomposition pyrolysis with a high heating rate. The main products are gases and bio-oil.

1.3.2.2. *Gasification*

Gasification is the exothermic partial oxidation of biomass with process conditions optimized for high yields of gaseous products (syngas) (Ciferno and Marano, 2002) rich in CO, H_2, CH_4, and CO_2 and some hydrocarbons (CH_4, C_2H_4, C_2H_6). Very small amounts of H_2S, NH_3, and liquid may also be produced (Pandey et al., 2019; Zhang et al., 2015c). Based on the gasification agents used, biomass gasification processes can be divided into air gasification using air (Wang et al., 2008a; Zhang et al., 2015c; Zhang et al., 2017), steam gasification using steam (Elorf et al., 2019; Jayaraman and Gökalp, 2015; Moghadam et al., 2014), oxygen gasification using oxygen (Niu et al., 2014), carbon dioxide gasification using carbon dioxide (Gao et al., 2016c), supercritical water gasification using supercritical water (Guo et al., 2015a).

The heat content of the syngas is dependent upon the type of the gasifying agent. The calorific values of the product gas from air, steam, and oxygen gasification are around 4–7, 10–18, and 12–28 MJ/Nm^3, respectively (Basu, 2010). Biomass gasification decreases the carbon-to-hydrogen mass ratio. Consequently, H_2 fraction is increased, which in turn enhances the calorific value of the output gaseous product. Feedstock parameters, such as particle size and shape, moisture content, heating value, carbon, and ash content, may significantly affect the performance of the gasifier. Therefore, information on the feedstock's volatility, its elemental analysis, heat content, and potential for slagging/fouling is very important in evaluating a gasification process (Ptasinski, 2008). In general, feeds with low volatile content are better for partial oxidation gasification, while biomass products with higher volatile content may be used as indirect gasification feedstocks. Biomass feedstocks come in a variety of forms, each with its own set of issues. Predicting specific biomass forms for a specific gasifier type under a range of conditions is critical. Although the chemical composition of biomass organisms or types is identical, the size and form of biomass feedstock particles are critical in deciding the difficulties in transporting and shipping the feedstock, as well as the behavior of the feedstock until delivered (Reed and Das, 1988). The gaseous products, or syngas can be cleaned and used directly as an engine fuel or upgraded to liquid fuels or chemical feedstocks to produce methanol or it can be used in the Fischer-Tropsch process to produce synthetic fuel (Huber et al., 2006; Wang et al., 2008b). One of the challenges of gasification is the management of higher molecular weight volatiles that condense into tars; these tars are both a fouling challenge and a potential source of persistent environmental pollutants, such as polycyclic aromatic hydrocarbons (Milne et al., 1998; Tanger et al., 2013).

1.3.2.3. *Combustion*

Combustion has been the most commonly used biomass conversion process since the dawn of humanity. Still today, a large majority of the human population relies on the burning of wood and agricultural residues in three-pot fires and stoves to supply heat and light energy for cooking and space heating (Kataki et al., 2015). This process is still the dominant bioenergy pathway worldwide. Furnaces and boilers are used typically to produce steam for use in district heating/cooling systems or to drive turbines to produce electricity (López González, 2013). During combustion, biomass fuel is burnt in excess air to produce heat. This process involves the production of heat due to the oxidation of carbon- and hydrogen-rich biomass to CO_2 and H_2O. However, the detailed chemical kinetics of the reactions during biomass combustion are complex (Babu, 2008; Jenkins et al., 1998; Tanger et al., 2013) and poor combustion results in the release of intermediates, including environmental air pollutants CH_4, CO, and particulate matter. Additionally, fuel impurities, such as sulfur and nitrogen, are associated with SOx and NOx emission (Tanger et al., 2013). In the combustion process, the main activities that occur are initial fuel drying, ignition and combustion of volatile constituents, and finally, the char's burning. The combustion is frequently proposed for the conversion of lignin-rich feedstocks. This process can be used to convert biomass in two ways: for direct conversion of the whole biomass or for parts of the biomass that exist after biochemical conversion (Kataki et al., 2015).

All the process described above uses dry biomass to transform it into energy. Therefore, it needs a previous drying. The reduction of water content in biomass, i.e., drying, results in the simultaneous increase in thermal value, preservation potential, ease in storage and transportation, less negative impact on the environment, and more uniform combustion. However, other thermochemical conversion processes do not require drying. These processes are known as wet biomass conversion processes or hydrothermal processes, including hydrothermal liquefaction (HTL) and hydrothermal carbonization (HTC).

1.3.2.4. *Hydrothermal liquefaction*

Hydrothermal liquefaction of biomass is the thermochemical conversion of biomass into liquid fuels by processing in a hot, pressurized water environment for sufficient time to break down the solid biopolymeric structure to mainly liquid components. Typical hydrothermal processing conditions are 250–374 ºC of temperature and operating pressures from 4 to 22 MPa of pressure (Elliott et al., 2015). The main products are liquid, as well as by-products in a gaseous, aqueous, and solid phase (Toor et al., 2011). HTL transforms 5% to 61% of the wet biomass into a liquid product called bio-oil, consisting of water-soluble components such as acids, alcohols, cyclic ketones, phenols, and naphthols, this bio-oil produced, with an energy value close to fossil petroleum (Jena and Das, 2011), is not directly suited as transportation fuel, but it is expected to be a suitable renewable feedstock for co-refining in existing fossil-based refineries. The recovery of the bio-oil is made by liquid-liquid extraction with hexane. A solid residue (20-49%) and a gaseous phase (15-30%), composed mainly of CO2 and CO, are also the by-products of HTL of the biomass (Beauchet et al., 2011; Xiu et al., 2010). The quality of the bio-oil in terms of oxygen content is increased with the use of catalysts; these decrease the production of solid residues. The catalysts such as Raney Ni and m-ZrO2 can be used (Beauchet et al., 2011). The literature has thoroughly identified and outlined the precise classification, reaction conditions, and reaction pathways for HTL processes of biomass (Behrendt et al., 2008; Toor et al., 2011; Zhang, 2010). Compared with pyrolysis, an HTL process can produce higher quality bio-oils with beneficial chemical and physical properties (e.g., lower oxygen content and smaller molecular weights, and increased heating values). Many literature studies have reported HTL technologies' ability to produce a variety of chemicals, such as vanillin, phenols, aldehydes, and acetic acids, among others (Behrendt et al., 2008; Toor et al., 2011; Zhang, 2010). For biomass liquefaction, Behrendt et al. (Behrendt et al., 2008) objectively analyzed different historical and existing HTL processes' theoretical implementations. HTL processes involving sub- and supercritical water were stated by Peterson et al. (Peterson et al., 2008) and Toor et al.(Toor et al., 2011). Furthermore, Zhang (Zhang, 2010) has published an overview of biomass HTL processes for various feedstocks. As reviewed by Akhtar et al.(Akhtar and Amin, 2011), the yield of bio-oil is highly dependent on different operating parameters such as feedstock form, solvent type, temperature, substrate concentration, reaction time, catalyst, and so on.

1.3.2.5. *Hydrothermal carbonization*

The HTC is a thermochemical process that occurs in subcritical water between 180 °C and 250 °C and can last from a few minutes to several hours. The pressure is autogenous with the saturated vapor pressure of the subcritical water and the gas produced during the HTC process (10-40 bars) (Arellanoa et al., 2016; Hitzl et al., 2015; Hoekman et al., 2011; Missaoui et al., 2017). During HTC, the feedstock undergoes a complex network of simultaneous reactions. The final products are a carbon-enriched residue (hydrochar), characterized by high carbon content (55–74 % (w/w) carbon) and high calorific value (21.1-30.6 MJ/kg) (Hoekman et al., 2011; Vassilev et al., 2010; Xiao et al., 2012), a liquid phase contains important chemicals, such as furfurals and small organic acids and a relatively small amount of gas, low in carbon and consequently harmless for greenhouse effects (Libra et al., 2011). Like HTL, the HTC process allows the treatment of substrates with a high moisture content >50 % (w/w) without requiring a drying pretreatment step (Libra et al., 2011; Missaoui et al., 2017). In recent years, the HTC process has been considered an alternative method of processing biomass for value-added products. The solid product created during HTC is called hydrochar in order to distinguish it from biochar or pyro-char. HTC process has several advantages over another thermochemical process, such as lower energy consumption and less emission over pyrolysis; it can be used for biomass with high moisture content. Therefore, a greater variety of feedstocks could be considered for processing into hydrochar since drying the feedstock is unnecessary for HTC. Compared to biochar produced at typical temperature ranges, hydrochar generally has a lower C content due to lower dehydration during the HTC process (Bargmann et al., 2013; Libra et al., 2011). Hydrochar has a much lower ash content than biochar; the ash in biomass enters the liquid phase during HTC, while biochar retains all of the ash in the biomass (Fang et al., 2015a; Fang et al., 2017). Consequently, hydrochar is slightly more acidic than biochar (Parshetti et al., 2014), has higher H/C ratios and less aromaticity than biochar, and little or no molten aromatic ring structure (Bejarano et al., 2017). Depending on the applications, the characteristics of hydrochar may be more desirable than those of biochar. The relatively low ash content of most hydrochars is desirable when they are to be used as a fuel (Demirbas, 2007; Yang et al., 2016b). Also, the surface area of biochar or pyrochar is much larger than hydrochar, since during HTC, reactions such as condensation and polymerization make pore formations much smaller than during pyrolysis. The physical, chemical, and mechanical properties of hydrochar make it susceptible to different uses. Hydrochar thus is used directly as a solid fuel that can be burned for energy or used to synthesize fuel cells, electrode supercapacitors, and batteries as a medium for converting and storing energy (Ding et al., 2012; Lin et al., 2015; Sik et al., 2015; Yang and Wang, 2016). Most hydrochars, particularly the ones derived from plant biomass, are considered an excellent potential solid fuel is owing to their low ash content; the inorganic minerals in the biomass enter the processing liquid during the HTC process (Fang et al., 2015a).

1.3.2.5.1. *Mechanism and steps of hydrothermal carbonization of biomass*

Many chemical reactions that can occur during the hydrothermal carbonization process are mentioned in the literature. Although there is a divergence of opinion between studies on the type of reactions that occur during hydrothermal carbonization, but it is known that the decomposition of biomass in the HTC process is governed in sum by hydrolysis (endothermic reaction), dehydration and decarboxylation (exothermic reactions). These reactions occur simultaneously, thus the functional groups of the biomass are removed to some extent (Funke and Ziegler, 2010; Yan et al., 2010; Zhang et al., 2018). However, the complex network of reactions and the combined mechanism for all these reactions is not yet known in detail. So, for the time being, only a separate discussion of the general reaction mechanisms that have been identified can provide useful information on the possibilities for manipulating the reaction. These mechanisms include hydrolysis, dehydration, decarboxylation, condensation, aromatization and polymerization (Kambo and Dutta, 2015; Kruse et al., 2013; Lu et al., 2012; Lucian et al., 2019; Volpe et al., 2018). The pathways of the main HTC reactions for lignocellulosic biomass are shown in **Figure 1-12**. The Liquid biocrude in the **Figure 1-12** is a complex liquid solution of condensation, aromatization and polymerization products. The reactions in the **Figure 1-12** are not necessarily consecutive or in series, but can form a parallel network of different reaction pathways. The nature and mechanisms of these reactions depend mainly on the feedstock. The main components of the biomass are hydrolyzed in large quantities from oligomers and monomers of sugars (pentose and hexoses) (Kumar, 2013). The extractives compounds of biomass are being eluted; most of these compounds have a good solubility in water in the HTC condition. The fragments of the extractives dissolved in water undergo further degradation mechanisms, such as dehydration and decarboxylation, while condensation reactions occur. These reactions form highly reactive intermediates such as furfurans, 5-HMF and its derivatives. They can also represent high value-added chemicals. During the polymerization reaction, they form humic acids, bitumen and insoluble solids that partially precipitate to form the main product of HTC (hydrochar).

In addition, there may be components of the biomass or oligomer fragments of the biomass that do not hydrolyze under the given reaction conditions, like crystalline cellulose (Funke and Ziegler, 2010).

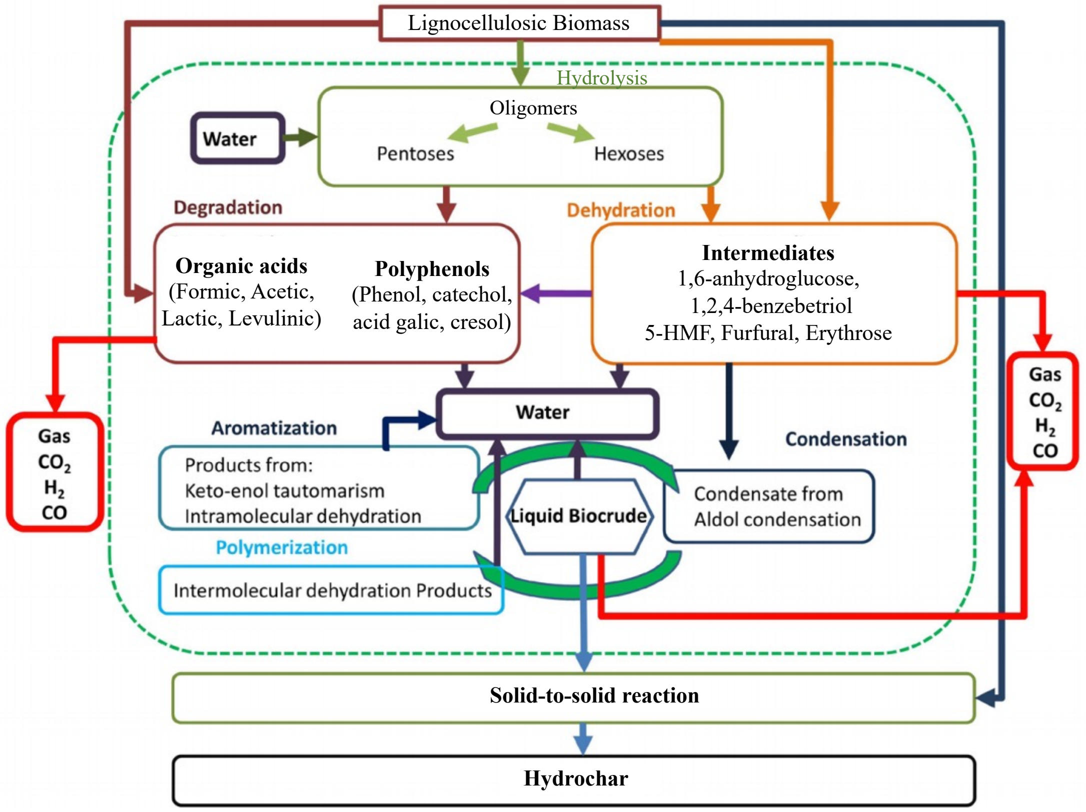

Figure 1-12: HTC reaction pathways for lignocellulosic biomass (Reza et al., 2014a))

Hydrolysis reaction

The hydrolysis reaction is endothermic; this reaction leads to the cleavage of mainly ester and ether bonds of the biomacromolecules by adding water. The hydrolysis has the lowest activation energy being the first step to be initiated in the HTC process (Fang et al., 2018; Gao et al., 2016a). The extensive product range in this reaction includes (oligo)-saccharides of cellulose and phenolic fragments of lignin (Fakkaew et al., 2015; Fang et al., 2018; Gao et al., 2016a). The complexity of the hydrolysis reaction can be summarized by the detailed mechanism of the D-fructose reaction explained by Antal Jr et al. (1990), since D-fructose is a specific substance in contrast to biomass. Next to other degradation mechanisms mentioned below, the resulting fragments are being further hydrolyzed, such as 5-HMF, erythrose, and aldehydes (Krylova and Zaitchenko, 2018), to yield levulinic and formic acid. Hemicellulose is readily hydrolyzed above 150 °C, but the detailed reaction pathways are less well known due to the complexity of its structure. Cellulose is being hydrolyzed significantly under hydrothermal conditions above approximately 180°C; details of the reaction mechanisms were summarized by Peterson et al. (2008). Hydrolysis of lignin is very complex; however, it is most likely at about 200 °C due to its large amount of ether bonds. Nucleophilic reactions form highly reactive products with a low molecular weight. One of them of potential interest is acetic acid, which is most likely formed by hydrolysis of the side chains (Funke and Ziegler, 2010). The number of different fragments formed is high, including the hydrolysis of selected components (D-fructose) (Concin et al., 1983). Most of these fragments are very reactive, and condensation reactions rapidly form precipitates. The different biomass components interact with each other. The effect of these interactions on hydrolysis is mainly unknown. In general, lignin is bonded to hemicelluloses by covalent bonds. Therefore, hemicellulose fragments interact with lignin and thus increase the solubility of their aromatic structures, which is consistent with the observation that lignin and hemicellulose from an oligomer that is usually stable under hydrothermal conditions (Funke and Ziegler, 2010). In the case of forced convection (e.g., stirring), the hydrolysis reaction is swift, and its rate is mainly determined by the adjusted flow rate and not by the reaction temperature. It can be concluded that the rate of biomass hydrolysis is mainly determined by diffusion and thus limited by transport phenomena in the biomass matrix; this may lead to the condensation of fragments in the biomass matrix at high temperatures (Hashaikeh et al., 2007; Mochidzuki et al., 2005; Shoji et al., 2005).

Dehydration reaction

The dehydration reaction is the removal of water from the biomass structure. Hydrothermal carbonization dehydration refers to all chemical reactions and physical processes, which remove water from the biomass matrix without changing its chemical constitution. Biomass dehydration reaction during the HTC process means reducing the H/C and O/C ratios. According to many studies, cellulose in biomass starts to decompose by pure dehydration according to the following reaction:

$$4(\mathrm{C_6H_{10}O_5})_\mathrm{n} \leftrightarrow 2(\mathrm{C_{12}H_{10}O_5})_\mathrm{n} + 10\mathrm{H_2O} \quad (1\text{-}1)$$

The meaningful decarboxylation is only observed after that specific amount of water is formed. Several experimental studies under hydrothermal conditions show that, at low HTC reaction conditions, dehydration can also be achieved without significant decarboxylation (Funke and Ziegler, 2010). Several experimental studies under hydrothermal conditions show that, at low HTC reaction conditions, dehydration can also be achieved without significant decarboxylation. However, the extent to which biomass can be carbonized without significant decarboxylation is mainly unknown (Titirici et al., 2007). The molar ratio between decarboxylation and dehydration (CO_2/H_2O) ranges from 0.2 for cellulose to 1 for lignite and is largely independent of temperature under HTC conditions. The rate of dehydration is higher or equal to decarboxylation. The removal of hydroxyl groups generally explains dehydration (Funke and Ziegler, 2010). There is practically no more detailed study of biomass dehydration reactions; however, it is reported that glucose dehydrates to form 5-HMF or 1,6-anhydroglucose (Funke and Ziegler, 2010; Kabyemela et al., 1999). For the case of lignin, the dehydroxylation of catechol is mentioned, and the possible formation of water during the cleavage of phenolic and alcoholic groups above 150°C and 200°C, respectively (Funke and Ziegler, 2010; Murray and Evans, 1972).

Decarboxylation reaction

Decarboxylation is a chemical reaction that removes a carboxyl group and releases carbon dioxide (CO_2). Detailed reaction mechanisms are largely unknown, including the effect of the presence of water (Peterson et al., 2008). Carboxyl and carbonyl groups rapidly degrade above 150°C, forming CO_2 and CO, respectively (Sevilla and Fuertes, 2009a). The gas formation (CO_2 and CO) increases with increasing temperature and reaction time (Missaoui et al., 2017). One likely source for CO_2 is formic acid, which is formed in significant amounts during the degradation of cellulose and decomposes under hydrothermal conditions to yield CO_2 and H_2O (Nelson et al., 1984). A significant decarboxylation reaction increases the formation of gas, thus increasing the saturation pressure of the system. The decarboxylation pathway involves the degradation of extractives, hemicellulose, and cellulose. Under hydrothermal conditions, these materials can degrade into monomers such as formic acid, acetic acid, and furfurans, which further degrade into CO_2 and H_2O (Hoekman et al., 2013). With the increase in temperature of HTC, most monosaccharides decrease substantially, degrading into carboxylic acids, such as acetic and formic acids (Hoekman et al., 2011; Hoekman et al., 2013). The presence of acids can be confirmed from the low pH of the liquid solution after HTC. Other possible decarboxylation pathways involve condensation reactions, resulting in the formation of CO_2 (Funke and Ziegler, 2010).

Condensation- polymerization reactions

The intermediates (5-HMF, furfural) formed from hydrolysis reactions in hydrothermal carbonization are highly reactive. Also, it depends on the type of biomass, as well as the degree of conversion. They are unsaturated compounds that readily polymerize by aldol condensation or intermolecular dehydration involving the removal of the carboxyl and hydroxyl groups. These reactions (dehydration and decarboxylation), explained above, create H_2O and CO_2, respectively (Reza et al., 2014b). Condensation reactions (e.g., of aromatic nuclei) may account for part of the CO_2 formation. A theoretical observation of possible condensation reactions can explain the experimental observations (formation and composition of gases, influence of temperature and pressure). Also, the carbonization rate is increasingly determined by steric influences with a higher degree of condensation of aromatics. Therefore, it can be argued that the formation of hydrochar during hydrothermal carbonization is mainly characterized by polymerization and condensation, specifically aldol condensation (Kabyemela et al., 1999; McCollom et al., 1999). Condensation proceeds mainly with the formation of H_2O. Free radical mechanisms can occur under hydrothermal conditions but are more likely to be dominant under supercritical conditions and at low density. Under subcritical conditions, the free radicals are effectively saturated by the water present and the hydrogen donated by aromatization (Sevilla and Fuertes, 2009b). Thus, condensation polymerization is most likely based on step-growth polymerization supported by the low polymerization rate observed during the experiments. In the case of lignin fragments (highly reactive), it has been reported that polymerization is completed in several minutes above 300 °C, whereas at low temperatures, it can take hours, even days (Funke and Ziegler, 2010; Masselter et al., 1995). Condensation reactions of monosaccharides are still slower, mainly since cross-linked polymerization competes with the recondensation to oligosaccharides. However, some degradation products of monosaccharides, such as 5-HMF, show higher reactivity, which may accelerate polymerization (Bobleter, 1994; Reza et al., 2014b). It has also been observed that hemicellulose fragments appear to stabilize lignin fragments, slowing down condensation reactions significantly. Therefore, the results from model compounds have clear limits for extrapolation to "real" biomass. Not everything is known about detailed polymerization sequences during HTC of biomass (Reza et al., 2014b). Polymerization that forms solid precipitation is usually considered an undesirable secondary reaction. It cannot be known whether the soluble hydrochar fraction is a precursor to the incompletely condensed non-soluble fraction (precipitate) or whether the two are components of distinct reaction pathways. However, it is known that it is not easy to distinguish analytically between the characteristics of the two hydrochars; because both appear as a single solid mass of char (Paksung et al., 2020).

On the other hand, the observation that the remaining insoluble fraction exhibits a specific surface area two orders of magnitude higher unfractionated hydrochar provides some evidence that the reaction pathways might be different. Other experiments reported that condensation fragments within the biomass matrix are able to "block" the remaining transport of biomacromolecules, thus trapping hydrolysis products inside the pore, impeding access of water to the pore. This phenomenon could also contribute to the increased hydrophobicity of HTC hydrochar (Garrote et al., 2001; Reza et al., 2014b).

Aromatization reaction

Although hemicellulose and cellulose are linear polymeric carbohydrate chains, they can form aromatic structures under hydrothermal conditions. Aromatic structures exhibit high stability under hydrothermal conditions and can therefore be considered as a fundamental building block of the resulting hydrochar (Funke and Ziegler, 2010). The cross-linked condensation of aromatic rings also constitutes the main components of natural carbon, which could explain the excellent agreement between natural carbonization and hydrochar (Peterson et al., 2008). Similar chemical structure characteristics of hydrochar and natural carbon have been mentioned in several publications. Based on these considerations, it is evident that the effect of hydrothermal treatment on oxygen content decreases with an increasing number of aromatic bonds. Aromatization appears to be significantly temperature dependent. Hydrothermal dehydration experiments of lignite and peat reported aromatization above 270°C (Funke and Ziegler, 2010); however, this depends on the type of biomass and the treatment time. Aromatization reactions increase the formation of polycyclic aromatic hydrocarbons (PAHs). The intermediate unsaturated compounds produced from dehydration and decarboxylation readily polymerize by aldol condensation, forming initially into long-chain aliphatic compounds. These hydrocarbons promote the formation of PAHs by aromatization reactions. As the temperature is increased, the ring number increases (Peng et al., 2017; Shen et al., 2017).

During HTC, there are some stable compounds with a crystalline structure and oligomer fragments that do not hydrolyze, and it is carried out from the solid-to-solid pathway reaction. Although their quantitative contribution is estimated to be considerably low at temperatures above 200°C (Funke and Ziegler, 2010), these reactions could become significant. However, Falco et al. (2011) reported that the solid-to-solid pathway dominates during the HTC of cellulose due to the large aromatic groups in the hydrochar.

The demethylation reaction has been used to explain the mechanism that results in a phenol becoming part of a catechol-like carbon structure. Several experimental setups measured the development of lower amounts of CH_4, which seems to confirm this mechanism (Bevan et al., 2020; Hatcher, 1995).

Also, it has been reported that pyrolytic reactions also compete with hydrothermal conditions; and could become significant above 200°C, although typical pyrolysis products (e.g., CO and tars) have not been reported to form in significant amounts during hydrothermal carbonization. Carbonization of biomacromolecules, which have no contact with H_2O because they have been blocked by precipitation of condensation fragments, has also been explained by pyrolytic reactions (Hashaikeh et al., 2007). Other reactions observed are the Fischer-Tropsch type; given the large amount of CO2 formed during HTC, they could play a role that has not been investigated in detail so far (Funke and Ziegler, 2010; McCollom et al., 1999).

The main product of HTC is hydrochar, a solid material 55-74% rich in carbon, is the stable, a lignite-like material which is characterized by a high calorific value (21.1–30.6 MJ/kg) (Danso-Boateng et al., 2013) and its physical, chemical, and mechanical properties make it susceptible to different uses. Hydrochar can thus be used directly as a solid fuel that can be burned for energy or produce syngas (Peng et al., 2017). Syngas produced from hydrochar can be used in Fioscher-Tropsch synthesis to produce synthetic fuels.

1.4. Fischer-Trospch process

The Fischer-Tropsch process (SFT) consists of the transformation of syngas (H_2 and CO) in a catalytic reactor to obtain liquid hydrocarbons (Hoek et al., 1985). Among the liquid products derived from this synthesis, gasoline, naphtha, diesel, methanol, among others, have a high added value.

The primary reaction of the SFT process is the synthesis of alkanes **Eq.(1-2)** and linear olefins or alkene **Eq. (1-3)**. However, several secondary reactions also occur, including the synthesis of oxygenated products **Eq. (1-4)** the water-gas shift reaction **Eq.(1-5)** and the Boudouard reaction **Eq.(1-6)** (Rojas et al., 2011). These reactions can be represented as follows:

Alkanes

$$nCO + (n+2)H_2 \rightarrow C_nH_{2n+2} + nH_2O \tag{1-2}$$

Alkene or linear olefins

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \tag{1-3}$$

Alcohols

$$CO + 2nH_2 \rightarrow C_nH_{2n+2}O + (n-1)H_2O \tag{1-4}$$

Water-gas shift:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{1-5}$$

Boudouard reaction

$$2CO \rightarrow CO_2 + C \tag{1-6}$$

Although the details of the mechanism of SFT are not fully understood, most researchers accept that hydrocarbon formation occurs through a polymerization reaction of CHx* units formed in situ on the catalyst surface from CO and H_2 and act as initiator and monomeric species in the chain growth process.

1.4.1. SFT reaction mechanism

The Fischer-Tropsch synthesis resembles an oligomerization reaction or polymerization with the following steps: (a) adsorption of reagents; (b) chain initiation; (c) chain growth; (d) chain termination; (e) desorption of products; and (f) re-adsorption and subsequent reaction of those products. The product distribution described in the previous section demonstrates the polymeric nature of the Fischer-Tropsch synthesis, but at present, a great deal of controversy persists about the nature of the monomer and, more specifically, the path followed by the hydrocarbon chain growth. Today there are many mechanisms of SFT (Adesina, 1996; Dry, 1996; Hindermann et al., 1993).The three main proposed reaction mechanisms are explained below:

1.4.1.1. *Mechanism of carbides*

It was proposed by Fischer and Tropsch (1926). The first step of the reaction is the dissociative adsorption of carbon monoxide on the catalyst surface, which gives rise to a metal carbide that subsequently transforms into the M-CHx species. The carbide mechanism is presented in **Figure 1-13.** Insertion into the metal-carbon bond of another similar neighboring species results in the formation of a hydrocarbon with more carbon atoms. Chain growth can be interrupted by adding or eliminating hydrogen, giving rise to the corresponding alkane or olefin, respectively. This mechanism does not explain the formation of oxygenated compounds (alcohols and aldehydes).

This scheme presupposes the formation of a metal carbide; this would be possible with Fe catalysts; however, other Fischer-Tropsch active metals such as Co or Ru cannot form carbides under the reaction conditions; this model would fail.

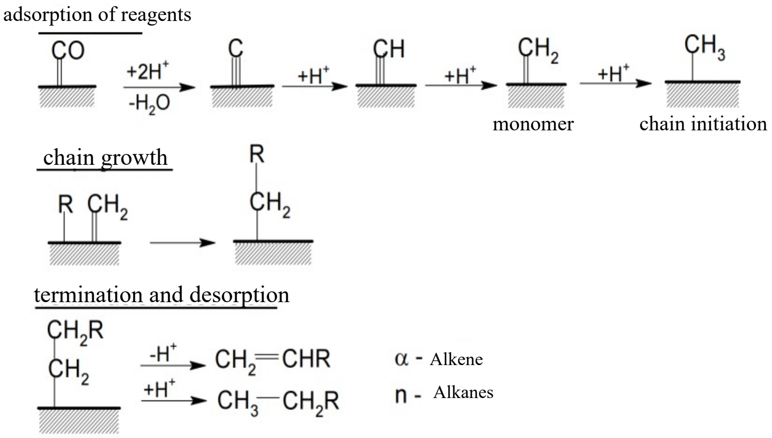

Figure 1-13: Mechanism of carbides (Fischer and Tropsch, 1926)

1.4.1.2. *Mechanism of hydroxy-carbenes*

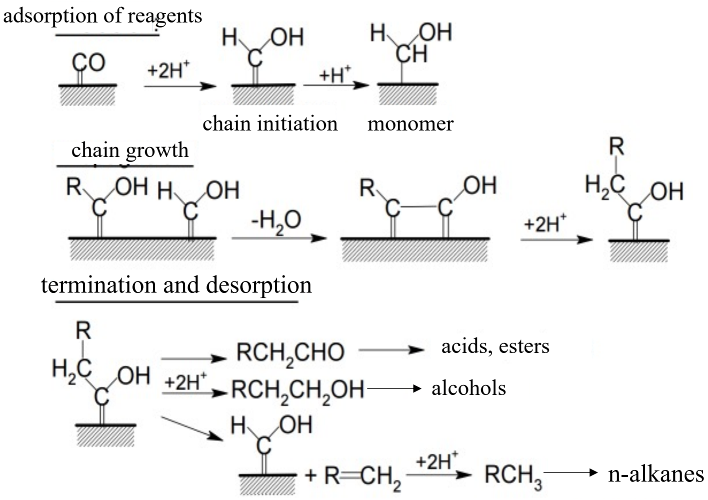

Figure 1-14: Mechanism of hydroxy-carbenes (Kummer et al., 1948).

This mechanism was proposed by Kummer et al. (1948). This mechanism consists of chain growth by condensation of two hydroxy-carbene species (M-CHOH) to eliminate water. First, a non-dissociative adsorbed CO molecule is partially hydrogenated to create the surface M-CHOH species. This model explains the formation of hydrocarbons and oxygenated compounds. In **Figure 1-14**, the mechanism of hydroxy-carbenes is presented.

1.4.1.3. *CO insertion mechanism*

In this mechanism, chain growth occurs by inserting a carbonyl intermediate (M-CO) into an alkyl chain metal bond. It was proposed by Pichler and Schulz (1970). In this case, the CO will act as a monomer, while the chain initiator will be the alkyl group. Chain growth occurs when CO is inserted into the M-CH3 bond, giving surface acetyl radical. The mechanism of CO insertion is presented in **Figure 1-13**.

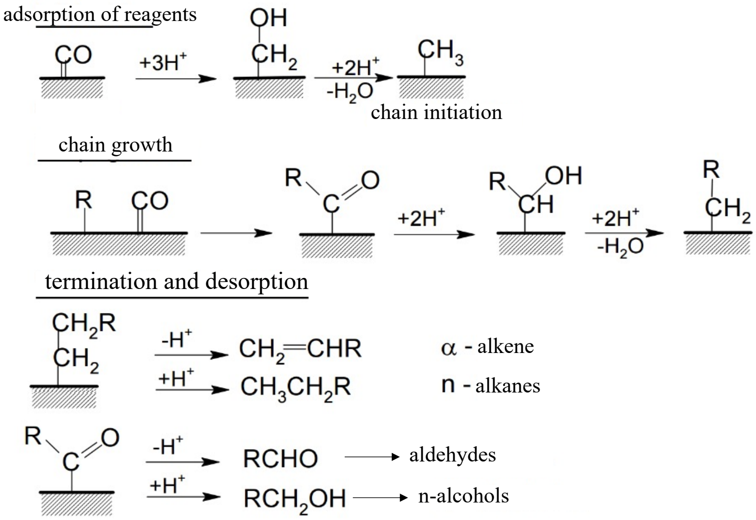

Figure 1-15: CO insertion mechanism (Pichler and Schulz, 1970).

These three mechanisms share an essential common feature: the presence of a single species responsible for chain growth (CH_2, CHOH, and CO). However, none of these mechanisms alone can explain the great diversity of products formed in SFT, so some researchers have proposed other mechanisms where more than one reaction intermediate is involved and presented in **Figure 1-16**. Thus, according to the mechanism proposed by Dry (1996), hydrocarbons are produced by the insertion of -CH_2- units into alkyl chains, while the insertion of CO produces the oxygenated compounds. This mechanism has been accepted by several researchers (Biloen and Sachtler, 1981).

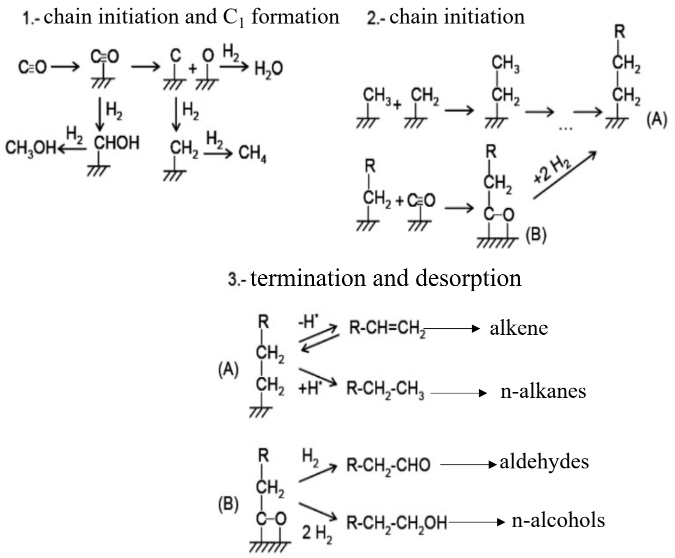

Figure 1-16: SFT reaction mechanism proposed by Dry (1996)

1.4.2. Product distribution and selectivity

The Fischer-Tropsch synthesis has been characterized as a reductive CO oligomerization or polymerization. Then, the distribution of the products obtained can be determined from an analogy with oligomerization and polymerization, as performed by Anderson et al. (1958). Schematically it is proposed:

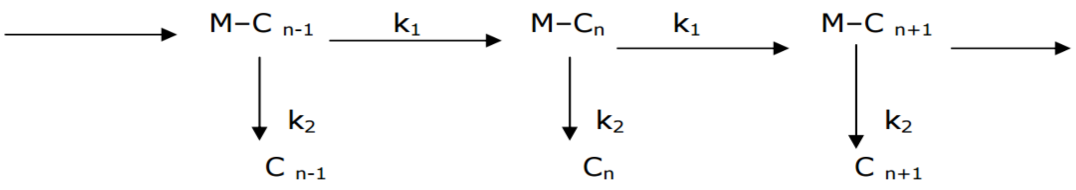

Figure 1-17: Diagram of the distribution and selectivity of the product proposed by Anderson et al. (1958).

This scheme shows that after each incorporation of a CO-derived "monomer" C1 into the growing chain, propagation of the chain with a rate constant k1 can occur, or the chain ends with a constant rate k2 by forming a product. In this simple method, it is assumed that under steady-state conditions, k1 and k2 are independent of chain length and that C2 or larger "monomers" are not inserted into the chain. As a result, the mass fraction Wn of each hydrocarbon produced decreases with the number of carbon atoms according to a geometric progression:

$$\frac{W_n}{n} = \alpha^{n-1}(1-\alpha)^2 \tag{1-7}$$

where Wn is the mass fraction of the hydrocarbon of n carbon atoms, n is the number of carbon atoms, α is Schulz-Flory coefficient, α = k1 / (k1+k2) (the probability of chain growth or degree of polymerization).

If k1 << k2, essentially low molecular weight products such as methane or C2-C4 are formed if k1 ≈ k2 the reaction could produce hydrocarbons in a wide range C1-C20 and k1 >> k2, the reaction will allow obtaining high molecular weight products such as waxes or poly-methylene.

Figure 1-18 depicts the selectivity towards various product groups as a function of α-chain growth probability. In any case, it should be noted that in Fischer-Tropsch synthesis, a broad spectrum of C1 - C50+ hydrocarbons are produced, being one of the significant challenges of this process to find catalysts that manage to produce the desired product or product fraction selectively. Generally, this fraction is the one between C13 -C18 (diesel fraction) since it has excellent properties, such as a high cetane number (>70) (Rojas et al., 2011).

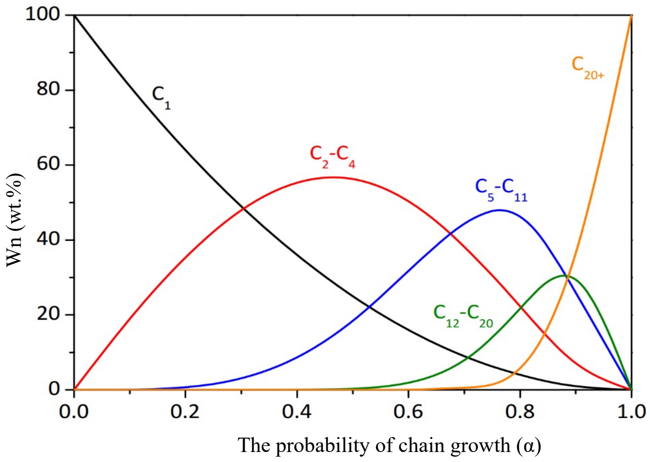

Figure 1-18: Distribution of products as a function of parameter α (Rojas et al., 2011).

Typically, SFT is carried out in a range of pressures between 2 and 6 MPa and temperatures: low temperature (200-250 ºC) and high temperature (300-350 ºC). In the first case, iron (Fe) or cobalt (Co) catalysts are usually used, obtaining mainly long-chain hydrocarbons, while in the second process, mainly Fe catalysts are used, forming lighter hydrocarbon fractions (*Rojas et al., 2011*).

In general, the conversion of biomass into synthetic fuels or energy is complex, involving complex chemical reactions, different transport phenomena, and different reactor structures. The study of this process in a laboratory and pilot plant is very tedious and expensive. For this reason, other researchers have looked for alternatives such as modeling and simulation studies, which are undoubtedly necessary and complementary to experimental studies. Besides, this contributes to the design, operation, optimization, and control of the process.

1.5. Modeling and simulation studies of biomass conversion processes

As we have seen before, biomass conversion strategies include thermochemical conversions, such as pyrolysis, gasification, hydrothermal carbonization, combustion, and biochemical conversions. The performance of each of these processes is highly dependent on transport phenomena, i.e., the mechanisms by which heat, mass, and momentum are transferred throughout a system and, of course, the kinetics of chemical reactions and reactor hydrodynamics.

In the case of thermochemical biomass conversion, transport phenomena are very important. For example, in fast pyrolysis, effective heat transfer combined with the rapid escape of volatile products is essential to reducing char formation and optimizing the yield of desirable products (bio-oil). The rapid heating rates combined with reactor residence times on the order of a few seconds will shift pyrolysis products' yields toward condensable gases while minimizing char formation. (Bridgwater, 1999; Wiley, 2017). In processes that involve heat transfer between solid and fluid phases, the rate at which heat can move across the solid/fluid interface is of critical importance. Jacque Lede explains the difficulties related to the experimental determination of the biomass particle's temperature in their recent critical review on the "Scientific Challenges and Related Recommended Research Topics" regarding biomass fast pyrolysis reactors and heat transfer rates (Lede, 2013). He points out that using a thermocouple to measure the temperatures of very fine biomass particles passing through the reactor quickly during fast conversion reactions is virtually impossible. The mathematical simulation of biomass conversion processes can be very useful, since it allows to predict the products yields and their characteristics. Modeling and simulation of biomass thermochemical is very complex, because it requires to take into account chemical, fluid dynamic, and thermodynamic phenomena (Gagliano et al., 2018).

Accurate representation of heat transfer, mass, momentum, and chemical reaction kinetics inside a reactor is critical when modeling processes that combine heat conduction through solids (biomass particles) and convective heat from fluids (inert gas or water). In this context, modeling and simulation-based on generalized biomass particle geometry, heat and mass transfer; physical constants; reaction kinetics, and reactor hydrodynamics can facilitate the understanding of biomass-to-energy conversion. Understanding these phenomena can help optimize and provide more reliable process models to reduce commercialization's economic uncertainty.

In general, there are several investigations on modeling and simulation of the biomass-to-energy process. However, there is little research on the modeling and simulation of the hydrothermal carbonization process to date. The great variety of phenomena that take place during the HTC process of biomass make the analysis of the process and its simulation difficult; only a few studies have been carried out in this aspect, focusing mainly on pure materials instead of heterogeneous biomasses, for example, (Álvarez-Murillo et al., 2016), who studied the kinetics of cellulose HTC. Besides, (Reza et al., 2013) proposed the kinetics of hemicellulose decomposition as a first-order reaction. However, most studies on HTC kinetics have been limited to the solid phase, while research on the liquid phase's evolution and gases during the process is relatively scarce. Besides, progress in the development of models capable of describing the kinetics and governing mechanisms of the process is very important for designing the equipment and operating conditions required to produce hydrochar with the desired characteristics. Most of the mathematical models describing the biomass HTC process's kinetics have been developed in recent years, but there is room for improvement of the proposed models. Most of the kinetic models reported for biomass HTC processes are (0D) models that analyze the process's kinetics by a simple analytical expression. Mathematical models describing the thermochemical conversion process of biomass can be divided into three categories: kinetic models, statistical models, and computational models. The advantages and limitations of these are summarized in **Table 1-2**. There is some overlap between these categories of models since each variable's mass balance is the basis for all mathematical models. Statistical models are empirical models, i.e., they are based on direct observation, measurement, and experimental data that allow us to predict the system's behavior without understanding the mechanisms that are occurring. In contrast, computational models based on the laws of physics are mechanistic because they try to explain the process, analyzing how experimental conditions affect chemical reactions, such as the transfer of mass, heat, and momentum. In the computational model, the entire process domain is discretized. The most commonly used discretization methods are the finite difference method, the finite element method, and the finite volume method, the latter being the most widely used in Computational Fluid Dynamics (CFD). With these methods, the continuous domain is exchanged for a discrete domain, where a set of control volumes is used to represent the original domain (Mattiussi, 1997).

Table 1-2: Advantages and limitations of biomass conversion process models.

Models	Advantages	Limitations
Kinetic	Easy to implement	- It does not provide sufficient information for large-scale installations.
Statistical	Qualitative and quantitative analysis of the effect of process parameters.	- Empirical models - Its application is limited to raw materials and experimental conditions.
Computational	-Complete descriptions of space and time variations -Combines reaction kinetics and physical laws to produce accurate simulation of full-scale applications. -Effective and intuitive visual analysis of results	- Numerical simulation is very complex

1.5.1. Kinetic models

Kinetic models provide essential information on kinetic mechanisms to describe the chemical reactions involved in biomass conversion, which is crucial for designing, evaluating, and improving reactors. These models are based on chemical reaction rates and can predict both overall performance and profiles of gas and liquid compositions with time and inside the reactor. Kinetic models are based on the evaluation of the kinetic constants k(T) of the chemical reactions used to simulate the thermochemical conversion processes (Gagliano et al., 2018) . The kinetic models are known as 0D model i.e., no influence of spatial variables; the system behaves in the same way at any point of the reactor. These constants can be calculated by an analytic technique known as thermogravimetric analysis (TG) (White et al., 2011). Indeed, TG allows the evaluation of the Arrhenius kinetic parameters, that is, activation energy (Ea) and preexponential factor (A), necessary for the determination of the constant rate of a chemical reaction through the Arrhenius mathematical expression (Doherty et al., 2009).

1.5.2. Statistical models

The Design of Experiments - Response Surface Methodology (DoE/RSM) approach has proven to be a handy tool to investigate several variables' influence on a given magnitude .The implementation of a DoE/RSM approach allows to identify the importance of each variable, as well as their interactions, by developing a model with input parameters (processing variables) and output functions (parameters of interest); therefore, it can provide information on the effect of experimental conditions on the direction and magnitude of the measured response. In this way, it has enormous potential to study and optimize a wide range of engineering systems and has often been used in energy production processes such as pyrolysis, gasification, hydrothermal carbonization, so forth. Furthermore, this methodology allows the design of experiments under particular conditions to maximize the information that can be extracted from the results and, provided that the model works and the fit of the experimental data is good, it can be used to predict the behavior of the system under different conditions (Álvarez-Murillo et al., 2015b).

1.5.3. Computational fluid dynamics models

Computational fluid dynamics modeling is based on the principles of fluid mechanics, utilizing numerical methods and algorithms to solve problems that involve fluid flows. CFD models attempt to simulate the interaction of liquids and gases where the surfaces are defined by boundary conditions. They also track the flow of solids through a system. These models employ the principles of the Navier-Stokes equations. Simulations are then conducted by solving the equations iteratively as either a steady-state or transient condition (Tillman et al., 2012). Three-dimensional (3D) computational models offer a versatile approach to study the complete descriptions of space and time variations inside the reactor, combines kinetics reactions with mass, temperature, and velocity fields to produce an accurate simulation of full-scale applications. Practical and intuitive visual analysis of results can help us determine, for example, transport of dissolved components, rates of energy dissipation, biomass particle trajectories inside the de reactor, and determine volumes of high mixing intensity and stagnant zones, based on reactor geometry and operating conditions. These models provide an accurate picture of the processes taking place in the HTC reactor and verify the validity of the 0D kinetic model and constant temperature assumption. However, the versatility of three-dimensional models has disadvantages because errors may occur for simple models or simplified boundary conditions; also, computation time may extend for large models and complex geometries. Every CFD problem has the same workflow, which can be divided into three basic steps: (1) Pre-processing, which includes preparing geometry and meshing the geometry. (2) Processing: specifying the numerical parameters, i.e., setting up solver parameters, discretization schemes, setting boundary conditions, initial conditions, defining the properties of different phases (gas, liquid, and solids), and selected numerical method on the calculation mesh. (3) Post-processing: The results of calculations are visualized, and the major part of any numerical simulation is interpreting the results; this is done in post-processing (Blocken and Gualtieri, 2012; Gyurik et al., 2019; Román et al., 2018). The CFD solution's accuracy is strongly dependent on the mesh quality while the computational time increases with the number of mesh elements. When the accuracy is not changing significantly with the increasing number of mesh elements, the calculation can be considered mesh independent (Egedy et al., 2013; Gyurik et al., 2019). Once the results are validated as mesh independent, and the results are validated with experimental data, the CFD model can be used to design, scale up, test, and optimize the process.

1.6. Conclusion

- In the last twenty years, global energy consumption has increased by more than 50%. Most energy consumption comes from fossil fuels (oil, coal, and natural gas). Today, fossil fuels account for more than 80% of the world's primary energy consumption. These fuel resources are not sustainable and cause Green House Gas emissions responsible for global warming. Clean and sustainable fuels productions are the main challenges facing the next energy crisis and global warming. In recent years, it has become clear that climate change is no longer strictly an environmental problem, but an economic and safety problem related to the energy sector, the leading emitter of greenhouse gases.
- Renewable energy can solve the great challenge of the energy future and reduce the environmental problem. There are different renewable energy sources, such as solar energy, wind energy, hydro energy, geothermal energy, and biomass energy. Based on the recent REN21 report, renewables contributed 19.3% to human beings' global energy consumption. This consumption is divided into 8.9% from traditional biomass, 4.2% as heat energy (modern biomass, geothermal and solar power), 3.9% hydropower, and 2.3% is electricity from wind and other renewable energy. The exploitation of these

renewable energy has its advantages and some disadvantages due to the current technology available.

- Hydropower has many benefits over most other forms of renewable or sustainable energy. High reliability, proven technologies, high performance, relatively low operation, and maintenance costs, and the ability to easily respond to load changes are only a few of them. Many hydropower plants are built next to reservoirs, which provide the city with electricity, flood protection, and recreational opportunities. However, the high initial facility costs; reliance on precipitation (no control over the volume of water available); changes in stream regimens can impact fish, vegetation, and biodiversity by altering stream flows, flow patterns, and temperature; inundation of land and wildlife habitat; and relocation of people living in the reservoir area are only a few of the disadvantages of hydropower.
- Solar energy is non-polluting and does not create greenhouse gases, such as oil-based energy, nor does it create waste that must be stored, such as nuclear energy. It is also far quieter to create and harness, drastically reducing the noise pollution required to convert energy to an application form. The main disadvantage of solar energy is its high cost. Despite technological advances, solar panels continue to be expensive. Even if the panels' expense is not taken into account, the device used to store and use the energy can be very expensive. Geothermal power operations produce few emissions. The disadvantages of geothermal energy power plants are their location since it is difficult to locate suitable sites for these power plants. The number of places where geothermal power plants can be built is minimal.
- Bioenergy can minimize greenhouse gas emissions, reduce reliance on oil, and benefit local agriculture and forest product sectors. Agro-industrial wastes, urban wastes, and other biomass feedstocks are the most common biomass feedstocks for energy production. Corn grain (for ethanol) and soybeans are now the most widely used feedstocks for biomass fuels (biodiesel). The planting and use of specific energy crops, such as fast-growing trees and grasses, as well as algae, are among the long-term plans. Additionally, bioenergy can also be used, stored, and transported in different forms such as solids, liquids, and gases, depending on the transformation technology. Nevertheless, bioenergy production is very complex, involving complex chemical reactions, different transport phenomena, and different reactor structures. The study of this process in a laboratory and pilot plant is very tedious and expensive. For this reason,

including tools such as modeling and simulation can be necessary and complementary to experimental studies. Besides, this contributes to the design, operation, optimization, and control of the process. Several mathematical models have been described to simulate the biomass-to-energy process, and these models include kinetic models, experimental design models, and CFD models. Each type of these models has its advantages and disadvantages, as the models have different approaches to handle the complicated process involving hydrodynamics, heat and mass transfer, and various chemical reactions.

Chapter2 RESEARCH APPROACH

2.1. Justification

The clean and sustainable fuels productions are the main challenges facing the next energy crisis and global warming. In recent years, it has become clear that climate change is no longer strictly an environmental problem, but an economic and safety problem related to the energy sector, which is the main emitter of greenhouse gases.

In the last twenty years, the global energy consumption has increased by more than 50% (BP, 2017). The majority of consumption comes from the fossil fuels (oil, coal and natural gas). In fact, today, fossil fuels satisfy more than 80% of the world's primary energy consumption (BP, 2017). However, the percentage contribution of renewable energy to global demand has remained almost constant over the last 20 years.

Additionally, the continued growth of agro-industrial waste such as *Agave Salmiana* bagasse, avocado stone and cacao shell can represent a serious environmental problem. In Mexico, it is estimated that millions of tons per year are generated in these biomasses (Chávez-Guerrero and Hinojosa, 2010; García-Fajardo et al., 1999; González-Alejo et al., 2019). Besides, their nature represents a major problem. Therefore, most of the waste generated is incinerated to reduce its volume to ashes and facilitate its management.

Consequently, the main objective of this project is to determine the appropriate technology and conditions for converting these biomasses (*Agave salmiana* bagasse, avocado stone and cacao shell) into fuels and high added value chemical products. To realize this project, studies of HTC of these biomasses will be carried out. The development of thermochemical processes for biomass conversion and proper equipment design requires knowledge and proper understanding of the several chemical and physical mechanisms which interact in the thermal degradation process. Mathematical modeling and simulation of the HTC reactor and simulation of the pyrolysis and gasification processes represent a very useful tool for understanding the operating condition of these processes. The performance of this process is highly dependent on transport phenomena and chemical reactions. Understanding these transport phenomena and kinetics of chemical reactions in the context of real biomass will facilitate their optimization and control of the products, the results of which can be used in the design and control of large-scale converters. This study comprises an experimental part and a simulation of the different processes. Four typical biomass species have been selected for the processes. These are *Agave salmiana* bagasse, avocado stone, cacao shell, and cellulose.

2.2. Hypothesis

Through the process of thermochemical conversion, agro-industrial waste such as *Agave salmiana* bagasse, avocado stone, cacao shell and cellulose can be transformed into products of interest, such as synthesis gas and synthetic fuels, with energy values similar to fossil fuels.

2.3. Research Objectives

2.3.1. General objective

To propose a sustainable alternative for the use of biomass as a renewable energy resource through the thermochemical conversion process, with the help of modeling and simulation of the process and the analysis of the factors that contribute to its viability.

2.3.2. Specific objectives

The specific objectives and approaches of this research are:

- To characterize biomass used in thermal processes
- To study the hydrothermal carbonization process of the biomasses
- To characterize the HTC process liquid in terms of identification and quantification of the intermediate components produced at different reaction temperatures
- The modeling and simulation of HTC reactor during HTC using COMSOL Multiphysics ® (hydrodynamics, heat transfer and kinetics reaction).
- To investigate the effect of reaction time, temperature, and biomass/water ratio on the mass yield, energy density, and combustion characteristics of the hydrochar samples.
- To determine the kinetic and reaction mechanism of HTC process.
- To study the gasification process of biomasses and hydrochars
- To determine and quantify the composition of the pyrolysis and gasification products.
- To determine the kinetic parameters of the pyrolysis process.
- To simulate the pyrolysis and gasification process in Aspen Plus ®
- To simulate the synthesis of the production of synthetic fuels in Aspen HYSYS ®
- To make an energy balance of the hydrothermal carbonization process.

2.4. Methodology of the project

This project consists of two main parts: The first part is the experimental studies of hydrothermal carbonization, pyrolysis, and gasification of the selected lignocellulosic biomasses. The second part consists of modeling and simulation of the experimental parts (hydrothermal carbonization, pyrolysis, and gasification) and a theoretical simulation based on the experimental data of the gasification (simulation of the production of synthetic fuels).

The experimental part of the project was carried out at the Institute of Aerothermal Combustion Reactivity and Environment "Institut de Combustion Aérothermique Réactivité et Environnement- Centre National de la Recherche Scientifique" ICARE-CNRS, Orléans-France. The modeling and simulation of this project were carried out in the Chemical and Food Process Simulation Laboratory (LSPQA) in the Faculty of Chemical Sciences at the Autonomous University of San Luis Potosí (FCQ-UASLP).

The different raw materials of biomass feedstocks, *Agave salmiana* bagasse (ASB), avocado stone (AS), cocoa shell (CS), and cellulose (CEL) was studied to investigate the effect of HTC on lignocellulosic biomass. The liquid by-product from the HTC process at different reaction temperatures was also characterized for the chemical composition. The study results were used for further modeling and simulation to optimize the design of an HTC reactor.

The hydrochars obtained, and the raw biomasses were used in the pyrolysis and gasification process. The products were analyzed and quantified using different analytical equipment. These results were used for the simulation of the chemical process. Subsequently, the syngas obtained were used to simulate a process for the production of synthetic fuels.

This part is only the global approach to address the problem; the specific methodology of each part will be described in detail in each chapter for a better understanding.

GENERAL CONCLUSIONS AND PERSPECTIVES

Conclusion

The objective of this work was to establish a suitable methodology for the conversion of wet biomass into synthetic liquid fuels. Different types of biomasses with high moisture content (mc), such as avocado stone AS (65-70 wt.%), *Agave salmiana* bagasse ASB (>70 wt.%), and cocoa shell CS (10 wt.%). Also, cellulose CEL was used in all studies as model biomass for a comparative study.

The compositional analyses showed different chemical structures of the studied biomasses. The results obtained showed a high content of extractives and lignin in the CS, which gives it a higher energy content. The high content of HHV in CS may be necessary for its use as an energy source. However, its high content of extractive compounds may impede its utilization during the thermochemical conversion process. Perhaps the best method to convert CS to energy is the chemical process due to its high oil content. The chemical characteristics of AS, ASB, and CEL made their comparative studies during the thermochemical conversion process interesting. The AS contains 76.4 wt.% hemicelluloses and 3.6 wt.% cellulose; this is interesting because it can be used as model biomass for hemicellulose. ASB has 43.8 wt. % of hemicelluloses and 40.7wt.% of cellulose; this biomass can be used as a mixture of hemicellulose and cellulose. Finally, the cellulose (CEL) was used to complement the comparative studies of the three biomasses, during the hydrothermal carbonization process, where only cellulose and hemicellulose are decomposed.

According to the total solids yield analysis of the HTC study, the AS and CS decompositions can be divided into four main zones. The initial induction period in the first zone where the reaction rate is relatively slow (up to 160 °C), followed by a maximum loss of total solids yield up to 200 °C for AS and 210 °C for CS. The third zone corresponds to the stabilization zone, dominated by condensation reactions; stability was observed from 200 to 220 °C for AS and 210 to 230 °C for CS. The last zone corresponds to the increase in total solid mass yield. The increase in total solid mass yield is related to aromatization and polymerization reactions. The results of the GC-MS study of the tar solution indicate that the tar contains aliphatic compounds and PAHs. Nevertheless, no PAHs were detected in CS. PAHs in hydrochars may be an impediment to use as a fertilizer since hydrochar is a favorable soil amendment, increasing cation extraction capacity and reducing the bulk density of solids.

Kinetic study of the HTC process indicates that the activation energy of the hydrolysis reaction depends on biomass composition. Indeed, the higher the hemicellulose content, the lower the activation energy. The activation energy of CEL hydrolysis (136.24 kJ/mol) is higher than in the case of AS and AB, which is 63.08 and 85.02 kJ/mol, respectively. Therefore, more energy is required for CEL hydrolysis than for AS or AB. This was also confirmed by the low solid conversion rate of CEL at low temperatures compared to AS and AB. Furthermore, for all biomasses, the activation energy for the formation of furfural and 5-HMF is higher than for forming organic acids, which was by the concentration of these intermediate products.

The application of design of experiments and response surface methodology (DoE/RSM) permitted to relate the process operating conditions to the hydrochar properties, including mass yield and thermal combustion behavior. The optimized HTC process allowed us to increase the energy content of AS from 18.6 to 26.98 MJ/kg and CS from 23.0 to 32.3 MJ/kg at 250 °C and 2 hours of reaction time.

The CFD study shows that the ideal stirring speed to obtain a homogeneous mixture inside the reactor is 550 rpm, given a turbulent regime. The average velocity corresponding to the dispersed phase is 0.24m/s, owing to AS particle's high density. The application of CFD simulation allowed the model construction that describes the heat transfer inside the reactor during the HTC of the AS, taking into account the kinetics of the HTC reaction. The model considers the reactor heat-up time, inside the reactor biomass concentration, and the water thermal properties evolution, and the thermal properties of biomass during the HTC process. This model can be extrapolated for use in any biomass with the known kinetic parameter and ultimate analysis. The CFD simulation results show that the difference between the thermal properties of biomass and water under HTC conditions is negligible. The biomass-to-water ratio has an effect on heat transfer during the HTC process. It is crucial to consider the biomass concentration in the kinetic model of the HTC process and heat-up time. The present modeling approach thus shows a promising way to simulate biomass HTC processes on an industrial scale. In addition, with the help of this model, the enthalpy of the HTC reaction can be determined.

The results obtained in the three models were used in the simulation of the HTC process, pyrolysis and gasification, using AspenPlus®. First, the experimental design models determine the optimal HTC conditions, determining the kinetic parameters. Then, use the kinetic results in the CFD simulation to study hydrodynamics and the effect of transport phenomena. These results would help the scaling up of the biomass conversion process and the design of the plant for the production of clean and sustainable energy.

Additionally, an energy balance was performed for the HTC process, where the results showed that the biomass to water ratio inside the reactor and temperature is a fundamental factor for the process scale up. The overall energy efficiency of the HTC process is as high as 85%, without considering the possible uses of the HTC liquid phase (which contains many valuable compounds), with the energy integration of the HTC process. This efficiency shows that hydrochar can store 85% of initial energy within the biomass after HTC, thus showing that the HTC process is ideal for biomass pretreatment with high moisture content. Also, the study of the economic feasibility of using hydrochar as fuels showed that hydrochar pellets can be competitive with commercial wood pellets, with an initial capital recovery period of less than 4 years in normal condition.

Finally, the experimental results of syngas from the gasification were used to predict the production of synthetic fuels in Aspen HYSYS®. The main products obtained in these studies were gasoline with 19.98%, diesel 8.15%, naphtha 5%, kerosene 5%, liquefied petroleum gases 11.57% and the rest of the product was water.

Perspectives and recommendations

Several scientific perspectives for further research on HTC conversion of biomass into an energy source or other uses emerge from this work:

- To study the behavior of hydrochars in combustion and gasification with different gasifying agents such as steam, pure oxygen, CO_2, son on. Also, to study the isothermal gasification process of hydrochars at temperatures higher than 1000 ºC.
- To study the behavior of hydrochars as fertilizers and base for catalysts to see their efficiency. AS hydrochars are not recommended for use as fertilizer due to their high PAH content.
- It is recommended to use the cocoa shell (CS) for biodiesel production due to its high oil content (>25%).
- Use hydrochars to remove heavy metals and dyes in the water and compare the yield with biochar (char obtained by pyrolysis).

- To exploit the experimental methodology developed in this work to understand the complex steps and reaction mechanism of biomass decomposition in aqueous media by characterizing the solid and analyzing the liquid and gas phases.
- Try to valorize the by-products of HTC and optimize its recovery, as it contains high value-added products (furfurals, 5-HMF, organic acids, and many more). Moreover, the liquid phase of the HTC process represents the main problem related to the application of the HTC process to treat wet organic materials. In this work, two alternatives for treating the liquid generated by the HTC process have been studied (using the liquid to produce biogas or recirculating it into the HTC process).

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Quantification and Kinetic Study of the Main Compounds in Biocrude Produced by Hydrothermal Carbonization of Lignocellulosic Biomass

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ABSTRACT

The biomass hydrothermal carbonization (HTC) reaction pathway to the formation of primary and secondary hydrochar is proposed in this study. Total sugars were the main product in biocrude at low temperature; their concentration decreased as the temperature increased, producing organic acids and furans. Kinetic study reveals that the hydrolysis activation energy increased as hemicellulose content decreased. Indeed, a value of 63.08 kJ/mol was found for biomass rich in hemicellulose (avocado stone) while for biomass composed of a hemicellulose-cellulose mixture (agave bagasse) the value was -85.02 kJ/mol, and for α-cellulose it was -136.24 kJ/mol. Contrastively, the activation energy for furans formation was higher than that for organic acids in any case. A proposed14-reactions mechanism adequately describes the HTC process considering intermediate to final products (R^2>0.98). The higher heating value (HHV) of hydrochars was between 22 and 26 MJ/kg, with an energy densification of 34 to 49 % compared to the corresponding feedstock.

1. Introduction

Hydrothermal carbonization is a method of thermochemical conversion by which wet biomass is heated in a batch autoclave reactor to temperatures from 180 °C to 250 °C, under autogenous pressure of saturated vapor from 1 to 4 MPa and reaction time or holding time from a few minutes to several hours (Liu and Balasubramanian, 2012; Missaoui et al., 2017; Tradler et al., 2018). The main HTC product is hydrochar; however, a large amount of by-product is generated as liquid (biocrude mixed with water) and small gas fractions (Becker et al., 2014). Recently, different biomasses have been investigated to produce hydrochar. Nevertheless, the quality of hydrochar obtained depends principally on the types of biomasses and operating conditions of the process. The hydrochar obtained is a solid material rich in carbon (55–74% carbon), stable, a lignite-like material that is characterized by a high heating value (21.1–30.6 MJ/kg) (Sangare et al., 2020b); its physical, chemical and mechanical properties make it susceptible to different uses. Hydrochar has wide applications; in agriculture, for soil amendment purposes (Kambo and Dutta, 2015), supercapacitor and CO2 capture (Demir et al., 2018), or as a fuel source (Libra et al., 2011). During the HTC process, hydrochar formation can be carried out in two reaction pathways. The formation can proceed from the reaction of the solid-solid pathway known as primary hydrochar (P-HC) and the intermediate products called secondary hydrochar (S-HC). In the HTC process of cellulose, it has been reported that the solid-solid reaction pathway was the dominant reaction due to the large aromatic groups in the hydrochar structure (Falco et al., 2011). However, secondary hydrochar formation may be favored by a high content of 5-hydroxymethylfurfural (5-HMF) in HTC liquid (Chuntanapum and Matsumura, 2009). Furthermore, Paksung et al. (2020) reported that it is not easy to distinguish analytically between P-HC and S-HC; because both appear as a single solid mass of char.

Under HTC process conditions, water behaves like an organic solvent. Indeed, it acts as a catalyst for biomass reactions, such as hydrolysis, decarboxylation, dehydration, condensation, aromatization, and polymerization (Kambo and Dutta, 2015; Volpe et al., 2018). The main products of the HTC process are solid hydrochar and a liquid by-product containing several valuable organic compounds, such as sugars (pentoses and hexoses), furans (furfural and 5-HMF), organic acid mixtures (formic, acetic, lactic), as well asphenolic products and their derivatives (phenol, gallic acid, catechol, and p-cresol) (Fujimoto et al., 2018; Kambo et al., 2018; Kang et al., 2012). The concentration of these compounds depends on the type of biomass and the operating conditions. However, their valorization in biorefineries requires their identification and recovery process, as well as knowing the chemical mechanism of formation and reaction kinetics (Kambo and Dutta, 2015).

The biomass conversion process by HTC has been largely investigated. However, the main challenge remains the process design and the operating conditions optimization. This is because reaction pathway and kinetics are still largely unknown. Even though different approaches are currently used to

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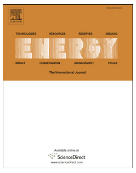

Hydrodynamics, heat transfer and kinetics reaction of CFD modeling of a batch stirred reactor under hydrothermal carbonization conditions

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ABSTRACT

Computational Fluid Dynamics simulation was used to study hydrothermal carbonization of avocado stone (AS) in a batch stirred reactor, using an open-loop controller system. The corresponding simulations were carried out in COMSOL Multiphysics 5.2. The different biomass-to-water ratio was investigated. The hydrodynamic study shows that the ideal stirring speed to obtain a homogeneous mixture inside the reactor is 550 rpm, due to the high density of AS particles (1547.64 ± 27.33 kg/m^3). However, a stagnant zone was observed just below the impeller. To validate the CFD simulations temperature profiles with experimental data, the heat transfer coefficient of the insulator was determined (11.66 W/m^2.K), this value was used to set the heat loss in the CFD simulation. According to the model, the difference between the thermal properties of biomass and water under hydrothermal carbonization conditions is negligible. However, experimentally, an increase in temperature was observed with increasing biomass to-water-ratio; this is due to the global hydrothermal carbonization of AS is exothermic reaction. The heat released during 8 h, including heat-up time, was −7.25 ± 0.32 MJ/kg of feedstock. Finally, a kinetic model was proposed taking into account the influence of temperature, heat-up time, reactor volume, and biomass concentration.

1. Introduction

The production of clean and sustainable fuels is the main challenge of the upcoming energy crisis and climate change. The potential of lignocellulosic biomass as an abundant source of renewable energy. Although there are different processes to convert biomass into energy, its direct use as fuel, faces several challenges (inefficiency of conversion facility, low-energy, biological instability, high moisture content, and so forth [1]. Pretreatment processes are necessary to improve the organic feedstock characteristics for most biomass to energy conversion processes.

Hydrothermal carbonization (HTC), also known as a wet thermochemical process, emulates the natural process of coalification, virtually no pretreatment is required [2]. HTC is a thermochemical conversion process by which biomass is converted into carbonized material (hydrochar), liquid (bio-oil mixed with water) and small fractions of gases; this process is performed in the temperature range of 180–250 °C under autogenous saturated vapor pressure between 10 and 40 bars, and a residence time range from a few minutes up to several hours [3–5]. The performance and composition of the final products are directly related to biomass type, and process conditions such as reaction temperature, residence time, and water-to-biomass ratio. HTC process has investigated distinct types of biomass; sugarcane bagasse [6], corn cob [7], tomato waste [8], olive pomace [4], olive stones [9], and so forth. Most of these biomasses are agro-industrial wastes, in Mexico, one of the most significant agro-industrial wastes generated is avocado stones (AS). The products of HTC can be used directly as a solid fuel, soil amendment, and so on [10–12].

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Research article

Modeling of *Agave Salmiana* bagasse conversion by hydrothermal carbonization (HTC) for solid fuel combustion using surface response methodology

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Abstract: Hydrothermal carbonization (HTC) of *Agave Salmiana* bagasse was investigated to assess the potential of hydrochar as an energy resource. The effect of operating conditions on the mass yield and the energy quality of hydrochar was examined by varying the temperature and the holding time over the ranges of 180–250 °C (T) and 0–60 min (t), respectively. These parameters were screened using the response surface methodology through a Doehlert design. Performances of HTC were assessed on the basis of the hydrochar mass yield higher heating value ultimate and proximate analyses. In the studied domain, the modeling results indicated that the hydrochar mass yield varies between 45% and 86% and higher heating valuesfrom18 to 23 $MJ.kg^{-1}$, which is similar to that of peat. In addition, the volatile matter and fixed carbon fractions of hydrochars ranged from 54 to 80% and between 12 and 36%, respectively. Energy yield modeling indicated that the mass yield is the most influent parameter. The maximal energy yield value was obtained at 180 °C with time equal to 0 min. Globally, the evolution of H/C ratio is amplified for temperatures greater than 215 °C by increasing the holding time from 30 to 60 min. For O/C ratio the maximal variation is below these conditions. It is concluded that increased hydrothermal carbonization conditions favor dehydration reactions, while decarboxylation reactions are favored in mild HTC conditions. The combustion characteristics such as ignition peak and burnout temperatures were significantly modified for hydrochars. The model results

In the process of publication

Kinetic Studies of Hydrothermal Carbonization of Avocado Stone and Analysis of the Polycyclic Aromatic Hydrocarbon Contents in the Hydrochars Produced.

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Abstract:

Model-free and model-fitting kinetic approaches were used to investigate the hydrothermal carbonization of avocado stone. The kinetic parameters and reaction mechanism were determined in two temperature zones, from 150 to 210 ºC and 210 to 250 ºC. In the first zone, the decomposition of avocado stone during the hydrothermal carbonization process followed a random nucleation reaction mechanism (Avrami-Erofeev-1) with the activation energy of 87.84 ± 3.28 kJ/mol. In contrast, in the second zone, it followed a first-order reaction model, and the activation energy was 230.96 ± 28.84 kJ/mol. Analysis of PAHs with gas chromatography-mass spectrometry showed that the number of PAHs in the hydrochar increases with an increase in temperature from 190 to 250 ºC. The 3-4 rings PAHs were dominant in the hydrochars prepared at a temperature between 230 and 250 ºC, while two rings were largely prevalent in the hydrochar obtained at low temperatures.

Keywords: Avocado stone; Hydrothermal carbonization; Kinetic model; PAHs

Pyro-gasification of Biomass: Use of TGA Coupled to μ-GC for Analysis and Quantification of Gas Evolution.

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ABSTRACT:

This study is focused on the pyro-gasification of agave salmiana bagasse (AB) and cellulose by employing a combined thermogravimetry and gas chromatography experimental setup. The thermogravimetric analysis (TGA), and derivative thermogravimetry (DTG) were performed to examine the thermal degradation of both biomasses. The product gas composition (CO, CO_2, CH_4 and H_2) produced during pyro-gasification was analyzed systematically by using an online and offline TCD-micro gas chromatograph (μ-GC) analyzer. The influence of different air to biomass ratio (ABR) and heating rate on product gas composition was investigated during AB pyro-gasification. The thermal behavior and the evolution of the gases produced during the pyrolysis of both biomasses showed that significant part of CO and CO_2 were mainly released at a temperature below 450 °C and followed almost the same pattern. The CH_4 started to evolve at a temperature above 300 °C, while the maximum H_2 production was obtained between 600-700 ºC. The experimental results showed that with an increment in ABR from 0.125 to 1.0, the combustible gases composition of H_2, CO, CH_4 decreased in the range of 26.27–7.02 mol.%, 27.38–11.39 mol.%, 5.92–2.07 mol.% while the fraction of non-combustibles gases was increased from 14.78 to 19.8 mol.% and 24.56 to 59.71 mol.% for CO_2 and N_2, respectively.

Hydrothermal Carbonization of biomass: Laboratory Trials, Energy balance, Process Simulation, Design and Cost Analysis*

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ABSTRACT:

The energy balance of the hydrothermal carbonization (HTC) process is fundamental to determining the application of hydrochar as an energy source. In this work, an HTC process is designed and modeled from experimental data obtained for two representative agro-industrial wastes: avocado stone (AS) and cocoa shell (CS). The process was simulated, including all the steps and equipment necessary to convert these biomasses into dry hydrochar and pellets. The energy balance study of the process showed that the energy efficiency of the process can reach 83.12% for AS and 71.36% for CS, while the thermal efficiencies were 4.12 for AS and 4.49 for CS. The result of the simulation allowed that the HTC process is economically feasible and competitive price of pelletized hydrochar compared to palletized bulk pine wood. Moreover, under the conditions studied, the initial capital recovery period (CRP) is lower at 3.8 years for each of the biomasses. This study could encourage the development of HTC plants and, therefore, the market for hydrochar pellets.