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Gasification of Biomass Feedstocks in CREC Riser Simulator

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A thesis submitted in partial fulfillment of the requirements for the Master of Engineering Science degree in Chemical and Biochemical Engineering

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ABSTRACT

The recent discovery of an increase in greenhouse gas levels, specially CO₂, raises concerns regarding the quality of life for future generations. Renewable energy sources such as biomass could contribute to solve this issue. Effective use of this available biofuel would improve the world's ability to reduce toxic air emissions, greenhouse gases, and its dependence on oil supply. Gasification arises as a potential alternative for converting biomass into a clean fuel. With the addition of steam as a gasifying agent, the problem on nitrogen in the syngas is neglected.

This research work investigated the effects of temperature, oxidizing agent and biomass composition in the quality of syngas from steam biomass gasification. Gasification of wood pellets, broza and bark was carried out with changes in temperature from 550°C to 600°C. The atmosphere for gasification was also varied using He and CO₂. Gasification of biomass materials are performed in a CREC Riser Simulator Reactor Unit under the expected conditions of a twin circulating fluidized bed gasifier.

Steam gasification performance was affected by changes in temperature, as well as endothermic reactions involved in the process. Thus, higher temperature favored steam reforming and carbon conversion with modest changes due the biomass type. The atmosphere in which gasification was carried out was found also to have an impact in the produced syngas. Gasification of biomass under a water-CO₂ atmosphere reached higher dry gas yields compared to steam gasification under water-helium. It is hypothesized that the decrease in the H₂ yield was driven by the reverse water gas shift reaction.

This study also revealed the importance of the catalytic effect of the ash content in biomass. Ash content affects the quality of syngas, with high-quality synthesis gas (H₂/CO >2) suitable for direct alcohol synthesis, obtained under water-helium atmospheres.

Changes in the gasification product yields and their variation with operating parameters are found to be in general agreement with the chemical equilibrium predictions. Moreover, product yields approach chemical equilibrium as the ash content in biomass is larger. In this respect, syngas yields from water-helium and water CO₂ gasification of broza, with an ash content of 12% were found to be close to the expected syngas yields at chemical equilibrium.

Keywords: *Steam gasification of biomass, steam reforming, syngas quality, water gas shift, thermodynamic model, Broza.*

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Nomenclature

CREC	Chemical Reaction Engineering Center
FCC	Fluidized Catalytic Cracking
FB	Fluidized bed
GC	Gas Chromatography
GC/TCD	Gas Chromatography/Thermal Conductivity Detector
HHV	Heat of Combustion (MJ/m ³)
ICAFC	Instituto del Café de Costa Rica
K	The equilibrium constant
MW	Molecular Weight
OECD	Organization for Economic Co-operation and Development
S/B	Ratio between Steam and Biomass feedstock
Syngas	Synthesis Gas
TCD	Thermal Conductivity Detector
TOC	Temperature Programmed of Desorption
UWO	The University of Western Ontario
WGS	Water-gas shift reaction
CBCC	the Conversion of Biomass Contained Carbon
Wt%	Weight percent
y_i	Mole fractions of species i
ΔC_p	Standard Heat Capacity change (J/K)
CH_xO_y	Unit composition of biomass
ΔG°	Standard Gibbs energy change of reaction (kJ/mole)
ΔG_{298}°	Standard Gibbs free energy change of formation at 298 K (kJ/mole)
ΔH°	Standard enthalpy change of reaction (kJ/mole)
ΔH_{298}°	Standard enthalpy change of formation at 298 K (kJ/mole)

Y_i Incremental Yield

Subscripts

C_2H_4 Ethylene

C_2H_6 Ethane

α Product H_2 /biomass feed ratio (mole/mole)

β Product CO /biomass feed ratio (mole/mole)

γ Product CO_2 /biomass feed ratio (mole/mole)

ψ Product H_2O /biomass feed ratio (mole/mole)

ζ Product CH_4 /biomass feed ratio (mole/mole)

Ω Product C_s /biomass feed ratio (mole/mole)

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CHAPTER 1

1. Introduction

1.1. Background

In modern society, energy is used for activities including transportation, heating, cooling, industrial and agricultural production. Therefore, it is important to guarantee the energy supply for future generations. The US Energy Information Administration prepared an International Energy Outlook in 2010 that predicts a 50 percent increase consumption worldwide by 2035. [1] Estimation involved the participation of the Organization for Economic Co-operation and Development (OECD) member countries as well as non-OECD members. Studies showed that the future energy consumption would come from non-OECD countries which are mostly developing countries looking forward to large urbanization. At the moment, in these countries, rural populations are mainly large yet access to electricity and power is limited.

It is estimated that the energy requirement per person in these rural communities is less than 1 percent that of an average person in the United States (0.08 kWh/day/person). [2] Even this small amount of energy can be quite costly and hard to access in these rural areas. On the other hand, due to geopolitical reasons, energy supply is still one of the concerns in the future. For this reason, energy production utilizing regional resources is ideal for developing countries.

Renewable energy is derived from naturally replenishing resources such as the sun, wind, rain, tides and geothermal heat. While domestic fossil fuels are not accessible in many countries, a wide variety of renewable energy sources is distributed much more evenly. Biomass energy is plentiful in the ecosystem. It is derived from plants. Plants convert solar energy and soil elements via photosynthesis into complex organic molecules.

Biomass represents all organic biological material composed mainly of carbon, hydrogen and oxygen. The main sources of biomass for energy usage are wood, agricultural products and municipal waste. Gasification, a thermochemical conversion of biomass, is a process of converting carbon based fuels into simpler gaseous fuels.

Biomass has the potential to be one of the world's largest energy sources. With a wide variety of feedstocks, the annual biomass is predicted to be 1500 EJ/yr by 2050. However, nowadays, biomass represents only 10% of the world's energy supply (45 EJ/yr). Figure 1.1. illustrates a biomass breakdown by percentages.

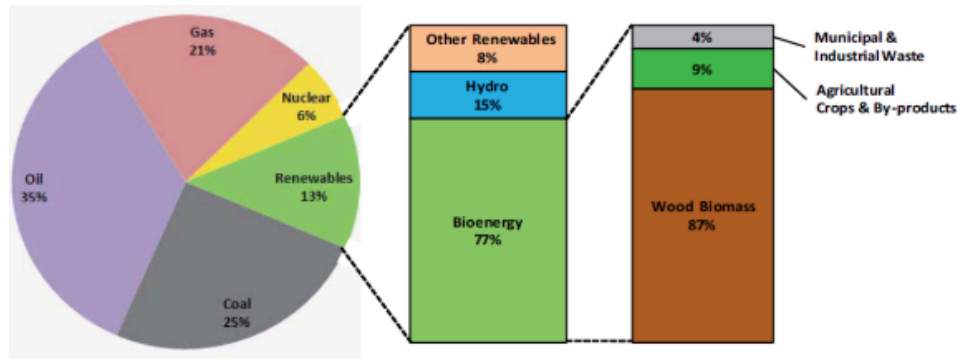


Figure 1.1. Biomass Contribution Towards World Energy Supply [3]

According to Figure 1.1, wood represents the largest percentage of biomass. This is mainly due to its use in domestic heating and in power plant combustion. As many of the newer technologies and technology enhancement enter the market, this balance will begin to shift. Gasification is an oxygen-limited technology that transforms biomass into a synthesis gas (syngas) with several advantages over thermochemical conversion processes. When gasifying biomass, the gaseous fuel burns more efficiently and produces less emissions to the atmosphere.

A gasification process is a series of temperature dependent thermochemical conversions of carbonaceous material. The kinetics of these reactions varies between the different types of gasifiers, but the fundamentals remain the same. In a typical gasifier, the process is initiated with the dehydration of biomass. The resulting steam evaporated from the biomass is drawn into the gas flow, and depending on the temperature may be involved in a number of reactions. Biomass undergoes pyrolysis, which occurs in the presence of an oxidizing agent such as air or steam. Pyrolysis, involves the breaking down of the biomass into char, gaseous H_2 , CH_4 and tars.

In the presence of a reducing agent, a combustion process also occurs. The volatiles and char react with the gasifying agent to form carbon dioxide and release heat. This heat is used to sustain pyrolysis and cause the subsequent thermochemical reactions. Char reacts with steam to produce H_2 and CO . Simultaneously, the reversible water-gas shift reaction, is an equilibrium reaction that sets the concentrations of the gasification products to concentrations determined by chemical kinetics and thermodynamics.

There are several types of gasifiers. This study focuses on the novel Riser Simulator Reactor, an internal recycle batch reactor with an impeller located above the biomass basket. The high speed rotation of the shaft induces a recirculation gas flow upward through the bed. The result is a fluidized state of the solids.

1.2. Scope of the Study

The present study focuses on the evaluation of the effects of temperature, oxidizing agent and biomass composition on the syngas quality from steam biomass gasification. The process temperatures studied of 550°C and 600°C, are proposed considering the energy efficiency, ash agglomeration and chemical reactions involved in the gasification process. A study of He-water and CO₂-water as gasifying agents is required. The twin fluidized bed gasifier unit, simulates the same reaction regime as in an industrial riser, which makes the Riser Simulator a suitable technology for large scale biomass processing.

Three biomass species were involved in this study. The first biomass feedstock analyzed were wood pellets provided by CANMET Energy. The applicability of steam gasification to Broza or coffee pulp provided by ICAFE Costa Rica was also considered. Bark, a wood residue provided by KMW a London, Ontario based company was also investigated as an alternative feedstock for syngas production.

This research work also establishes structure-reactivity relationships of biomass feedstocks using characterization and gasification results. The best biomass material performance is determined in terms of conversion, yield and synthesis gas quality. In addition, the performance of this biomass adjusts to the equilibrium predictions of a thermodynamic steam gasification model developed in this study.

1.3. Thesis Structure

The major findings of this study are organized in the following chapters:

- Chapter 2: Provides a review on biomass characteristics, gasifier design and operation and biomass steam gasification.
- Chapter 3: Describes the experimental methods and equipment used to carried out this study.
- Chapter 4: Demonstrates the effect of operational and non-operational variables in the steam biomass gasification process.
- Chapter 5: Reports the thermodynamic model for steam gasification of biomass developed in this study. The experimental gasification results with the variation of operating parameters are also compared with the yield equilibrium predictions.
- Chapter 6: Provides concluding statements and recommendations for future work.

CHAPTER 2

2. Literature Review

The objective of this chapter is to review the recent technical literature on biomass gasification and its reaction mechanisms. It is apparent that the effectiveness of biomass gasification is strongly influenced by the operational process variables and feedstock properties. Thus, this literature review chapter considers the effect of these variables.

2.1. Introduction

Energy plays an important role in the economy of every country. For a long time, oil supply has raised further concerns due the instability of the large world oil reserves in middle eastern countries. The fear of energy security was intensified in the 1970s oil shortage crisis. This motivated the development of sustainable renewable energy technologies. [4]

Even though fuel scarcity was an issue in the past, nowadays, in several rural areas in North America and South America, the effect of the continues fuel production demand has influenced the world economy.

Recent findings of greenhouse emission level increments in the earth's atmosphere represent a risk to the quality of life of future generations. To reduce the concentration of gases in the atmosphere and fight global warming, 169 nations signed the Kyoto protocol in 2005. The Kyoto protocol is an international treaty that aims to reduce emissions of CO₂ from fossil fuel combustion. [5]

2.2. Historical Background

The concept of the gasification process was used in blast furnaces over 180 years ago to produce combustibles from organic feeds. The alternative of using this gas for energy purposes was encountered and emerged in Europe. European gas systems fed charcoal and peat as feedstocks for their use in heating and power generation. [6]

During the 20th century, petroleum became an important fuel, acquiring wider use. However, World War II led to its insufficiency. The lack of available oil triggered research into new alternatives to fossil fuels. Therefore, the process of gasification was reintroduced as a potential alternative to generate energy in current and new chemical plants. By 1945, gasification systems were supplying power to transportation machinery. [7]

When World War II was over, the availability of cheap fossil fuels caused the gas industry to decline. Nevertheless, Sweden conducted research in the area of producer gas technology in 1956; including the development of use of gasifier emergency plants for the country [8]. Thus, studies into suitable designs of wood gasifiers, essentially for transport use, were carried out at the National Swedish Institute for Agricultural Machinery Testing and are still in progress.

2.3. Theory of Gasification

Gasification is the controlled partial oxidation of a carbonaceous material. It is achieved by supplying less oxygen than the stoichiometric requirement for complete combustion. A central process between combustion (thermal degradation with excess oxygen) and pyrolysis (thermal degradation in the absence of oxygen), proceeds at temperatures ranging between 600°C and 1500°C. Depending on the process type and operating conditions, low- or medium-value producer gas (which is a combination of combustible and non-combustible gases) is formed. [9]

Gasification technology has been widely used to produce commercial fuels and chemicals. Current developments in the chemical manufacturing and petroleum refinery industries show that the use of gasification facilities to produce synthesis gas will continue to rise. A striking feature of the technology is its ability to produce a reliable, high-quality syngas product that can be used for energy production or as a building block for chemical manufacturing processes. [10]

In addition, it includes the ability to house a wide variety of gaseous, liquid, and solid feedstocks. Conventional fuels such as coal and oil, as well as low- or negative-value materials and wastes such as petroleum coke, heavy refinery residuals, secondary oil-bearing refinery materials, municipal sewage sludge, and chlorinated hydrocarbon byproducts have all been used successfully in gasification operations. [11]

Biomass and crop residues also have been gasified successfully. Gasification of these materials has many potential benefits over conventional options such as combustion or disposal by incineration. [12]

2.4. Biomass Properties

Biomass is a hydrocarbon material that consists mainly of carbon, hydrogen, nitrogen and minerals. It is considered an ideal renewable resource given its low ash and sulfur content and its contribution to lowering the level of carbon dioxide in the atmosphere. [13]. Because of its solid

form, there are promising processes in industry aiming to convert biomass to more conventional energy forms such as gas or liquid fuels.

Living species such as plants and animals form biomass from the instant a seed sprouts or an organism is born. Through photosynthesis, plants metabolize atmospheric carbon dioxide using sunlight, and grow as a result. On the other hand, animal growth is accompanied by the ingestion of food from biomass. Furthermore, biomass is a renewable resource reproduced in a considerably short time compared to fossil fuels. [14]

A great amount of biomass is formed through photosynthesis ever year. When the biomass is burned, the carbon dioxide released to the atmosphere represents the amount that the plants had absorbed previously from a few years to a few hours. Thus, biomass is considered a carbon-neutral fuel since it doesn't add any extra carbon dioxide to the earth's atmosphere. [15]

Even though there is a great amount of available biomass on the earth, only 5% can be mobilized to produce energy. This quantity is still large enough to provide about 26% of the world's energy consumption, which is equivalent to 6 billion tons of oil

Biomass covers a large range of natural products from plants to animals. Once harvested biomass consists mainly of 3 groups: cellulose, hemicellulose and lignin. Conversion of these lignocellulosic materials requires a thermochemical process or gasification.

Table 2.1. reports two types of harvested biomass and the potential products obtained through their thermochemical conversion [16]. It is important to mention that production of transportation fuels such as ethanol from corn, require large quantities of this good. Thus production of energy from corn like feedstocks may not be viable for various economic, social and political reasons, with only nonfood feedstocks being available.

Table 2.1 Sources of Biomass

Farm Products	Corn, sugar cane, wheat, sugar beet and others	Produce ethanol
	Rape seed, soybean, palm sunflower seed, Jatropha and others	Produce biodiesel
Lignocellulosic materials	Straw or cereal plants, husk, wood, scrap, slash	Produce ethanol, bioliquid and gas

Biomass being a solid creates an important barrier to a rapid conversion from fossil to biomass fuels. Some of the challenges of biomass management are related to handling, storage and transportation. The gasification process serves as a biochemical conversion of solid biomass into liquid and gaseous fuel capable of reducing these difficulties.

2.4. Biomass Potential for Energy Production

At the turn of the 21st century, many researchers together with the oil and gas industry showed strong commercial interest in biomass gasification. This is the result of a number of identified environmental and sociopolitical benefits.

2.4.1. Biomass Renewability

One of the major disadvantages of fossil fuels like oil, coal and gas is their lack of renewability. Biomass, on the contrary, is in principle a fully renewable resource assuming adequate sun irradiation and fertile land availability. [17]

In fact, conversion of biomass from plants, provides carbon-neutral energy and reduces the greenhouse effect. A recommended approach is to provide adequate plant replacement following cutting, as is done in the pulp industries. In this respect, fast-growing plants like switch grass and *Miscanthus* are being considered as a fuel for new energy projects. These plants have very short growing periods, taking place in just a series of months [18].

2.4.2. Environmental Benefits

With global warming, the importance of reducing greenhouse gas emissions has become a great societal and individual responsibility. Biomass represents a good alternative as a potential fuel since it makes no net contribution to carbon dioxide emissions in the atmosphere. [19]

One of the environmental benefits related to the biomass conversion is the zero net addition of CO₂ to the atmosphere and the little amount of sulfur emitted. Furthermore, CO₂ emissions from the gasification are slightly less than those from its combustion and this on a unit heat release basis. [20]

Moreover, fresh biomass sulfur content ranges from a small amount to no sulfur. Variation of the sulfur content depends on the type of biomass. While biomass derived feedstocks such as waste agricultural products do contain sulfur, the amount of sulfur in the fresh biomass is essentially zero. [21]

2.4.3. Sociopolitical Benefits

In order for a biomass-based power plant to be economically feasible, the biomass supply needs to come from a reduced distance. This shows the importance of developing associated industries in a close range area where biomass growth, biomass collection and transportation take place. In addition, it is estimated that a biomass power plant creates up to 20 times more employment than a coal-based plant. Hence, the biomass industry has a positive impact on the local economy. [22] [23]

The use of biomass as an energy source, may also have a political dimension. Biomass-based fuel technology reduces countries reliance on imported fossil fuels and us dollar currency. Due the global political situation, around fossil fuels supply, local production of energy from biomass may thus, provide a much more reliable energy availability for third world countries. [24]

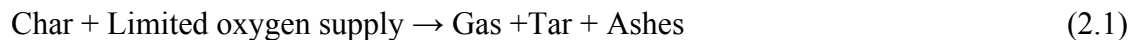
2.5. Biomass Gasification

Gasification processes convert biomass into combustible gases containing a high fraction of the energy originally present in the biomass. Generally, gasification can convert 60% to 90% of the energy in the biomass into fuel. Gasification processes occurs in the presence of a gasifying agent, such as steam and CO₂. It can be either direct (using air or oxygen to generate heat through exothermic reactions) or indirect (transferring heat to the reactor from the outside). [25]

This thermochemical conversion of biomass fuel uses high temperatures, involving partial oxidation of the fuel elements. The product syngas consists mainly of carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂), water vapor (H₂O), methane (CH₄) and nitrogen (N₂). However, gasification products include small quantities of hydrocarbons and contaminants, such as carbon particles, tar and ash.

Gasification takes place in a reactor in the presence of an oxidizing agent. Inside the gasifier, a set of endothermic reactions occur between the gas and the solid fuel which are devolatilized excluding the oxygen.

In biomass gasification, the material is heated, causing a series of physical and chemical changes in the volatile products and carbonaceous residues. The amount of volatiles produced and their compositions depend on the reactor temperature and the characteristics of the fuel materials. [26] The final product composition gas depends also on the chemical equilibrium of different reactions. Syngas composition and carbon conversion are mainly attributed to the water-gas shift reaction. The gas-phase reaction that best represents the gasification of char with reactive gases is shown in equation (2.1):



When char is gasified in the presence of steam, the gas produced is composed mainly of CO, CO₂, H₂ and CH₄. Steam is usually added from an external source. Operating at lower temperatures, lower heating rates and longer reaction times, makes secondary reactions more prevalent. Under these conditions, primary volatile products remain extended periods in the reaction zone contributing to tar formation. On the other hand, at high temperatures, high heating rates and shorter reaction times allows primary volatile products to be removed quickly reducing as a result, tar yield. [27]

2.5.1. Steam Gasification

In order for steam to act as an oxidizing agent and given the overall endothermic nature of steam gasification, an energy supply is required. Thus, a mixture of steam and air are typically co-fed as gasifying agents. In this respect, combustion of a biomass fraction with the oxygen from air has provides the required energy. Furthermore, the elevated temperature helps in the devolatilization process of biomass to produce various gases. In particular, steam reacts with carbon monoxide to produce hydrogen and carbon dioxide, with this water gas-shift reaction being one of the main ones during steam gasification. [28] [29]

Compared to air gasification, steam gasification produces a higher energy content producer gas. Boateng [30] determined the effects of reactor temperature and steam to biomass ratio on producer gas composition and energy recovery. The produced gas was found to have a heating value ranging from 11.1 MJ/m at 700°C to 12.1 MJ/m at 800°C. Energy recovery varied from 35-59% within the same temperature range.

Hoveland [31] studied corn grain-dust gasification in a fluidized bed gasifier using steam as a fluidizing agent and a mixture of sand and limestone as the bed material. The produced gas dry yield increased from 0.13 m/kg at 867 K to 0.73 m/kg at 1033K. The gas heating value increased from 9.4 to 11.5 MJ/m within the same temperature range.

Walwender [32] gasified alpha cellulose in a bench-scale fluidized bed reactor using steam over a temperature range of 873-1073 K. The major components of the produced gas were H₂, CO, CO, and CH₄ and the volumetric gas yield was 0.5-1.4 m/kg. The average gas higher heating value was 11.8 MJ/m. The energy recovery as well as carbon conversion ranged from 32-90%.

Walawender [33] gasified straw with steam in a fluidized bed reactor with changes in the temperature ranging from 552-757°C. The fraction of feed converted to gas ranged from 32% at 552°C to 73% at 757°C. The heating value of the gas exhibited a parabolic temperature variation with a maximum value of 16.3 MJ/m obtained at 672°C. There was a continuous external energy input to the system, which resulted in higher than expected heating values.

The gasification of rice husk was studied by Chen and Day [34] over a temperature range of 873-973K in a fluidized bed reactor. The bed consisted of fused alumina sand. The fluidizing medium was heated steam. As a result of this set-up, the gas yield increased from 0.38 to 0.55 m/kg and the heating value varied from 16.8 to 18.5 MJ/m. Over this temperature range, H₂, CH₄, CO, and CO₂ contents experienced significant augmentations.

2.5.2. Mechanism of Gasification

In gasifiers, as air is circulated through the fuel bed, drying, pyrolysis, gasification and oxidation zones develop in the reactor. The location of these zones in the gasifier depends on the relative movement of the fuel and air. These zones are mainly differentiated by the variety of reactions or processes occurring and the temperature regimes in these areas. The depth and relative importance of each zone depends on the chemical composition of the feedstock, its moisture content and particle size, the mass flow rate of the gasifying agent, and the temperature. [27]

2.5.2.1. Drying Zone

The drying zone receives its energy through heat transfer from other zones. The rate of drying depends on the temperature, velocity, and moisture content of the drying gas. Other influential factors are the biomass surface area and biomass moisture content. As the untreated biomass enter the drying zone, their internal temperature is increased to 100-150°C. [28] Low density materials change dimensions slightly due to shrinkage and compression whereas negligible size changes are experienced by feedstocks with high densities. No chemical reactions take place in this zone.

2.5.2.2. Devolatilization Zone

Heat transfer from the neighboring hot reduction zone causes devolatilization of the biomass fed. Temperature in the devolatilization zone increases rapidly due to the large temperature difference between the fed biomass and the hot gases. In this zone, the rate of temperature rise is controlled by heat transfer. As the fed biomass moves through this zone, rapid charring and reduction in their volumes results, causing considerable variations in the structure as well as in the physical and thermal properties of the fed biomass. [35]

The products from the devolatilization zone are mainly permanent gases, tar and char. Production of undesirable tars should be controlled and minimized in gasifiers. The amounts of each of these

reduction zone products vary depending on the zone temperature, rate of heating, biomass structure, and composition. [36]

2.5.2.3. Oxidation Zone

In the oxidation zone, there are a number of chemical and physical changes occurring as the oxygen in the air, is introduced into the fuel bed material. The oxygen burns a portion of the carbon in the fuel material until almost all free carbon is released. Oxidation processes occur usually at temperatures of 975 to 1275 K. [37]

Heterogeneous reactions between oxygen and a solid fuel, produce CO and this when air is used as a gasifying medium. In addition, the oxygen content decreases from 21 to 0%, while the CO₂ production percentage increases proportionally [38]. Due to the exothermic nature of the reactions involved in this zone, the temperature reached is the highest within the whole process. The main reactions in the oxidation zone are listed below.



2.5.2.4. Reduction Zone

In the reduction zone, a number of high temperature chemical reactions occur in the absence of oxygen. [39] Assuming a gasification process using biomass as a feedstock, the first step of the process is the thermochemical decomposition of the lignocellulose components with the production of char and volatiles [40] [41]. The main gasification reactions that occur in the reduction process are mentioned below:



The main reactions listed above show the heat requirements during the reduction process are considerable. As a result, the temperature of the gas decreases in this reduction zone. If complete gasification occurs, all the carbon is burned or reduced to carbon monoxide, with some mineral matter eventually vaporized. The unconverted biomass remains as ash and char. [42]

2.6. Gasifier Types

A variety of biomass gasifier types have been developed. They can be grouped into three major types: updraft, downdraft and fluidized bed gasifiers. Differences of gasifier types are based on the means of supporting the biomass in the reactor vessel, the direction of flow of both the biomass and oxidant, and the way heat is supplied to the reactor. [43]

2.6.1. Updraft Gasifier

The updraft gasifier is the earliest and simplest type of fixed-bed gasifier. Figure 2.1 illustrates an updraft gasifier where the flow of the fuel and gases are countercurrent to each other. In this gasifier, the biomass moves downward, being dried by the upflow of hot product gas. After the drying zone, the solid fuel is pyrolysed and the vapors are carried upward by the hot product gas. Char, which continues to move down to be gasified, is obtained through pyrolysis. [44]

The tar content in the vapor can be either cooled and condensed or carried out of the reactor with the product gas. The condensed tars are recycled back to the reaction zones, where they are cracked enhancing gasification efficiency forming gas and char. [45]

In the updraft gasifier, the gasification zone is located at the bottom of the gasifier, where the solid char and tar are partially oxidized by the incoming oxidizing agent. Combustion gas also goes through the gasification zone reacting with the char. Thus, this set of reactions release the heat that the process requires. [46]

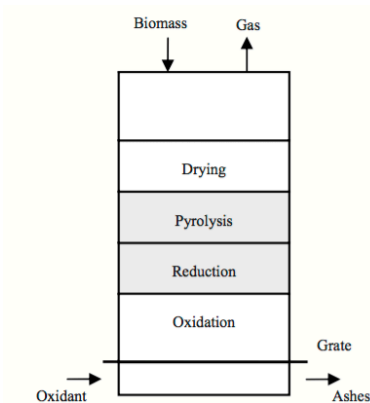


Figure 2.1. Updraft Gasifier

The gas produced from an updraft gasifier is rich in hydrocarbons and tars since it exists at low temperatures (400°C). Due to the significant proportion of tars in the fuel gas, cleanup is required for further processing. In order to increase the H₂ levels in the syngas, steam can also be added.

The syngas composition from an updraft gasifier include higher CO contents and less CH₄ yields than gas from other gasifiers. In addition, the amount of minor products like ethane and acetylene in the synthesis is also reduced.

2.6.2. Downdraft Gasifier

Reaction zones in a downdraft reactor are similar to those in an updraft reactor, except that the oxidation and reduction zones are located differently (Figure 2.2). In a downdraft unit, the oxidizing agent is fed from the bottom of the gasifier while pyrolysis products move downwards. The main difference between this unit and an updraft reactor is that the char is able to pass through the high temperature oxidation zone, where further decomposition takes place. [47] The gas continues moving down, until gasification takes place. The design of this reactor, guarantees less tar content and reduces its calorific power. This is because of the pyrolytic gases that are burned to provide the energy required for endothermic reactions. [48]

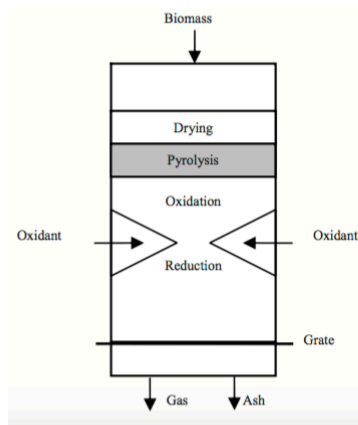


Figure 2.2. Downdraft Gasifier

It is important to mention that, in the downdraft gasifier the moisture content of vaporized biomass, enters the gasification zone and serves as a gasifying agent. The final syngas leaves the gasifier from the bottom at a high temperature (700°C), with a significant reduction in the amount of tar compared to updraft gasifiers. [49]

The major advantage of downdraft reactors is related to their ability to produce gas with low tar and oil contents, which reduces cleaning before use in internal combustion engines. This gas is economically feasible since it can be used as a fuel with minimal filtering for spark ignition and diesel engines. However, due to slagging issues, downdraft units are not suitable for materials with high ash content and low ash fusion temperatures, such as crop residues.

2.6.3. Fluidized Bed Gasifiers

The main advantage that fluidized bed (FB) gasifiers have over fixed-bed gasifiers is the uniform distribution of temperature accomplished in the gasification zone. This uniformity is achieved using a fine bed material (e.g. sand). The bed material is fluidized with air/steam and mixed with the combustion gas and biomass feed. The two main types of fluidized bed gasifiers are circulating fluidized beds and bubbling fluidized beds.

2.6.3.1. Bubbling Fluidized Beds.

In bubbling FBs, fine granular material is placed into a vessel with an upward flow of gas circulating in it. The biomass is introduced into the moving bed of material (Figure 2.3). The excess of gas circulates through the bed in the form of bubbles, that grow as they rise in the bed. The pressure drop across the bed, which is affected by the characteristics of bed particles, is an important variable to consider when developing a bubbling fluidized bed.

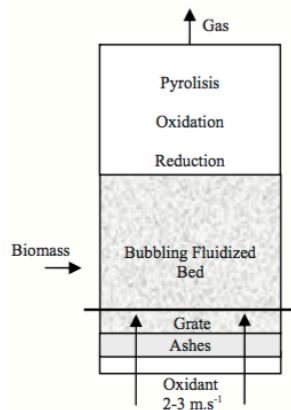


Figure 2.3. Bubbling Fluidized Bed Gasifier

In this type of reactor, the bed temperature is regulated by controlling the air/biomass ratio. The pyrolysis of biomass fed takes place in the bed, forming char and gaseous compounds. Cracking of tars occurs by contact with the hot bed material, producing a low tar content syngas. [50]

2.6.3.1. Circulating Fluidized Beds.

In this type of gasifier, the bed material circulates between the vessel and a cyclone separator, where the removal of the ash is carried out. The bed material and char are returned to the reaction vessel (Figure 2.4). Circulating FB gasifiers are used for the gasification of bark and other plant-based biomass in the paper industry. The design of these gasifiers allows them to be operated at high pressures.

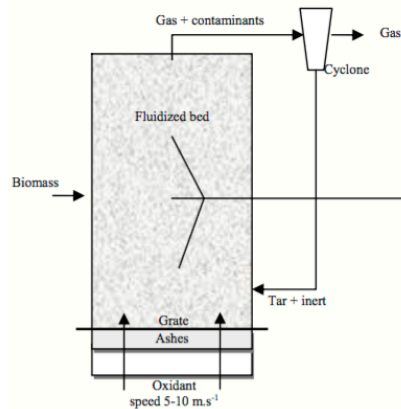


Figure 2.4. Circulating Fluidized Bed Gasifier

Some of the main advantages of circulating fluidized beds are the allowances of high heat transport rates due to the high heat capacity of the circulating bed material. Thus, rapid reactions leading to high conversion rates and low tar are favored in circulating FB gasifiers.

The choice of one type of gasifier over other is dictated by the biomass fuel, its available form, particle size, moisture content and ash content. [51] Table 2.2 lists some of the main advantages and disadvantages generally found for various types of gasifiers.

Table 2.2 Advantages and disadvantages of various gasifiers

Gasifier Type	Advantage	Disadvantage
Updraft	-Small pressure drop -Good thermal efficiency	-Great sensitivity to tar and moisture content of fuel

	-Little Tendency towards slag formation	-Relatively long time required for start-up of the engine unit -Poor reaction capability with heavy gas load
Downdraft	-Flexible adaptation of gas production to load -Low sensitivity to charcoal dust and tar content of fuel	-Design tends to be tall -Not feasible for very small particle size of fuel.
Fluidized Bed	-Flexibility derived from temperature control -Ability to deal with fine materials	-Feeding problems -Instability of the bed.

2.7. Syngas Characterization

Syngas quality is affected by several operating operational variables. For instance, the product composition and distribution have been found to be influenced mainly by the type of fuel, bed temperature and oxidizing agent [52]. These parameters are interrelated and affect the gasification rate, the char reactivity and the product gas heating value.

2.7.1. Effect of Biomass Type

Every biomass has a distinctive atomic ratio such as $C_{10}H_{14}O_6$ [15]. One should also notice that biomass chemical composition and gasification products are interrelated. Biomass composition may also affect char reactivity. [53]

The main components of biomass are cellulose, hemicelluloses, and lignin, which are chemical species containing carbon, hydrogen, and oxygen. Other minor biomass components in typical available biomasses such as wood, are fats, resins, and waxes. All these are combustible components. [54] On the other hand, major non-combustible component of wood is water, which makes up to 50% of freshly cut wood. Ash content may be relatively low (1%-10%). Given the high oxygen content, the heating value of biomass ranges in the 16-20 MJ/kg.

Most wood species have ash contents below two percent and are therefore, suitable fuels for fixed-bed gasifiers. As wood contains high volatile matter, an updraft gasifier system produces a gas containing tar, which needs to be cleaned out before use in engines. Gas cleaning is a difficult and labor-intensive process. Hence, wood is not suitable for an updraft gasifier coupled with internal

combustion engines. However, the gas containing tar from an updraft gasifier can be used for direct burning. Downdraft systems can be designed to deliver a virtually tar-free product gas when fueled by wood blocks or wood chips of low moisture content. After passing through a relatively simple cleanup train, the gas can be used in internal combustion engines.

2.7.2. Influence of Bed Temperature

Several works have stated the importance of the reaction temperature in gasification. According to Emami [55], the bed temperature is one of the most influential parameter in gasification. It is therefore essential, depending on the type of biomass, to control this variable accurately due to ash accumulation.

Findings in gasification studies reported the increase of gas yield with temperature, regardless of the type of feedstocks and gasifiers used. Moreover, the temperature increase leads to an increase in the gasification reaction rates. Thus, the production of H₂ and CO is enhanced as well and hydrocarbons are eliminated. Less tar emissions are also observed at higher temperatures.

On the other hand, the reduction of the temperature causes lower char conversion and generates a higher concentration of tars in the syngas. This reduces the process efficiency and limits its use to certain electricity conversion equipment. [56] [57]

Numerous experiments have been carried out on gasifier operating temperatures for fuel utilization in pilot plants. Higher temperatures may produce desirable yields of H₂ and CO and low tar yields. The optimal temperature for gasification to achieve high carbon conversion and steam reforming is 900°C. However, under these conditions gasification may face challenges due to ash melting with lower temperatures being recommended. [58]

2.7.3. Influence of the Oxidizing Agent

It has been reported in the literature that the H₂ content in the syngas is higher when gasification uses steam rather than when it is made with air. [59]

Table 2.2. reports experimental results of wood gasification using different types of gasification agents. There is evidence that the use of steam or O₂ favors the production of H₂ and CO. In the case of the fixed-bed reactors, an increase of methane yields is also verified when using O₂ and steam as oxidizers.

Table 2.3 Influence of the Oxidizer in the Final Composition of Gas.

Oxidizing agent	Composition (% vol, dry base)				HHV (MJ/m ³)
	H ₂	CO	CO ₂	CH ₄	
Air	17	21	13	1	5.7
O ₂	32	48	15	2	10.4
Steam	52	23	18	7	n.d.

2.8. Conclusions

- Most frequently used biomasses for gasification are charcoal and wood. However, in the future agricultural residues are likely going to be preferred feedstocks for gasification.
- Fixed-bed gasifiers are relatively easy to deploy and operate, but are more suitable for small or medium power generation. On the other hand, fluidized and circulating fluidized beds are more suitable for larger scale gasifiers offering uniform bed temperatures for gasification.
- Changes in the composition of the syngas are influenced by biomass type, reactor type, and reactor operational conditions.
- Operational parameters influence char reactivity in the gasification process.
- Steam gasification generates a syngas of high energy quality with a higher heating value compared to air gasification. However, excessive steam can lower gasification temperature and diminish product gas quality.
- Temperature is considered the most influential factor in gasification. Higher temperatures favor H₂ production and gas yield. Excessive high a temperature may lower gas heating value and contribute to ash melting.
- Synthesis gas can be used for driving internal combustion engines and producing heat and/or electricity.
- Integrated gasification processes may facilitate biomass drying of agricultural residues making biomass gasification economically viable.

CHAPTER 3

3. Experimental Methods

3.1. Introduction

This chapter describes materials, equipment and experimental methods involved in the research of this MEd thesis. Regarding the materials section of this MEd thesis, three feedstocks are considered with their respective characterization, This is followed by a description of the operating conditions at which these samples were gasified. With respect to operating conditions, carrier gas flow, sample weight, total pressure, temperature, and reaction time, among others; are provided in the experimental procedure section. Finally, the product analysis section describes various devices that were used to analyze the produced gas as well as an illustration of the typical chromatogram obtained from biomass gasification.

3.2. Materials

Three different types of feedstocks were considered for biomass gasification in the context of the present study, namely wood pellets, bark pellets and Costa Rica coffee waste (broza). The wood pellets were provided by CANMET, the wood bark by KMW Energy and the broza or coffee waste by ICafe Costa Rica.

The chemical compositions of the feedstocks were obtained by sending approximately 1kg of each material to a certified laboratory. These analyses provided technical data regarding moisture content, heating value, elemental composition, ash content and volatile matter.

All biomass samples were extensively dried during seven hours and kept in an OCa dryer container waiting for their use during experiments. Description of both elemental composition and ultimate analysis for the three feedstocks studied are reported in the upcoming chapter 4.

3.3. Reaction System

Experiments were carried out using a novel CREC Riser Simulator developed by Professor Hugo de Lasa at the Chemical Reactor Engineering Centre (CREC) at the University of Western Ontario. This experimental device allows one to evaluate catalysts and processes for the manufacturing of

clean fuels; reproducing closely the conditions found in industrial riser units. Some of the processes that can be developed and studied in this reactor are: a) gasoline desulphurization, gasification of biomass, b) catalytic cracking, c) steam and dry methane reforming, d) methane oxidative coupling and e) FCC studies. A schematic representation of the CREC Riser Simulator is shown in Figure 3.1.

The CREC Riser Simulator operates as a fluidized batch reactor. The reactor volume is 50.7 cm³. The CREC Riser Simulator is comprised of an upper and lower shell, both sealed with a metallic gasket. This set-up, allows the feeding and unloading of the biomass into a basket, located in the lower shell. In the CREC Riser Simulator basket, the biomass is kept between two porous grids under high recirculation of chemical species. This is achieved as a result of the impeller rotation in the upper section of the unit. There is a cooling jacket that keeps the impeller cone at the adequate temperature avoiding overheating (de Lasa (1991)).

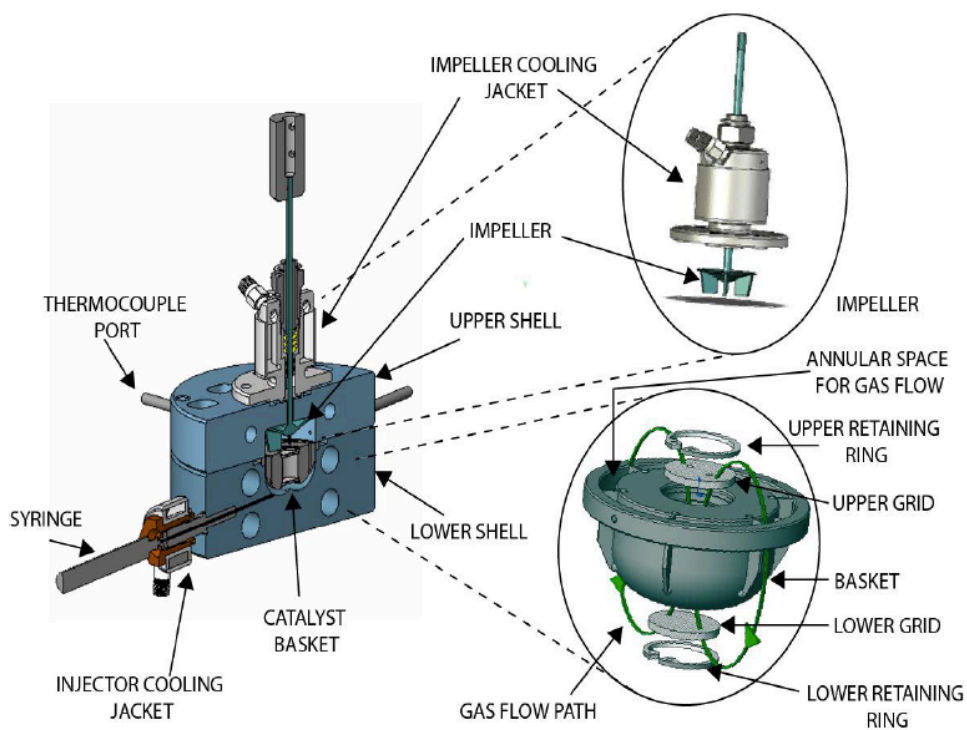


Figure 3.1 Schematic Representation of the CREC Riser Simulator (Adapted from Mazumder [60])

The CREC Riser Simulator operates in conjunction with a series of sampling valves. The set of accessories that compose the sampling system involve a four-port valve (4PV), a timer, a sampling port and a vacuum pump. These valves allow the injection of hydrocarbons and the withdrawal of reaction products in short periods of time.

The four-port valve allows gases to be recirculated through the reactor, with the reactor and the vacuum bottle being isolated. There is also timer coupled to an actuator. This actuator operates the 4PV and controls the reaction time. This total reaction time can be modified. It can be set for instance, at 30 minutes. Once the set time is reached, products are quickly evacuated from the reactor and transferred to the vacuum box. The purpose of the vacuum box is to collect the sample from the reactor. Consequently, the reaction is terminated once the evacuation process is completed.

The sampling system allows directing the reaction product sample to the analytical system. Detailed descriptions of various CREC Riser Simulator components and the sequence of injections and sampling can be found in Figure 3.2

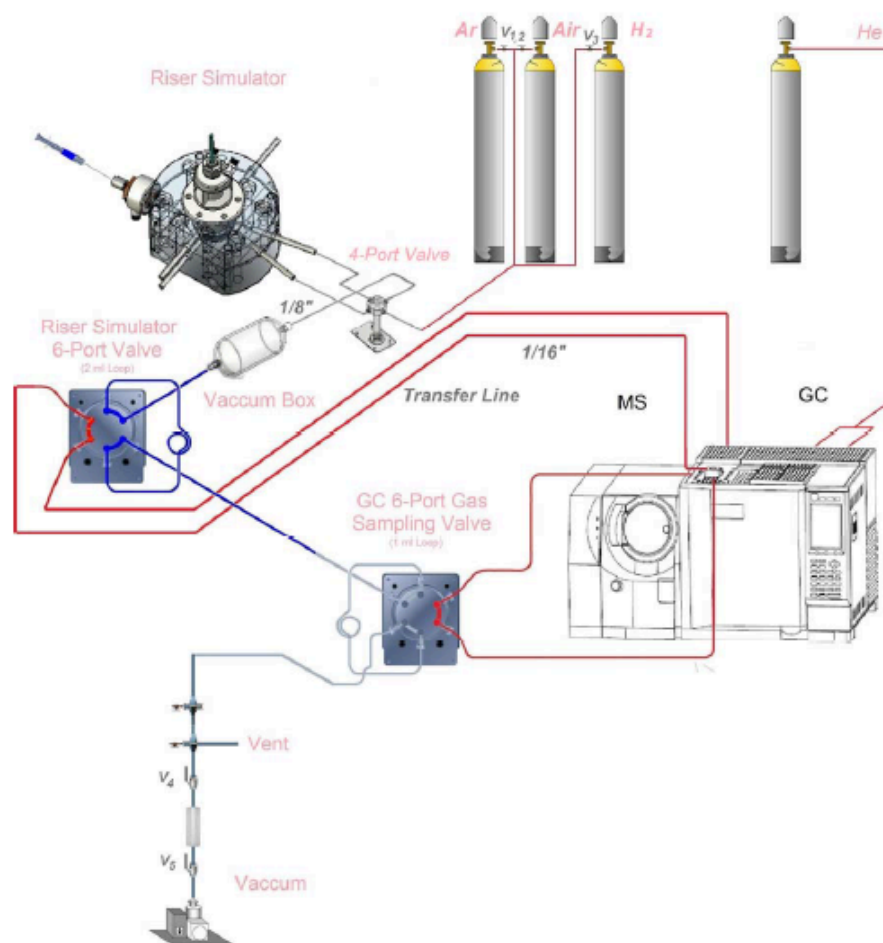


Figure 3.2. Schematic Description of CREC Riser Simulator, Associated Valves and Accessories (Adapted from Salaices [61])

The CREC Riser Simulator is also equipped with three ways valves: V_1 and V_2 . The V_1 valve is used to select the either He or CO_2 , to feed the reactor and vacuum system. Helium or Carbon Dioxide was used for this purpose, during the reaction period. The V_2 valve has three main functions: a) Venting the system, b) Creating a vacuum in the system and c) Helping to connect the vacuum box to the vacuum pump.

Valves V_{3a} and V_{3b} are on-off valves which separate the vacuum box from the vacuum pump. All valves are of the solenoid type and are controlled from the control panel.

The 4PV connects the reactor with the He/ CO_2 supply at one end, as well as with the vacuum system at the other. In the "open" position, the following is accomplished: The gases (He or reaction products) in the reactor, flow through the 4PV, entering into the reactor through the inlet port. Gases leave the reactor through the outlet port, going back into the valve and finally reaching the vacuum bottle. In the "closed" position, the reactor is completely isolated from the rest of the system. Thus, the carrier gas or reaction products going to the 4PV, bypass the reactor, flowing directly into the vacuum bottle.

The vacuum bottle volume is $1175 \pm 3 \text{ cm}^3$. This volume includes the vacuum bottle, the connecting lines, a six-port valve (6PV) and sample loop. Its large volume allows quick and easy removal of gas products, as well as unreacted feed from the smaller volume CREC Riser Simulator.

Additionally, a large pressure difference is set using a vacuum pump. This allows one to effectively remove the reactor contents.

A 6PV is installed after the vacuum box. This valve has two positions: load and inject. These two valve positions provide two independent paths for the carrier gas. The "load" position allows the sample loop to be filled. The "inject" position connects the sample loop with the carrier gas flow and allows the product sample to be send "on-line" the GC for analysis.

The chromatographic valves (4PV and 6PV) and vacuum chamber are located inside of the heated box. A thermocouple placed inside the heated box is used to measure and control the temperature of the vacuum system. The vacuum box temperature was consistently set at 195°C . The temperature of the line connecting the 6PV and GC was also kept at 220°C , using a heating tape. This temperature setting avoid condensation of tar products.

Pressure transducers are installed in both reactor and vacuum box chambers to monitor the progress of each experiment. Figure 3.3 reports an typical example of a pressure profile in the CREC Riser simulator. Total pressure increase is the combined effect of temperature and increase in the number of moles as a result of the gasification.

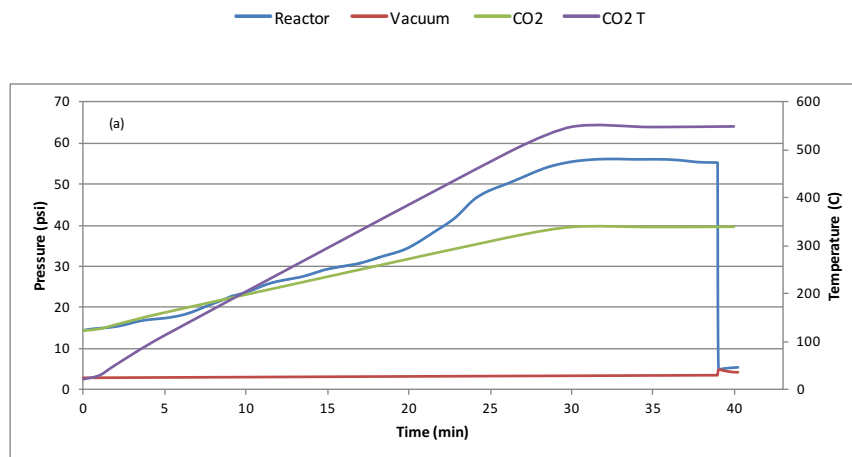


Figure 3.3. Pressure and Temperature Changes during the Gasification of Wood Bark at 550°C in the CREC Riser Simulator for a total reaction time of 40 min. Gasifying agents: CO₂ and H₂O. Note: Purple line: Temperature in the reactor, Blue line: Pressure in the reactor, Red line: Pressure in the vacuum box. Green line: Pressure for temperature rise.

3.4. Experimental Procedure

Thermal gasification experiments were developed in the CREC Riser Simulator described previously. Three different feedstocks (Costa Rica coffee waste, CANMET pellets and bark) were gasified by varying the temperature, the carrier gas and the amount of water. All the experiments were developed under close to atmospheric pressure. The rotation of the impeller and the total reaction time remained constant throughout the run. Temperature was increased gradually using a set temperature ramp until the desired temperature was reached.

Conditions selected for the thermal biomass gasification studies were as follows: a) 550°C and 600°C, b) He and CO₂ carrier gas, c) Dry biomass was loaded using 0.04 g of material. Dry biomass weight fed remained constant throughout the whole study. Water was added at 8µl of water to the dried biomass, to provide a desirable biomass/water ratio.

Experimental runs in the CREC Riser Simulator were developed using a number of steps as follows:

- a) A biomass sample was first loaded in the CREC Riser Simulator basket, placing the basket in the lower shell section of the unit. Then, the upper and lower shells were sealed using a metallic gasket and six inconel tightening bolts.
- b) The CREC Riser Simulator temperature was set to 23°C and the pressure was set to 24 psi, with helium gas flowing for approximately 10 min. During helium flow, the 4PV was kept with the reactor and the vacuum box connected. This “purging” step ensured that the

- reactor was free of any remaining chemical species from previous experiments, or contaminants that could have been introduced while opening the reactor to the atmosphere.
- c) Once the purging process was complete, the reactor pressure was set to atmospheric conditions. At this point, the 4PV was turned to the “disconnect” position with the reactor and vacuum chamber being isolated.
 - d) Following this, the vacuum box pressure was lowered to 2.8 psi to provide a significant pressure differential. This helped in transporting gasification products from the reactor to the vacuum chamber.
 - e) Once the pressure in the vacuum box reached, the target temperature for the upper and lower reactor was set (e.g. 600°C). Following this, a linear temperature ramp function was activated in the temperature controller. For example, the temperature was programmed to increase linearly for 30 min from room temperature until reaching the desired target (e.g. 600°C). Once this step completed, the CREC Riser Simulator was ready to carry out the experimental run. Pressure and temperature recording started at this point.
 - f) The impeller rotational speed was set to 600 rpm to achieve good gas mixing during the run.
 - g) Once the desired 30 min. of reaction time elapsed, the 4PV reconnected the reactor to the vacuum box. Under these conditions, the gas mixture was transferred to the vacuum chamber due the high pressure differential. Gas phase sampling of the reactor continued until pressures reached equilibrium.
 - h) After reaching the equilibrium pressure in both the reactor and the vacuum box, the 4PV was set back to the “disconnection’ mode in order to isolate the reactor from the vacuum box.
 - i) Furthermore, in order to ensure that the sample loop was filled with reaction products, the vacuum box contents were discharged for approximately 1 min.
 - j) Finally, gas products were sent to the gas chromatography unit for analysis and product quantification.

Once the run was completed, the CREC Riser Simulator was cooled down and char samples was discharged, weighted and kept for further analysis.

3.5. Product Analysis

Reaction product analysis was carried out using gas chromatography (GC) with a thermal conductivity detector (TCD). Product quantification was developed by a Shimadzu GC connected to a TCD and a packed column Agilent HayeSep D 100/12, with an inner diameter 2 mm and a nominal film thickness of 2 µm. This permitted the separation of the various chemical species in the samples. The packed column was connected to the back of the GC with a splitter coupled to the TCD, allowing the identification of the chemical species. Biomass gasification products

included permanent gases such as H₂, CO, CO₂, CH₄, water, and light to heavy hydrocarbons. Figure 3.4 provides a chromatogram of a typical gas mixture obtained from GC/TCD.

The quantification of permanent gases and light hydrocarbons was effected using calibration curves that correlated calculated areas to concentrations of C in hydrocarbon mixtures. Calibration curves for various chemical species are reported in Appendix B: Calibration curves

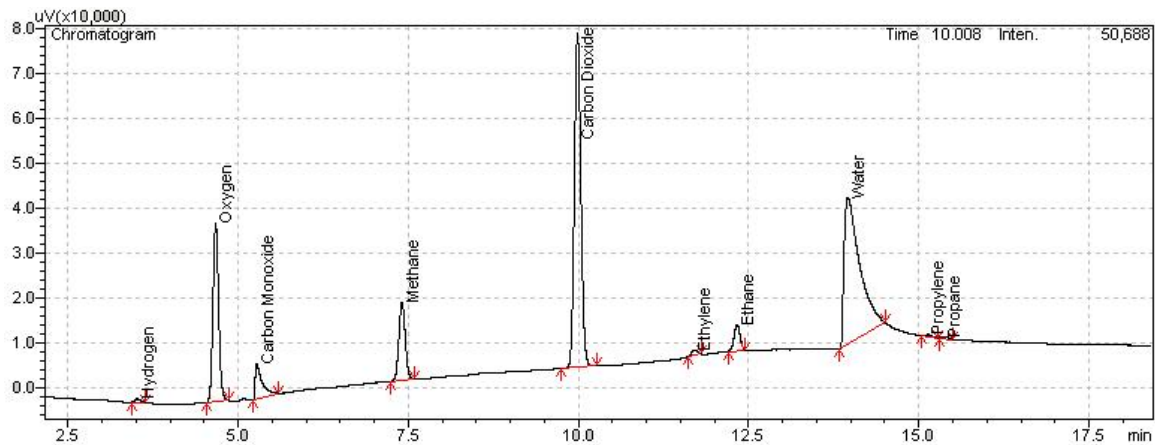


Figure 3.4. GC/TCD typical chromatogram of permanent gases of biomass gasification

The GC/TCD analytical system was operated using a Mandel GC Solution software. This is an integrated software that performs various tasks associated with GC/MS data acquisition, data processing and reporting. Table 3.1 reports the method used for gas chromatograph analysis in the present study.

The GC oven program was run using a thermal ramp as follows: a) Initially, the oven temperature was set to 35°C for 3 min, b) Following this, the temperature was increased at 25 °C/min to 250°C for 8.40 min and c) Finally, and once 250°C was reached, this temperature was kept constant for 9 min.

Table 3.1 Gas chromatography method

Parameter/Setting	Value
Inlet	
Mode	Direct
Gas	He
Temperature	250 °C
Pressure	9 psi
Total Flow	25 ml/min

Column	Agilent HayeSep D 100/12
Detector	TCD
Outlet	Ambient
Mode	Constant flow
Inlet	Back
Temperature	35 °C
Detector	TCD
Temperature	250 °C
Make up gas	He
He Flow	8 ml/min
Sampling rate	40

3.6. Conclusions

- a) The required method for reaction engineering studies for biomass feedstocks were implemented using the CREC Riser Simulator and related auxiliary equipment.
- b) The developed method was successfully employed using several biomass samples from different sources.
- c) The various gasification products were analyzed using the the required GC column and TCD
- d) The formed residual char was analyzed using TOC analysis.

CHAPTER 4

4. Steam Biomass Gasification. Experimental Results

4.1. Introduction

This chapter reports a series of experiments designed and conducted to study the effect of two operating variables, namely the temperature and the carrier gas composition and their impact on the syngas quality. Data was obtained in a fluidized bed using different biomasses types. The reaction temperatures selected were 550°C and 600°C. The two gasifying agents considered were He and CO₂. The feedstock used were woodchips, wood pellets and “broza” (pulp coffee waste).

Experiments were carried in the CREC Riser Simulator. The rotation of the impeller was set to 600 rpm during the entire run. A mixture of 0.04 g of biomass and 20% water was loaded in the reactor basket. Temperature was increased progressively for 30 min using a 50°C/min temperature ramp. Once the highest temperature was reached, it was kept at this level for 10 min. Thus, the total reaction time was 40 min.

All runs were repeated at least 15 times to ensure reproducibility of the results and obtain enough solid char for further TOC analyses. At the beginning of the run, the vacuum box was under sub-atmospheric conditions. It is important to mention that the mass balance included all chemical species fed and removed from the reactor. More details of this calculation are provided in Appendix A Mass Balance.

Following every run, and once the GC analysis was completed; a carbon balance was effected as reported in the Appendix A. In this appendix, a carbon balance summary describing closure for a typical run of the series is provided.

Gaseous products were analyzed using a Shimadzu GC connected to a TCD (Thermal Conductivity Detector). The total pressure measurements both from the reactor and vacuum box were saved on a computer disk using a Personal Daq acquisition card, as described in the Section 3.5. The coke on the char was measured using a Total Organic Carbon analyzer (TOC-V) and a solid sample module (SSM-5000A) from Shimadzu. Analysis and quantification of tars are not included in this study.

Various experimental findings including gasification efficiency, gas yield, carbon conversion and

H₂/CO ratio are reviewed in the present section.

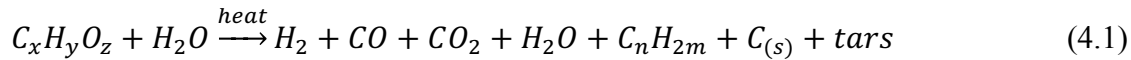
Mass balance closures were consistently in the ±11 %, with most of the mass balances closing in the ±7% range. The main chemical species involved in the balance were H₂, CO, CO₂, CH₄ and small quantities of C₂H₄ and C₂H₆.

4.2. Gasification Process

Gasification involves three important process steps: a) pyrolysis, b) oxidation reactions and c) reduction reactions. Reduction reactions; mainly gasification reactions are endothermic and require the heat produced from the prior oxidation reactions.

The most important reactions considered for kinetic studies involve carbon, CO, CO₂, H₂, H₂O and CH₄ as follows:

- a) The primary products of biomass gasification are formed via devolatilization (pyrolysis in the presence of steam):



- b) Higher hydrocarbons formed further, react with steam; yielding additional amounts of CO and H₂,



In fact, biomass gasification involves, a complex set of solid phase and gas phase reactions as summarized in Table 4.1.

Table 4.1 Chemical Reactions in the Steam Gasification of Biomass

Name of reaction	Chemical equation	$\Delta H_{298}^{\circ} \left(\frac{kJ}{mole} \right)$	$\Delta G_{298}^{\circ} \left(\frac{kJ}{mole} \right)$	Eq.
Water-gas shift	$CO + H_2O \leftrightarrow H_2 + CO_2$	-42.2	-28.538	(4.3)
Heterogeneous WGS	$C + H_2O \leftrightarrow H_2 + CO$	130.41	89.824	(4.4)
Steam methane-reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	205.81	140.098	(4.5)
Dry methane-reforming	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	123.76	168.635	(4.6)

Boudouard reaction	$C + CO_2 \leftrightarrow 2CO$	172.61	118.362	(4.7)
Hydrogenating gasification	$C + 2H_2 \leftrightarrow CH_4$	-74.9	-50.273	(4.8)
Ethylene formation	$2CO + 4H_2 \leftrightarrow C_2H_4 + 2H_2O$	-104.25	-111.651	(4.9)
Ethane formation	$2CO + 5H_2 \leftrightarrow C_2H_6 + 2H_2O$	-172.77	-212.787	(4.10)

Some of these reactions are strongly influenced by chemical equilibrium

$$K = \exp\left(-\frac{\Delta G}{RT}\right) \quad (4.11)$$

For instance, reactions with negative Gibbs free energy are considered not thermodynamically viable and shall be discarded from the analysis.

As a result, and given the importance of the Gibbs free energy determining chemical equilibrium for the individual reactions, one is looking to the minimization of the overall Gibbs free energy for the gasification process.

4.3. Experimental Runs

As described in section 3, steam gasification of biomass materials was carried out in the CREC Riser Simulator at 550°C and 600°C, using He and CO₂ as gasifying agents. The CREC Riser Simulator unit was loaded with a set amount of biomass. Once this operation was completed, the reactor was sealed to prevent leaks. Then, the reactor was leak tested under the selected gasifying medium and finally heated to the desired temperature.

The heating of the reactor was effected during 30 minutes using a thermal ramp at 17.7°C/min for 550°C and at 19.17°C/min at 600°C. Once the desired temperature was reached, it was held at this thermal level for about 10 min.

Once these steps were completed, the contents of the reactor were evacuated towards the vacuum box. Reactor and vacuum box pressure were recorded by the Personal Daq Acquisition software.

Figure 4.1 describes the typical temperature profile in both the reactor and the vacuum box for the heating period. Once the 30-minute time was reached, the temperature remained at a preselected constant level for 10 min.

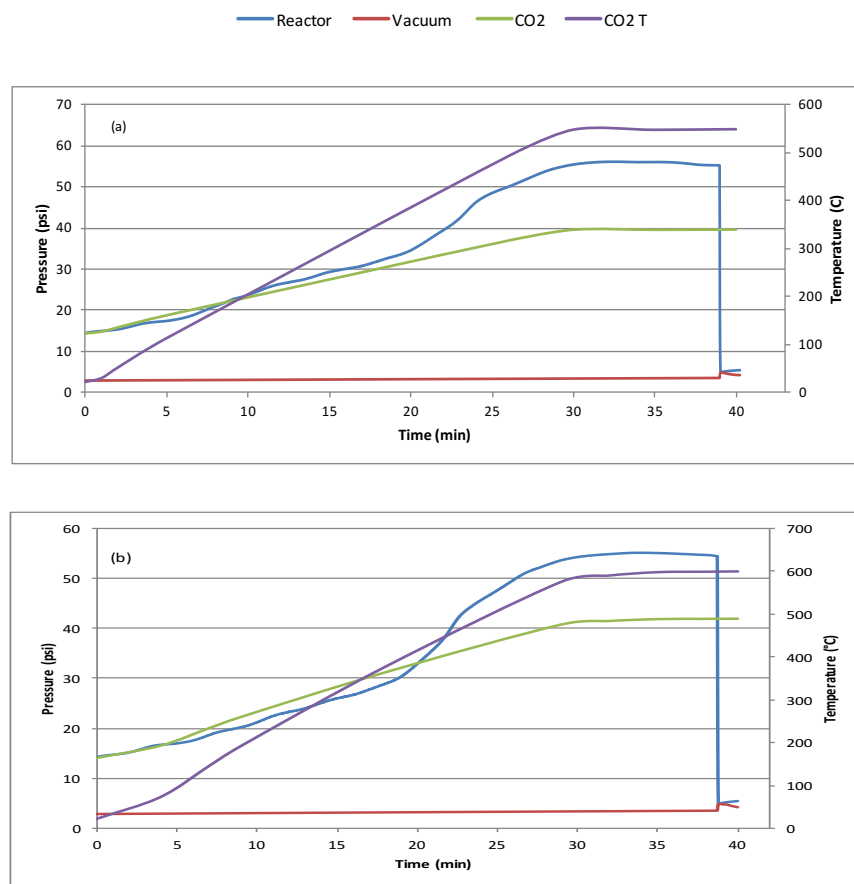


Figure 4.1. Gasification of 0.04 g of broza at (a) 550°C and (b) 600°C for a total reaction time of 40 min. Gasifying Agents: CO₂ and H₂O. Note: Purple line: Temperature in the reactor, Blue line: Pressure in the reactor, Red line: Pressure in the vacuum box. Green line: Pressure for temperature rise.

Figure 4.1 also reports the pressure changes for broza at 550°C and 600°C in both the reactor and in the vacuum box, at various reaction times. Similar pressure profiles were obtained for the other feedstocks studied.

One can see that the total reactor pressure remains consistently above atmospheric pressure while the vacuum box stays below atmospheric pressure. This is true for the entire experiment except at the very end. At that time the reactor and vacuum box are connected and the total pressure is equalized, with most of the reactor contents being transferred from the reactor to the vacuum box. [62]

Furthermore, and according to Figure 4.1, the progress of gasification can be shown using the total reactor pressure. One can observe that there is a progressive pressure increase with time superseding the expected pressure increase for the heating unreacted gases. One can notice that the

highest pressures reached at 550°C and 600°C were 51 psi and 56 psi, respectively, with this being significantly different than the expected 42 psi and 38 psi for the unreacted gases.

It is valuable to comment that this type of gasification experiment with a temperature ramp, was selected to simulate the KMW Power Generation System using the CREC Riser Simulator, where biomass is subject to a progressive temperature increase.

4.3.1. Variables Affecting Char Reactivity

Several variables have been reported to influence biomass gasification and product distribution. These parameters include: a) gasifier temperature, b) moisture content, c) fluidization velocity, and d) gasifying medium; among others [63]. One should notice that both operational and non-operational factors are interrelated and have an impact on the product composition. [64]

This study evaluates the effect that the bed temperature and the gasifying agent have on the char and syngas produced. The impact of the char characteristics as it is related to the feedstock and moisture content is also considered.

4.3.2. Biomass Type

The gasification of biomass in fluidized beds has been studied for many years. Previous studies have found that the feedstock affects the process significantly. The size, moisture and volatile matter are also major factors affecting gaseous products [65] [66] [67] [68].

To address the issue of feedstock characterization, proximate as well as ultimate analyses were effected using 1kg of biomass feedstock. This was done in order to have both quantitative as well as representative biomass analyses.

Table 4.2. provides a proximate analysis of each biomass fuel. These analyses include volatile matter, fixed carbon and ash content.

Table 4.2. Proximate Analyses of Wood Bark, Wood Pellets and Broza

Proximate Analysis (wt.%)	Wood bark	Wood pellets	Broza
Volatile matter	54.7	84.76	79.16
Fixed Carbon	19.8	14.83	8.84
Ash	2.92	0.42	12

One can notice in Table 4.2, the significant differences between the biomasses studied. For instance, broza and wood pellets display a high volatile matter content. For broza, as well one can notice a significantly high ash content.

Furthermore, a more detailed characterization of the biomasses considered is reported in Table 4.3 using the ultimate analysis.

Table 4.3. Ultimate Analyses of Wood Bark, Wood Pellets and Broza

Ultimate Analysis (wt.%)	Wood bark	Wood pellets	Broza
Hydrogen	4.05	5.7	4.26
Nitrogen	0.37	0.1	2.05
Oxygen	28.1	41	30.2
Carbon	49.4	46.3	37.78
Sulfur	0.04	<0.05	0.12

One should notice that the data presented in Table 4.1 and Table 4.2 are on a water free basis. This guarantees that the comparison of the various species contained in biomass is effected on the same basis.

On the basis of the above information of Table 4.3 one can calculate both the formula and the molecular weight of the biomass unit for each feedstock as CH_xO_y . This allowed to express any weight of biomass fed to the reactor as moles of the biomass unit fed or the equivalent as moles of carbon fed.

Table 4.4. Biomass unit elemental composition for wood pellets, broza and bark.

Feedstock	C	H	O	MW
		x	y	
Wood pellets	1	1.48	0.66	24.04
Broza	1	1.34	0.6	22.94
Bark	1	1.4	0.61	23.16

Table 4.4 reports the elemental composition of 1 unit of biomass for each biomass feedstock with its respective molecular weight.

4.3.3. Moisture Content of Fuel

Sadaka [69] and Klass [70] indicated that the moisture content of biomass is an important parameter to be considered in gasification studies. In this respect, one should also notice that the moisture content in biomass has a significant effect on energy gasification efficiency. This is the case given the significant energy required for water vaporization. In this respect, fuels with a moisture content of 15% are usually recommended for energy savings. [71]. Despite this fact, in steam biomass gasification, a water content of 20% is usually recognized as the optimum, in order to enhance the various gasification reactions involving steam.

According to Xiong [67], who developed sawdust gasification, increased moisture content in the feed improves gas yields and carbon efficiency. The introduction of a higher amount of water also decreased the quantity of tar present. In this respect, the addition of water appears to enhance both steam reforming and water-gas shift reactions. This increased amount of steam may decrease the temperature of the steady state process for the same run conditions.

In our experiments and in order to achieve an optimum moisture content of 20 wt%, 8 μ L of water were added to a dry biomass sample of 0.04 g.

4.3.4. Reactor Temperature and gasification results

Gasification calculations in the present study were done on the basis of product yields:

$$y_i = \text{Product Yield}_i = \frac{\text{Moles of product "i"}}{\text{Moles of C in biomass fed}} \quad (4.12)$$

One should notice that the moles of C in biomass fed were calculated following the procedures describe in chapter 3.

Given the fact that for every reported condition 15 runs were developed, an average y_i value and a standard deviation were calculated.

It is important to mention that every upcoming figure in this chapter reports both average yields values as bars and standard deviations values written in the caption of every figure.

The reactor temperature has a strong influence on the quality of the syngas and the combustion products. At higher temperatures, the yields of H_2 and CO were found to increase as tar yields decrease, with this being true regardless of the gasifying agent used. [72] [73].

In this respect, previous research involving several feedstocks, found that the major carbonaceous gas products and H₂ are affected by temperature. Hernandez [74] evaluated the impact of the temperature increase on the steam-gasification of sugarcane bagasse. This study revealed that the H₂/CO ratio is temperature dependent. Hence, the H₂/CO ratio increases with higher temperatures, and is reduced at lower thermal levels.

In addition, similar studies have attributed greater reaction rates to higher temperatures [75]. This indicates that the water–gas shift (WGS) is a dominant reaction, likely more dominant than the Boudouard reaction. [76]

In the present work, in order to assess the temperature effect, the reactor temperature was varied from 24°C to the desire temperatures of 550°C and 600°C using an average 18.43°C/min heating ramp.

Figure 4.2 reports the product gas yields and their variations with a temperature under a 1 atm of initial CO₂-water atmosphere. Product yields are reported in terms of number of moles over moles of biomass.

One can notice that the combined yield of product gases including H₂, CO, CO₂, and CH₄ improve at higher temperatures.

Figure 4.2 displays the changes in the dry gas yield with temperature from the gasification process of the three biomass materials under a helium-water atmosphere.



Figure 4.2. Changes of dry gas yields with temperature for steam-helium gasification of wood pellets, bark and broza. Gasifying agents: He at 1. atm and H₂O at 0.5 atm. Data reported is the average of at least 15 repeats with a +/- 3-6% standard deviation.

As shown in Figure 4.2, the production of the dry gas yield products is favored by temperature changes. With the temperature raise from 550°C to 600°C, the highest gas yield was produced by broza with 1.0 mole/mole biomass.

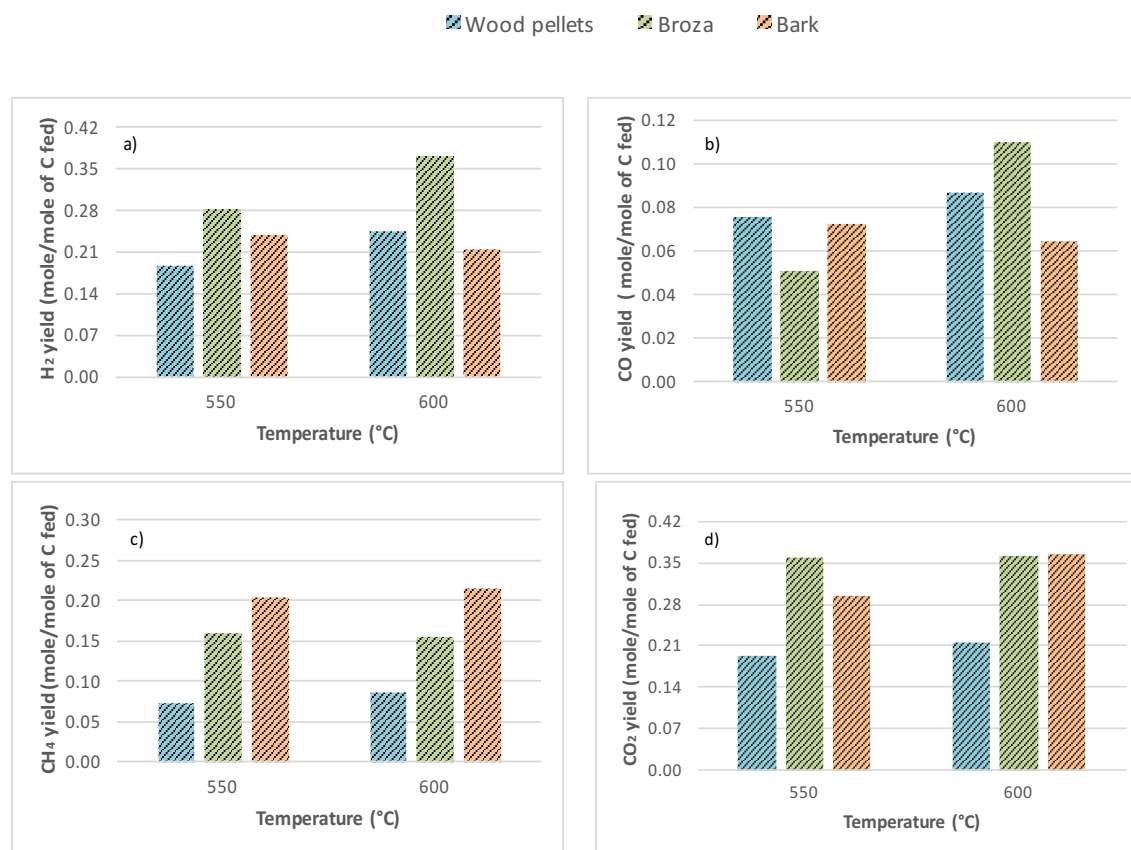


Figure 4.3. Changes of product gas yields (dry basis) with temperature (a) H₂, (b) CO, (c) CH₄, (d) CO₂ from steam gasification of wood pellets, bark and broza with a He-water atmosphere and 40 min reaction time. Data reported is the average of at least 15 repeats with a +/- 3-6% standard deviation.

Figure 4.3 shows the individual gas product yields and their changes with temperature for a He-water atmosphere. Figure 4.3 (a) reports that the highest H₂ content is achieved with broza with a yield of 39.8% at 600°C. H₂ yields are also enhanced at higher temperatures for wood pellets and bark with 32.5% and 26% yields respectively.

In addition, the CO production in Figure 4.3 (b) presents a similar trend with temperature increments for bark and broza. The CO yields are augmented from 7.5% to 8.5% for wood pellets and from 5.0% to 11% for broza. On the other hand, bark reached the highest CO yields at 550°C with a 7% value. At 600°C however, CO production was lower approximately 6.5%. This decrement shows that the CO yields for bark are not with temperature under a He atmosphere.

CO yields can be affected by the water gas shift reaction (4.3) ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$). Chemical equilibrium for this exothermic reaction decreases with increasing temperature. Consistent with this, the endothermic “reverse” water gas shift reaction is favored at higher thermal levels. This may lead to higher CO yields from biomass gasification. One can notice that as reported in Figure 4.3(b) the CO yields increase for bark and due the water-gas shift reaction occurring in the opposite direction.

Furthermore, biomass gasification involving, He-water and a temperature rise increased mildly CH_4 yields (Figure 4.3 (c)). For instance, using bark, the CH_4 yields augmented from 20% and 22%. For wood pellets CH_4 yields raise from 7% to 8%.

Temperature increase has however, a variable impact in CO_2 yields as reported in Figure 4.3 (d)) and this for all the samples. For instance, for wood pellets CO_2 yields are decreased and this appears to be consistent with an increased influence of the reverse water gas shift reaction.

Table 4.5 reports the yields changes with temperature for the various synthesis gas components using Incremental Yields %:

$$\text{Incremental Yield (\%)} = \frac{\text{Yield}_i \text{ at } 600^\circ\text{C} - \text{Yield}_i \text{ at } 550^\circ\text{C}}{\text{Yield}_i \text{ at } 550^\circ\text{C}} \times 100$$

Table 4.5. H_2 , CO, CH_4 and CO_2 Incremental Yield % for 550°C to 600°C increase. Steam gasification of wood pellets, broza and bark under a He-water atmosphere.

Incremental Yield (%)	Wood pellets	Broza	Bark
H_2	31.01	30.74	-10.00
CO	14.07	115.12	-10.81
CH_4	19.91	-1.88	5.45
CO_2	12.45	1.39	23.59

Figure 4.3 and Figure 4.4 report both the H_2/CO and the Converted Biomass contained Carbon for the experimental runs developed at 550°C and 600°C.



Figure 4.4. Changes of (a) H₂/CO ratio and (b) the Conversion of Biomass Contained Carbon (CBCC) into synthesis gas with temperature during steam gasification of wood pellets, broza and bark under a He-water atmosphere. 40 min reaction time. Data reported is the average of at least 15 repeats with a +/- 3-6% standard deviation.

Figure 4.4 (a) shows that broza can yield a H₂/CO mole ratio as high as 5.55, at 550°C. However, this yield is reduced to 3.36 at 600°C. Dissimilar trends are observed for wood pellets and bark with the H₂/CO mole ratio either augmenting mildly or remaining close to constant with temperature: a) for wood pellets from 2.46 to 2.83, b) for bark remaining at 3.33.

Figure 4.4(b) describes the Conversion of Biomass Contained Carbon (CBCC) into synthesis gas, CBCC increasing consistently with the thermal level in all cases. This appears to show that primary reactions are consistently favored at higher temperatures. For broza, the CBCC increases approximately from 35% to 45%.

Figure 4.5 displays the changes in the dry gas yield with temperature, from the gasification of the three biomass feedstocks, under a CO₂.water atmosphere.



Figure 4.5. Changes of Dry Gas Yield with Temperature, from Steam-CO₂ Gasification of Wood Pellets, Bark and Broza. Gasifying agents: CO₂ at 1 atm and H₂O at 0.5 atm. Data reported is the average of at least 15 repeats with a +/- 3-6% standard deviation.

Figure 4.5 reports the yields of the main gasification products and their changes with temperature. One can notice that temperature, when increased from 550°C to 600°C, gives for all three feedstocks, consistently increased dry gas yields. One can notice in particular, the following yields (moles of dry gas/mole biomass): a) 1.52 at 550°C and 1.59 at 600°C for wood pellets, b) 1.74 at 550°C and 2.12 at 600°C for broza, c) 1.46 at 550°C and 1.55 at 600°C for bark.



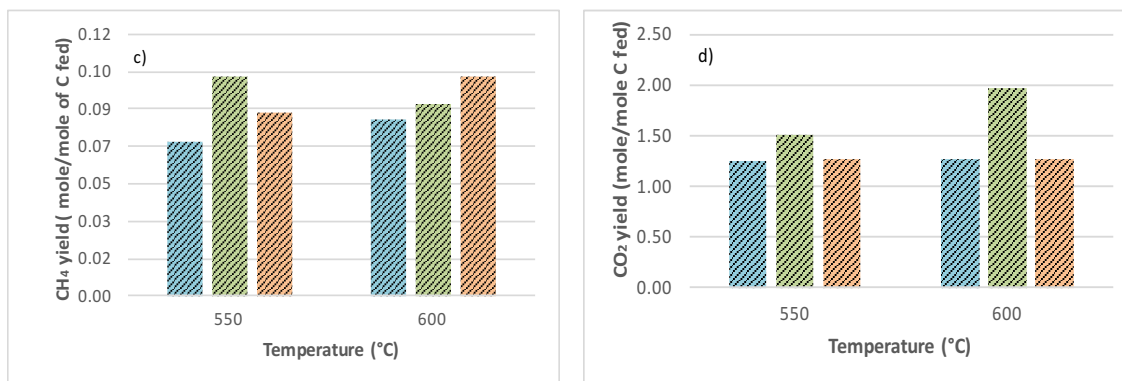


Figure 4.6. Changes of Product Gas Yields (dry basis) with Temperature (a) H₂, (b) CO, (c) CH₄, (d) CO₂; from Steam-CO₂ Gasification of Wood Pellets, Bark and Broza. Gasifying agents: CO₂ at 1.0 atm and H₂O at 0.5 atm. Reaction: 40 min. Data reported is the average of at least 15 repeats with a +/- 3-6% standard deviation.

Figure 4.6 (a) reports that higher temperatures favor H₂ production. This is a consistent trend observed for all three feedstocks. The observed H₂ yield values in the 0.06-0.13 range, obtained with a water-CO₂ atmosphere are, however, significantly lower than the 0.18-0.37 yields observed using the He-water atmospheres.

Figure 4.6 (b) describes the CO yields at both 550°C and 600°C. One can note again, improved CO yields at higher thermal levels and this for the three feedstocks. In this respect the following was recorded for CO yields expressed in moles of CO/mole of biomass: a) 0.08 at 550°C and 0.09 at 600°C for wood pellets, b) 0.04 at 550°C and 0.054 at 600°C for broza, c) 0.048 at 550°C and 0.08 at 600°C for bark.

Furthermore, a comparison of CO yields as the ones reported in Figure 4.3(b), for CO₂-water and He-water atmospheres, shows CO yields in a similar range. On this basis, one can speculate that addition of CO₂ enhances biomass gasification leading to comparable CO yields and a H₂/CO ratio in the range of 1 [77].

Figure 4.6 (c) reports CH₄ yields for runs under CO₂-water atmosphere. One can notice increased CH₄ yields at higher temperatures. This is consistent with the endothermic thermal cracking and endothermic steam and dry reforming reactions. These reactions are all favored at higher temperatures [78]. This is true for wood pellets and bark. It appears that broza is an exception to this trend, with methane yields being slightly reduced at 600°C. A significant observation is given by the CH₄ yields under CO₂ atmospheres, being 0.08-0.11 CH₄ yields with this being lower than the 0.07-0.21 CH₄ yields under helium-water atmospheres. It appears that under these conditions, there is a prevalent effect of the methane dry reforming reactions influencing the product distribution. [72] [73].

Finally, Figure 4.6 (d) reports the CO₂ yields for experiments using CO₂-water atmospheres. CO₂ yields reach in this case, values in the 1.24-1.9 range. One should emphasize that these CO₂ yields

of Figure 4.6 (d) incorporate the CO₂ amount initially injected in the reactor, prior to the experiment.

Thus, a more effective view of CO₂ yield changes with temperature and feedstock can be seen in Figure 4.7. Figure 4.7 uses the “net” CO₂ yield or the observed yield of CO₂ at the end of the run, minus the CO₂ yield at the start of the experiment.

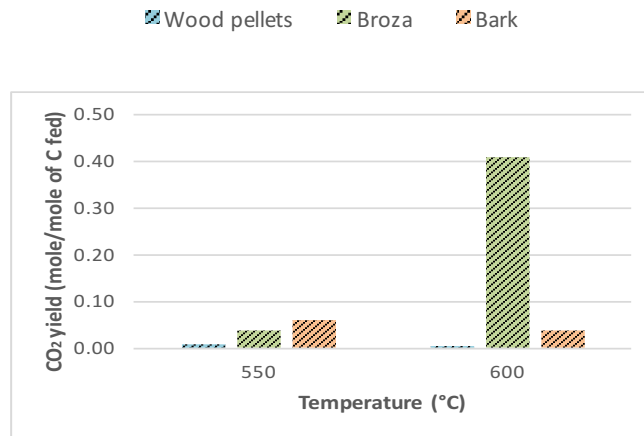


Figure 4.7. Changes of Net CO₂ Yield from Steam-CO₂ Gasification of Wood Pellets, Bark and Broza. Gasifying agents: CO₂ at 1.0 atm and H₂O at 0.5 atm. Reaction: 40 min [S/B=1 g/g] Data reported is the average of at least 15 repeats with a +/- 3-6% standard deviation.

One can observe that net CO₂ yields at the two temperature levels considered and for the three biomass feedstocks, remain close to zero with a slight positive deviation for broza at 600°C, with a CO₂ net yield of 0.40. Thus, one can consider that for broza, there is an increased influence of the water-gas shift reaction, moderating the endothermicity of the biomass gasification [79]

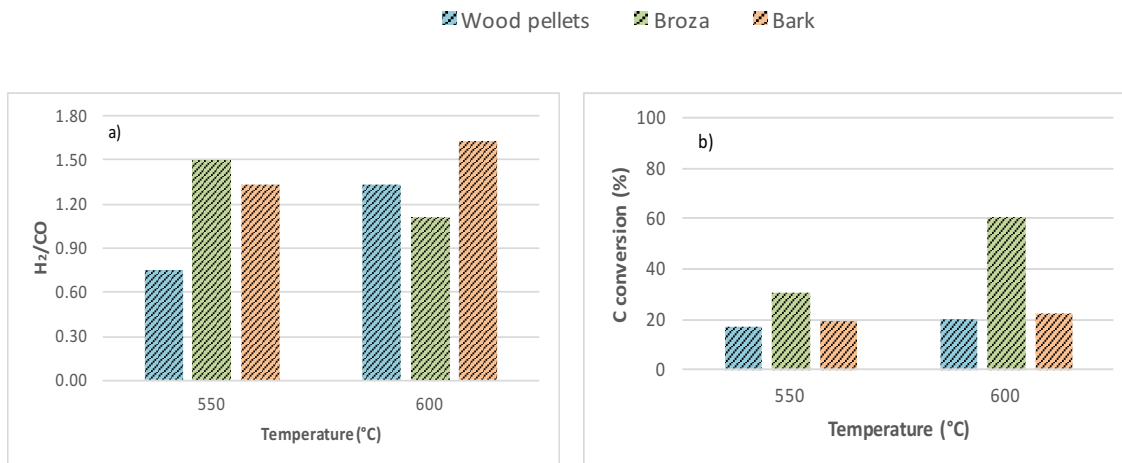


Figure 4.8. Changes of (a) H₂/CO ratio and (b) Conversion of Biomass Contained Carbon (CBCC) into synthesis gas with temperature; during steam gasification of wood pellets, broza and bark, under a CO₂ atmosphere; for 40 min reaction time. Data reported is the average of at least 15 repeats with a +/- 3-6% standard deviation.

Figure 4.8 (a) reports the H₂/CO ratio and its changes with temperature, for each experimental run and feedstock, having a CO₂-water atmosphere. One can notice that overall, temperature increases led to higher H₂/CO ratio. Broza however, is an exception, with temperature reducing the H₂/CO ratio [80] [81]. One can notice that the H₂/CO ratios achieved with all biomass samples studied under CO₂-water, are mostly higher than 1, except for wood pellets gasified at 550°C.

On this basis, it can be postulated that the H₂/CO ratios found in the gasification experiments under CO₂-water atmospheres, are affected by the reverse water–gas shift reaction. In fact, when the WGS reverse reaction is more dominant, more CO₂ and H₂ are consumed to produce CO and H₂O. Hence, higher temperatures also favor increased CO yields. The exception to this trend appears to be the broza, with high thermal levels reducing the H₂/CO ratio.

One can notice in Figure 4.6(b) that the CO content for wood pellets is relatively high. This led to a H₂/CO ratio smaller than 1 at 550°C. Furthermore, and for wood pellets, the H₂/CO ratio becomes larger than 1 at 600°C. Regarding the H₂/CO ratios, they stay consistently larger than one, for bark and broza.

In addition, the implementation of CO₂ as a gasifying agent, also influence the Conversion of Biomass Contained Carbon (CBCC), as shown in Figure 4.8 (b). Higher CBCCs were favored at higher temperatures with this being true for all materials. Among all biomass feedstocks, broza achieved a higher CBCC of 61%, while the CBCC for wood pellets and bark remained at 20 and 22% respectively. Thus, one can notice that the type of feedstock, as in the case of broza with its high mineral content, can affect the CBCC considerably.

One can also consider the yield changes with temperature and feedstock using the Incremental Yields %:

$$\text{Incremental Yield (\%)} = \frac{\text{Yield}_i \text{ at } 600^\circ\text{C} - \text{Yield}_i \text{ at } 550^\circ\text{C}}{\text{Yield}_i \text{ at } 550^\circ\text{C}} \times 100$$

As a complement to the previous data reported, Table 4.6 summarizes the Incremental Yield % for H₂, CO, CH₄ and CO₂ while the temperature was augmented from 550°C to 600°C.

Table 4.6 H₂, CO, CH₄ and CO₂ Yield Increases for 550°C and 600°C Temperatures, for the Steam Gasification of Wood Pellets, Broza and Bark under Water-CO₂ Atmospheres.

Yield Change (%)	Wood pellets	Broza	Bark
H₂	100	25.01	83.09
CO	12.53	35.00	63.59
CH₄	12.06	-3.50	16.66
CO₂	3.69	5.45	4.37

Table 4.6 shows the consistent impact of higher temperatures on both H₂ and CO yields. On the other hand for methane, the temperature effect increase is less clear, with wood pellets and bark displaying positive yields changes and broza showing a yield reduction. Finally, for CO₂, the influence of temperature increases with higher thermal levels having a positive effect on CO₂ yields [82].

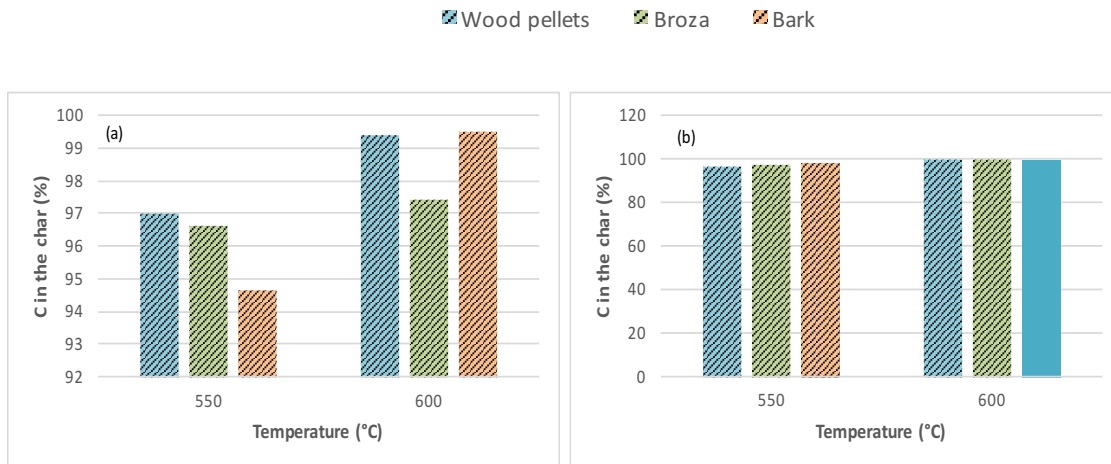


Figure 4.9. Carbon Contained in Char Following Gasification at 550°C and 600°C under: (a) A CO₂ -water atmosphere and (b) A He-water atmosphere. Data reported is the average of at least 15 repeats with a +/- 3-6% standard deviation.

Figures 4.9(a) and 4.9(b) report the carbon content in char after the gasification of wood pellets, broza and bark, at 550°C and 600°C, respectively. It can be noticed that the amount of carbon in char reached 90% and over, at 550°C. This was the case for all biomass feedstocks under water-helium atmospheres. In addition, the carbon in char content was enhanced further at 600°C, reaching 98-99%. Similar trends, were noticed as shown in Figure 4.9(b) under water-CO₂. The carbon content in char was in the 98-99%, in all cases. This is in agreement with previous findings on CO₂-steam gasification of wood [4].

4.4. Conclusions

- Biomass gasification and in particular the permanent gases produced, were observed to be strongly dependent on both biomass type (wood pellets, bark or broza) and gasification atmosphere conditions (water-helium or water-CO₂).

- Temperature increases in the 550°C-600°C range, consistently favor dry gas yields and the Conversion of Biomass Contained Carbon (CBCC). This is true for all feedstocks studied as well as for water-helium and water-CO₂ atmospheres.
- Gasifying atmosphere, either water-helium and water-CO₂ had a major influence on H₂, CO, CH₄ and CO₂ product species distribution. It was observed that water-helium atmospheres led to higher H₂ yields than the ones observed for water-helium.

- From all the feedstocks studied, broza appears to be the feedstock providing the highest H₂/CO ratios both under water-helium and water-CO₂ atmospheres. It is speculated that this is the result of the relatively high content of ash in broza promoting the water-gas shift reaction. This was also consistent with the consistently observed high CO₂ yields.
- For CO₂-water gasification, it appears that (with the only exception of broza at 600°C), the various feedstocks yield an essentially zero net yield of CO₂. This is encouraging because it could help set gasification in the context of a “zero” net CO₂ production gasification process.

CHAPTER 5

5. Thermodynamic Chemical Equilibrium Model

5.1. Introduction

A significant number of studies [83] [84] [85] [86] [87] have addressed the thermodynamic equilibrium modeling of biomass gasification systems. These studies have revealed the importance of approaching thermodynamic equilibrium in order to evaluate the feasibility of gasification processes.

This chapter discusses the chemical thermodynamic equilibrium analysis for the steam gasification of the biomass samples. Evaluations were carried out including the main components in biomass (C, H and O) and product species (H_2 , CO, CH_4 , CO_2 and H_2O).

The thermodynamic equilibrium model validates the effect of biomass composition, bed temperature and gasifying agent on the various gas product molar fractions. The study aims to compare thermodynamic equilibrium predictions with experimental data obtained in a CREC Riser Simulator. Results showed that the produced syngas from steam gasification using broza feedstock were close to equilibrium data.

The chemical thermodynamic equilibrium analysis was developed using the process simulation software Aspen-Hysys and a *Reactor Equilibrium* Module. Key stoichiometries were selected in order to analyze the reaction process. Using the *Reactor Equilibrium* Module, mass and heat balances were calculated concurrently under chemical reaction equilibrium conditions.

5.2. Chemical Equilibrium Model

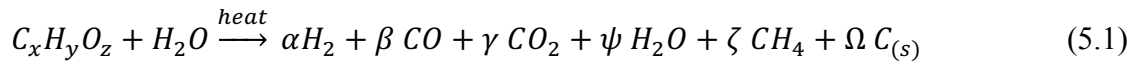
The chemical equilibrium model accounts for following assumptions:

- a) C, H, O in biomass feedstocks are considered using elemental analysis. All other elements such as N and S are neglected.
- b) Ash is considered negligible in all chemical equilibrium calculations.

- c) Char and tar are accounted for via the unconverted carbon lump.
- d) The significant gasification products were H₂, CO, CO₂, CH₄ and H₂O as observed during product analysis.
- e) A selected set number of 4 independent reaction pathways were adequate to describe the chemical equilibrium without redundancy.
- f) The heat of formation and the Gibbs Free Energy of Formation of biomass (CH_xO_y unit) are considered negligible as the one for carbon.

5.3. Thermodynamic Equilibrium Model for Steam Gasification of Biomass

Based on the previous considerations, the product species taken into account are the following: H₂, CO, CO₂, CH₄, H₂O and C. The effects of nitrogen and sulfur are not considered in this study due their minor contributions to the gasification process, in terms of equilibrium calculations [88] [89]:



With α , β , γ , ψ , ζ , Ω being the stoichiometric coefficients in eq(5.1).

Five equations can be considered to model the steam gasification of species. For the purposes of simulation, the concept of biomass was broken down and simplified into independent streams of C, H, and O:



An *Equilibrium Reactor* module was selected as a suitable unit to model equilibrium reactions simultaneously. In order to have an independent set of stoichiometric equations consistent with

the requirements with chemical equilibrium calculations, Eqs (5.2), (5.3), (5.4) and (5.6) were considered.

One should notice that the Equilibrium Reactor module in Hysis-Aspen includes the definition of the stoichiometry. Various chemical equilibrium constants are defined directly by the Hysis Aspen software.

5.4. Application of Equilibrium Criteria to Chemical Reactions

For a closed reactor system as in the CREC Riser Simulator module, at constant temperature and pressure, it is known that the total Gibbs Free Energy decreases during the process, reaching the following equilibrium condition [90]:

$$(dG^t)_{T,P} = 0 \quad (5.6)$$

Thus, for any type of reaction that is not at chemical equilibrium, the total Gibbs Free Energy must only decrease at a constant temperature and at a constant total pressure and this for any reaction change in the system.

Thus, when comparing the Gibbs Free Energy at the equilibrium state with the Gibbs Free Energy at any other surrounding state, at constant T and P, it can be predicted that the value at equilibrium is the lowest. This allows one to consider an alternative criterion for equilibrium: at a constant T and P, the total Gibbs Free Energy being minimum at chemical equilibrium.

5.5. Effect of Temperature on the Equilibrium Constant

Since the standard-state temperature is that of the equilibrium mixture, the standard property changes of reaction, such as ΔG^o and ΔH^o , vary with the equilibrium temperature. The dependence of ΔG^o on T is given by the following equation:

$$\frac{(\Delta G^o/RT)}{dT} = -\frac{\Delta H^o}{RT^2} \quad (5.7)$$

As well, given Eq (5.6) the following can be stated:

$$\frac{\Delta G^o}{RT} = -\ln K \quad (5.8)$$

Therefore, one can consider Eq. (5.9) to assess the effect of temperature on the equilibrium conversion as follows:

$$\frac{d \ln K}{RT} = \frac{\Delta H^o}{RT^2} \quad (5.9)$$

5.6. Equilibrium Constant

The calculation of the equilibrium constant K_{eq} for a chemical reaction ($Aa+bB \rightarrow cC+dD$) can be based on an ideal gas model for various gas chemical species (Eq (5.11)). In this case, having the fugacity coefficients equal to one, the reaction's equilibrium constant K_{eq} can also be defined as described in Eq (5.16):

$$K_{eq} = e^{\frac{-\Delta G}{RT}} = \frac{P_{H_2} P_{CO_2}}{P_{CO} P_{H_2}} = \frac{y_C^c y_D^d}{y_A^a y_B^b} \quad (5.10)$$

If the standard heat of reaction is known as a function of T, Eq (5.10) can be integrated analytically, as shown in the following equation:

$$\ln K = \int \frac{\Delta H^o}{RT^2} dT + I \quad (5.11)$$

with I being a constant of integration. The general expression for ΔH^o is:

$$\Delta H^o = J + \int \Delta C p^o dT \quad (5.12)$$

where J is as well, another constant of integration. Each $C p^o$, is defined as:

$$\frac{C p^o}{R} = A + BT + CT^2 + DT^{-2} \quad (5.13)$$

Then, the resultant expression for ΔH^o is described in Eq. (5.15) as follows:

$$\frac{\Delta H^o}{R} = \frac{J}{R} + (\Delta A)T + \frac{\Delta B}{2} T^2 + \frac{\Delta C}{3} T^3 - \frac{\Delta D}{T} \quad (5.14)$$

Substituting Eq (5.15) into Eq (5.12) and integrating, the following is obtained:

$$\ln K = \frac{-J}{RT} + (\Delta A) \ln T + \frac{\Delta B}{2} T + \frac{\Delta C}{6} T^2 - \frac{\Delta D}{2T^2} + I \quad (5.15)$$

5.7. Steam Biomass Gasification Thermodynamic Equilibrium Model

A thermodynamic equilibrium model for the steam gasification of biomass materials shall include: a) temperature, b) biomass composition c) pressure and d) gasifying agent as inputs for the equilibrium calculations.

This study focuses on the development of a thermodynamic equilibrium model for a fluidized bed gasifier and steam as the oxidizing agent. This model allows the simulation of the chemical composition of the produced syngas as a function of the biomass composition, carrier gas, pyrolysis and gasification reactions and operational parameters of the gasifier unit.

The gasification reactor was modeled using Aspen Hysys software as described in Figure 5.1. This includes an Equilibrium Reactor module, in which a set of 4 chemical independent reactions (eqs. 5.2, 5.3, 5.4 and 5.6) occurred at equilibrium. The Equilibrium Reactor solves this set of equations simultaneously calculating the yields of various products species (H_2 , CO , CO_2 , H_2O , CH_4 and C) at equilibrium. The enclosed figure provides a schematics of the Hysys-Aspen module used in the calculations:

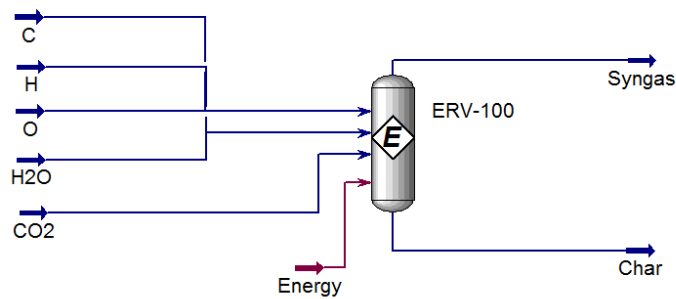


Figure 5.1. Schematic Diagram of the Steam Gasification Reactor using the Chemical Equilibrium Aspen-Hysys Module. Selected atmosphere: CO_2 . Note: Biomass is introduced in the module using the elemental composition (C, H and O).

Biomass compositions employed in the thermodynamic chemical equilibrium model are summarized in Table 5.1 in terms of moles of C, H and O. Biomass chemical formula follows the structure CH_xO_y

In the case of this particular fluidized bed gasifier, it is important to mention that differences in the temperature between the gaseous and solid phase are minimum, while differences in their concentration are not. This is due the superficial area augmentation when biomass is converted into small pieces before initiating the process. Thus, biomass superficial area is in contact with the gaseous phase, and chemical reactions take place in the reaction unit. Concentration gradients in biomass particles are neglected based on their reduced particle size.

The development of a thermodynamic equilibrium model for the steam biomass gasification of the feedstocks is based on mass balances of species for the solid and gaseous phase. Balances in the simulation software are based on the main generated gas: H₂, CO, CH₄ and CO₂ and H₂O. Validation of the model is made through comparison with experimental data and the ones achieved with the thermodynamic model.

5.8. Validation of the thermodynamic model

Comparison between the thermodynamic model and experimental data was developed on the basis of y_i which represent the moles of product “i” over the moles of C fed. Additional explanations about this parameter and its calculation are given in chapter 4.

Figure 5.2. reports the changes in the dry gas yield composition at the chemical equilibrium state and compares them with the ones obtained experimentally. To report results, darker colored bars followed by lighter-dashed colored bars are included in Figure 5.2. Dark blue bars represent equilibrium conditions and light-dashed blue bars report experimentally obtained results. The same applies to the “broza” and bark of the other two feedstocks of the present study.

■ Wood pellets Equilibrium ■ Wood pellets Experimental ■ Broza Equilibrium ■ Broza Experimental ■ Bark Equilibrium ■ Bark Experimental

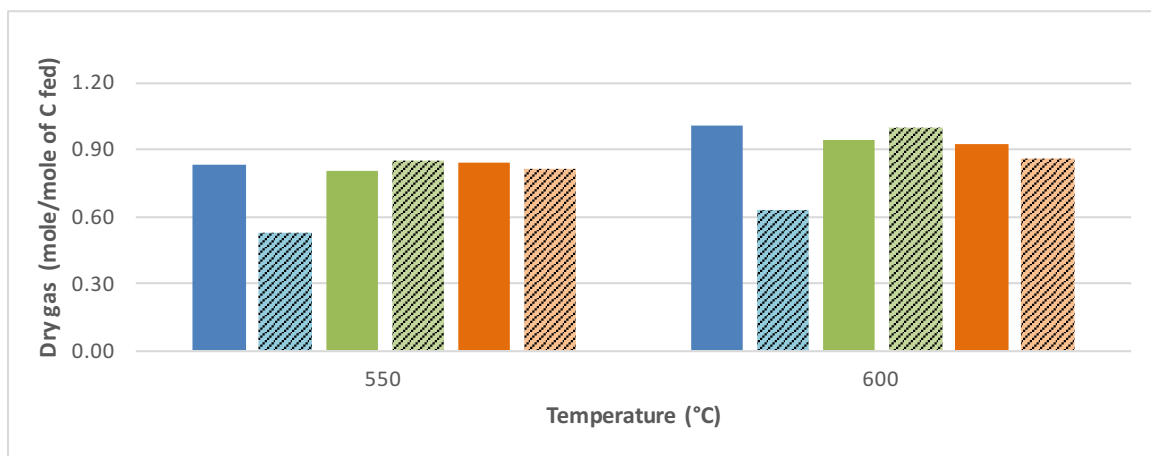
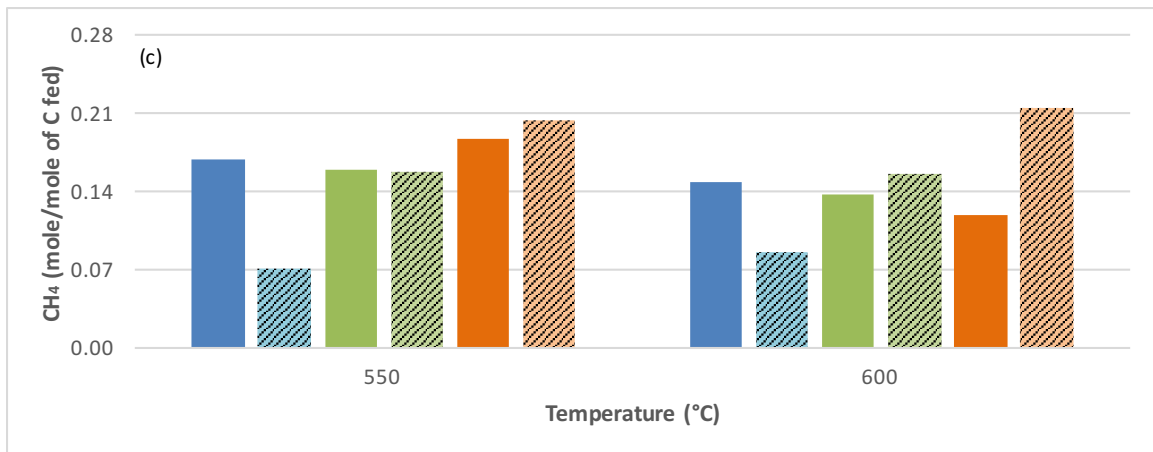
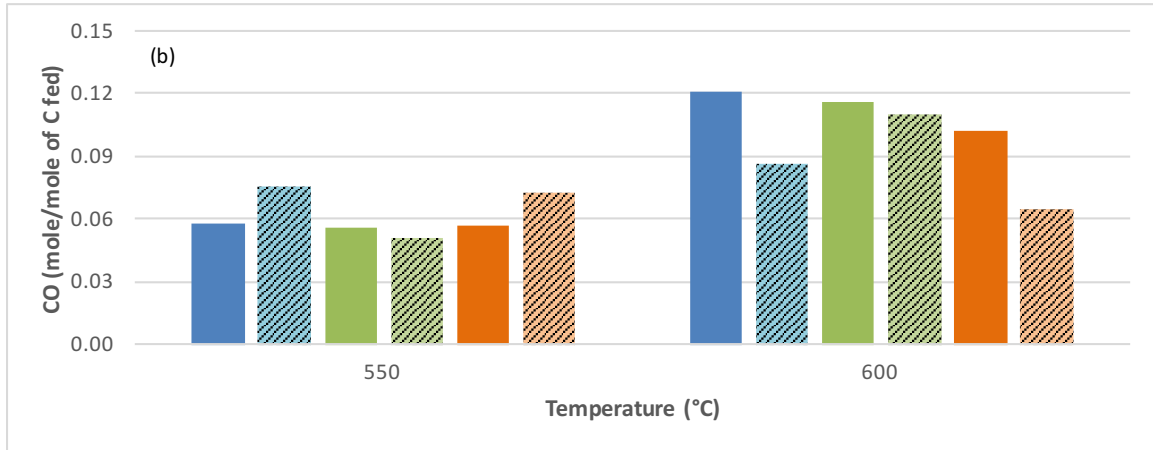
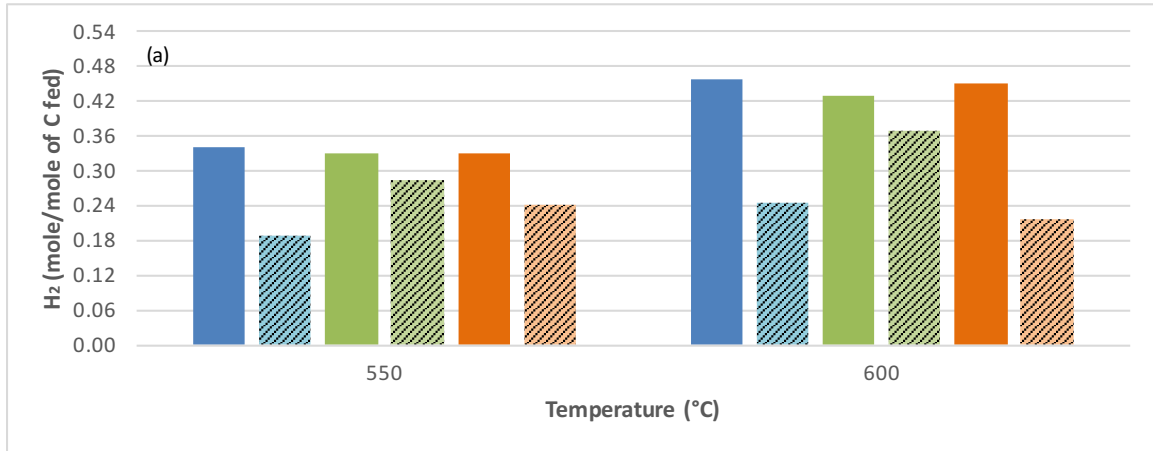


Figure 5.2. Changes of Dry Gas Yield with Temperature for Equilibrium Conditions and for Experimental Runs in the CREC Riser Simulator. Three feedstocks are considered, with these being wood pellets, broza and bark. Darker colors represent chemical equilibrium and light-dashed colors describe data from experimental runs. Selected atmosphere: inert gas (helium).

One can notice from Figure 5.2 that the dry gases as predicted by chemical equilibrium remain in a close range when using the various feedstocks, and increase with temperature. These dry gas yields at equilibrium consistently surpass the experimentally observed dry gas yields. Thus, one can safely hypothesize that the various chemical reactions as studied in the experimental runs of the present study are shifted from chemical equilibrium.

■ Wood pellets Equilibrium ■ Wood pellets Experimental ■ Broza Equilibrium ■ Broza Experimental ■ Bark Equilibrium ■ Bark Experimental



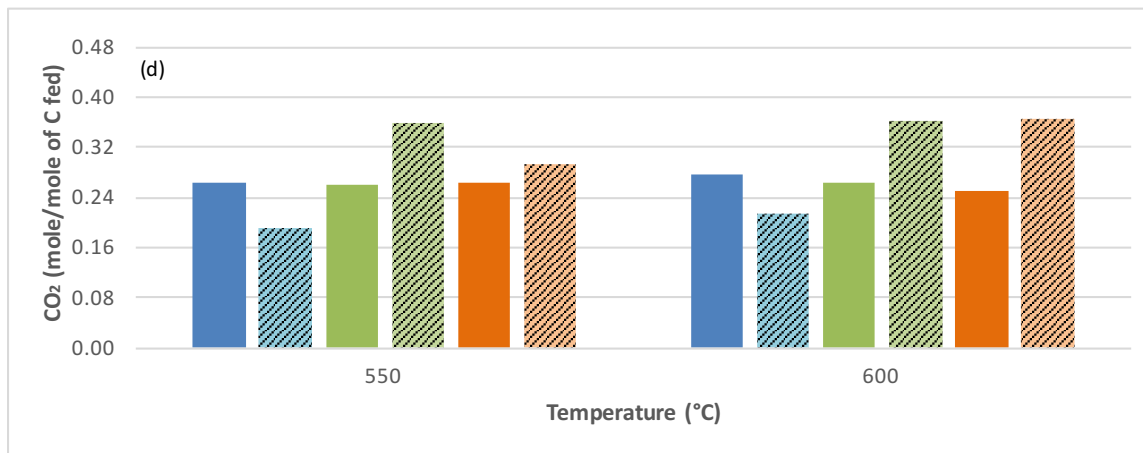


Figure 5.3. Changes of Various Product Gas Yields (Dry Basis) with Temperature for both Equilibrium Conditions and Experimental Runs in the CREC Riser Simulator. Codes: (a) H₂, (b) CO, (c) CH₄, (d) CO₂. Three feedstocks are considered with darker colors representing chemical equilibrium and lighter-dashed colors describing data from experimental runs using wood pellets, broza and bark. Selected gasification atmosphere: inert gas (helium).

Figure 5.3 (a) describes the changes in the composition of H₂ with temperature. It can be observed that H₂ yields at equilibrium were close to 0.34 mole/mole of biomass at 550°C and 0.44 mole/mole of biomass at 600°C. It can also be noticed that the actual experimental H₂ yields are 0.12-0.24 at 550°C and 0.18-0.22 at 600°C. Thus, both the thermodynamic model and the experimental data are in agreement with regard to the positive effect of the thermal level on the hydrogen yields.

Figure 5.3 (b) reports the CO yields for both the chemical equilibrium and the experimentally observed values in the CREC Riser Simulator. One can notice that CO yields at chemical equilibrium remain in a narrow range for the three feedstocks considered, at both 550°C and 600°C. One can see the consistently positive effect of raising the temperature of CO yields. In this case once again, the chemical equilibrium values, while being directionally correct provide an overestimation of the actually observed CO yields.

Figure 5.3 (c) describes the CH₄ yields for both chemical equilibrium and experimentally measured values. One can observe the following: (a) the consistency of CH₄ yields as predicted by the chemical equilibrium model for various feedstocks, (b) the underprediction of CH₄ for wood pellets, the close to equilibrium values of CH₄ for broza and the overestimation of CH₄ for bark. On the basis of this, one can hypothesize that methane reforming and its shift from chemical equilibrium are important factors affecting CH₄ yields. It appears that in cases like the one of “broza”, a feedstock with a high mineral content (ash) the CH₄ reforming reaction is favored.

Finally, Figure 5.3 (d) reports that experimentally measured CO₂ yields vary with feedstock type and thermal levels. This is in contrast with the little effect of the studied feedstocks on CO₂ yields both at 550°C and 600°C.

Figure 5.4 reports the H_2/CO ratio obtained when using both the chemical equilibrium and the experimentally determined yields and their changes. H_2/CO for the three biomasses of this study are reported.

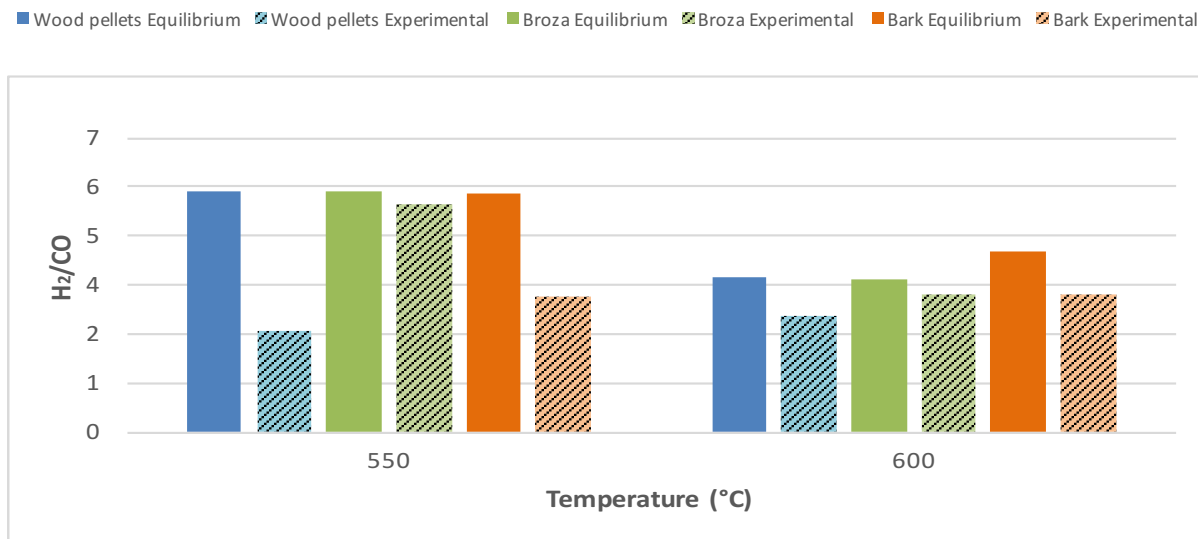


Figure 5.4. Changes of various H_2/CO Ratios with Temperature for both Chemical Equilibrium and the Experimental Runs in the CREC Riser Simulator. Three feedstocks are considered (wood pellets, broza and bark) with darker colors representing chemical equilibrium and lighter-dashed colors describing data from experimental runs. Selected atmosphere: inert gas (helium).

One can observe in Figure 5.4, that chemical equilibrium predicts high H_2/CO ratios in the 5.8 range for a $550^{\circ}C$ temperature, with this ratio being reduced to 3.7-4 ratio. One can also notice that in practice these high H_2/CO ratios at $550^{\circ}C$ are not achieved with wood pellets and bark. In fact, “Broza” is the only feedstock performing close to equilibrium as per the H_2/CO ratio observed experimentally. This behavior can once again be attributed to the high content of ash in the broza, which promotes gasification reactions. Despite this, research is lacking on the evaluation of the effect of ash on synthesis gas composition. Previous findings determined the catalytic effects of ash in the steam biomass gasification process [90]. The characterization of ash has shown that elements encountered in bottom ash include oxides such as SiO_2 , Fe_2O_3 , Al_2O_3 , CaO and MgO . Ellis [91] also mentioned the potential of aluminosilicate species with iron and calcium catalysts.

In any event, one can also see that under the conditions employed in the CREC Riser Simulator, the three feedstocks studied yielded a $H_2/CO > 2$ which are the required conditions for methanol synthesis ($CO + 2H_2 \rightarrow CH_3OH$). Thus, and on the basis of the above, one can argue that the various feedstocks at the selected conditions, are excellent for the synthesis of alcohols.

Furthermore, Figure 5.5 reports carbon converted into synthesis gas, as observed both experimentally and using the chemical equilibrium model. Data consistently shows from both

experimental runs and chemical equilibrium, that gasification under the selected conditions of the experiments yields 35-50% of the feedstock converted into synthesis gas. This is a favorable condition given biomass gasification as in the present study, is considered for co-production of biochar and synthesis gas.

■ Wood pellets Equilibrium ▨ Wood pellets Experimental ■ Broza Equilibrium ▨ Broza Experimental ■ Bark Equilibrium ▨ Bark Experimental

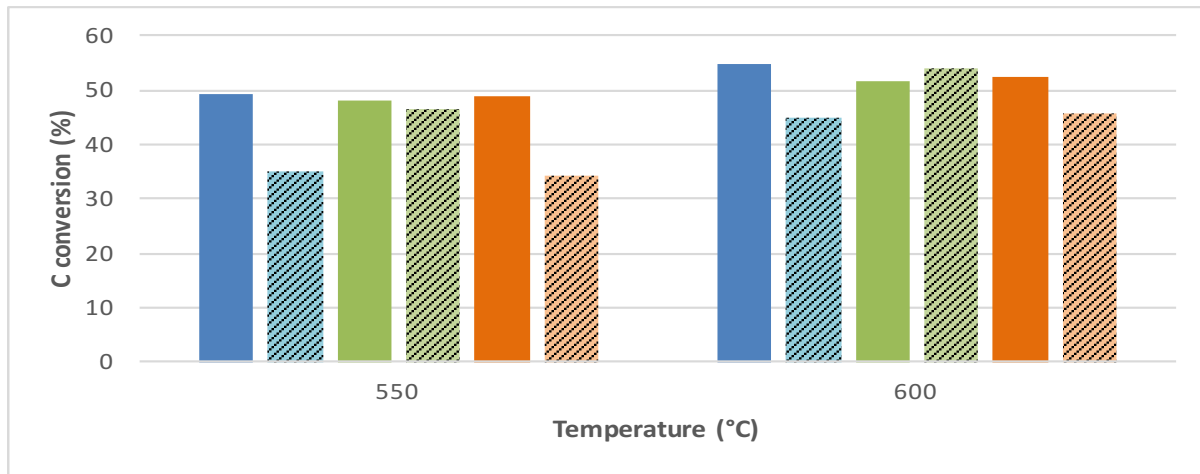


Figure 5.5. Changes of the Conversion of Biomass Contained Carbon into Synthesis Gas as Predicted by Chemical Equilibrium and as a Result of Experimental Runs in the CREC Riser Simulator. Three feedstocks are considered (wood pellets, broza and bark) with darker colors representing chemical equilibrium. Lighter-dashed colors describe data from experimental runs. Selected atmosphere: inert gas (helium).

Regarding the studies developed in the context of the present MESc thesis, once the experimental runs with inert gas (e.g helium) atmosphere were completed, they were followed with experimental runs using CO₂ as a co-gasifying agent. To provide a better discussion of the results obtained, chemical equilibrium calculations were developed for the gasification of the three feedstocks of the present study.

Figure 5.6 reports the changes in the dry gas yields at chemical equilibrium and obtained experimentally at both 550°C and 600°C.

■ Wood pellets Equilibrium ■ Wood pellets Experimental ■ Broza Equilibrium ■ Broza Experimental ■ Bark Equilibrium ■ Bark Experimental

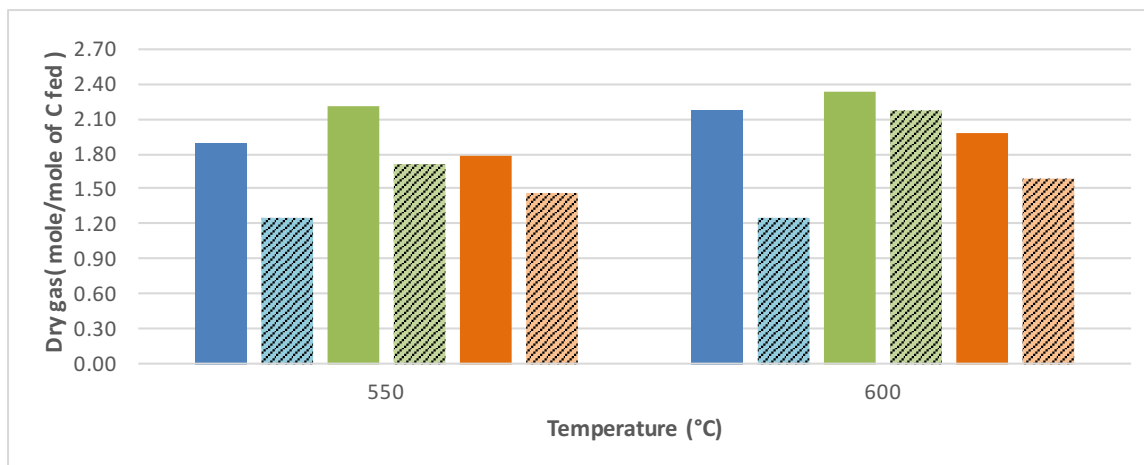
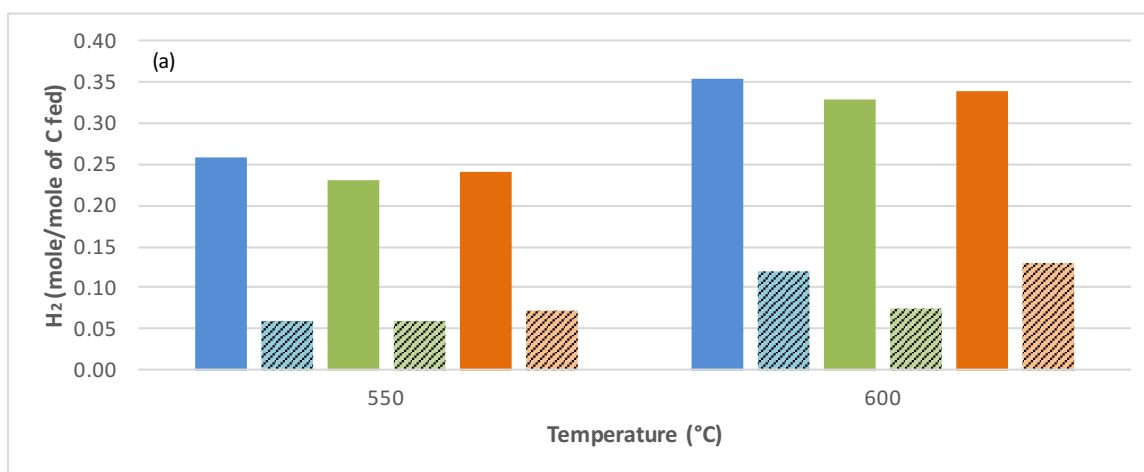


Figure 5.6. Changes of Dry Gas Yield with Temperature for both Equilibrium Conditions and Experimental Runs in the CREC Riser Simulator. Three feedstocks are considered (wood pellets, broza and bark) with darker colors representing chemical equilibrium. Lighter colors describe data from experimental runs. Selected atmosphere: CO₂.

Figure 5.6 shows the modest effect of temperature on dry gas yields, with the chemical equilibrium model consistently overpredicting the dry gas yields.

Furthermore, Figure 5.7 reports the changes of product gas yields with temperature for both chemical equilibrium and from experimental runs using the H₂, CO, CH₄ and CO₂ yields. Three biomasses (wood pellets, broza and bark) were used in the gasification experiments under a CO₂ atmosphere.

■ Wood pellets Equilibrium ■ Wood pellets Experimental ■ Broza Equilibrium ■ Broza Experimental ■ Bark Equilibrium ■ Bark Experimental



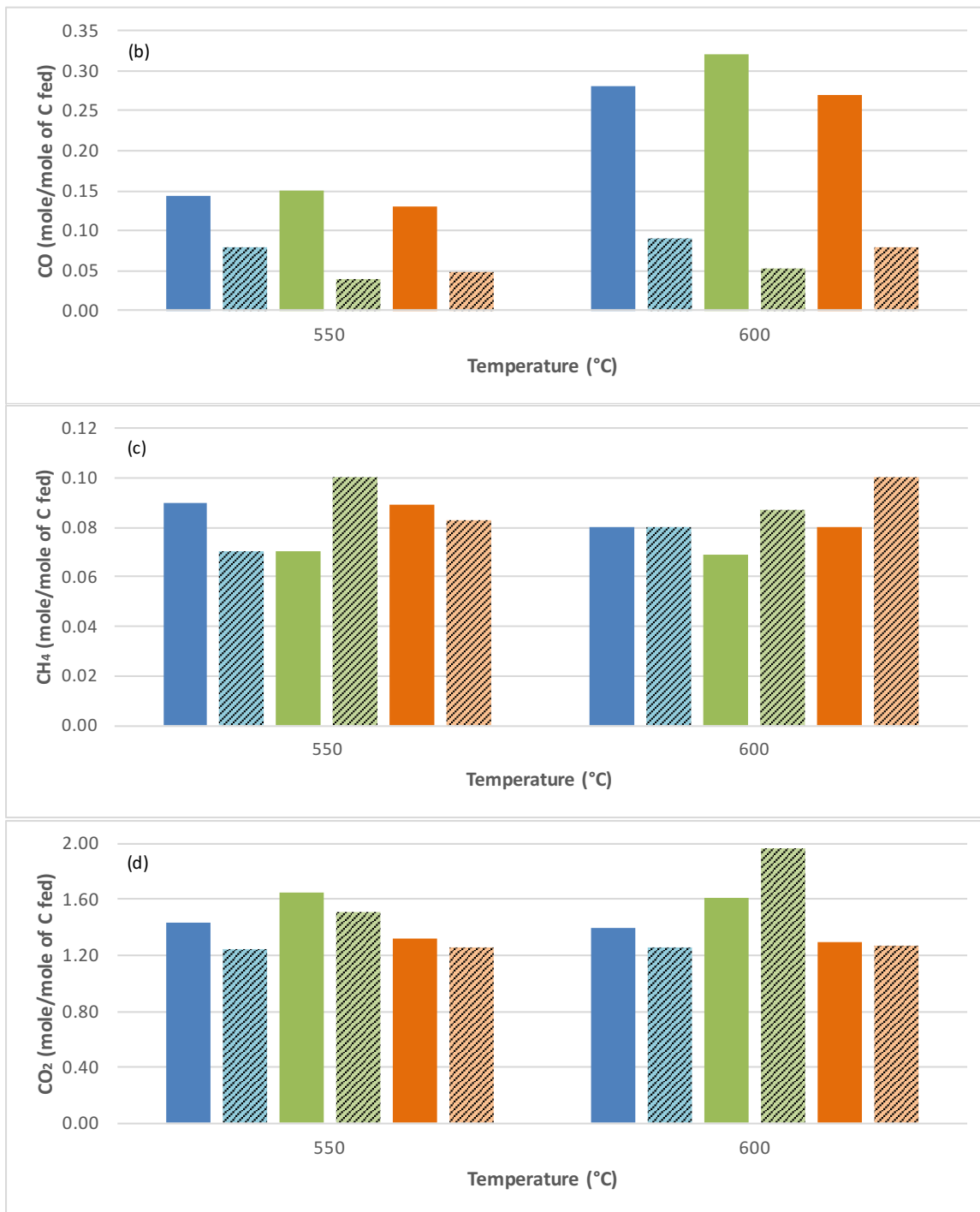


Figure 5.7. Changes of Various Product Gas Yields (Dry Basis) with Temperature for both Equilibrium Conditions and Experimental Runs in the CREC Riser Simulator. Codes: (a) H₂, (b) CO, (c) CH₄, (d) CO₂. Three feedstocks are considered (wood pellets, broza and bark) with darker colors representing chemical equilibrium. Lighter-dashed colors describe data from experimental runs. Selected gasification atmosphere: CO₂.

On the basis of this data, when CO₂ was used as a gasifying agent, one can notice the following:
a) There is a significant deviation between the equilibrium model and the experimental data. This

is the case for H₂, CO and CH₄ yields, b) The presence of CO₂ enhances consistently and significantly the CO yields while reducing H₂ and CH₄ yields

In addition, there are other important consequences for biomass gasification when using CO₂ as a gasifying agent, as reported in Figure 5.8 and 5.9.

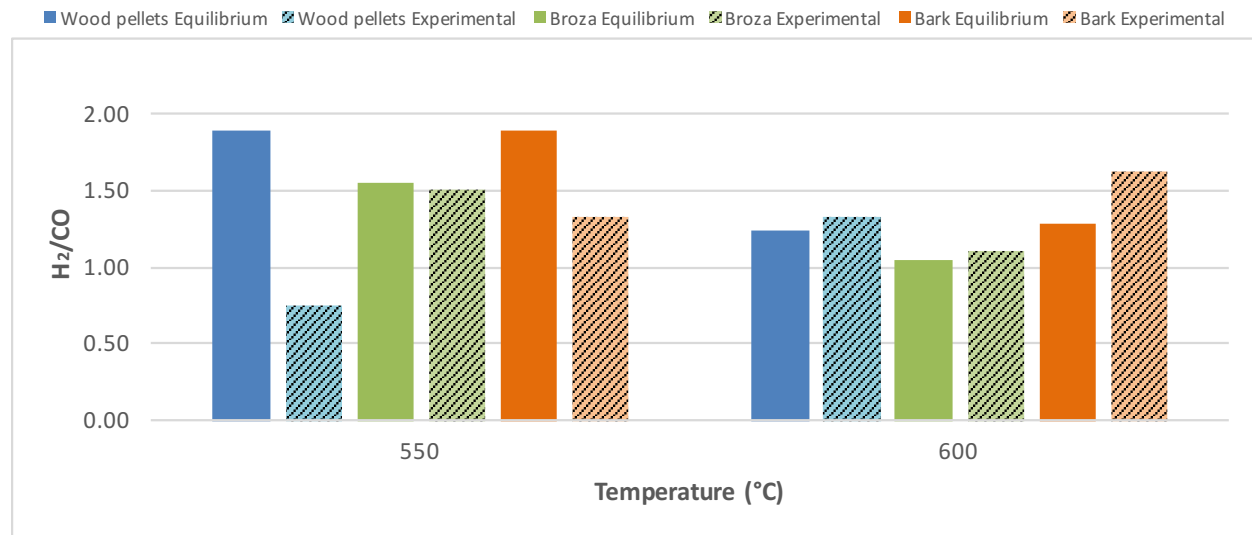


Figure 5.8. Changes of Various H₂/CO Ratios with Temperature for both Chemical Equilibrium and for the Experimental Runs in the CREC Riser Simulator. Three feedstocks are considered (wood pellets, broza and bark) with darker colors representing chemical equilibrium. Lighter-dashed colors describe data from experimental runs. Selected gasifying atmosphere: CO₂.

Figure 5.8 shows a comparison of the thermodynamic model yield predictions for biomass gasification under CO₂ atmosphere. One can notice that for broza, product yields become close to the ones observed experimentally. For instance, at 550°C, the H₂/CO ratio for broza is 1.5 for the experimentally measured values, while staying at level 2 for chemical equilibrium being 2. On the other hand, when the temperature is increased to 600°C, the H₂/CO ratios for chemical equilibrium as well as those experimentally observed are 1.4 and 1.2, respectively. These results appear to be in agreement with Wang [92]. This author mentioned the potential effect of ash on the biomass gasification reactions in a CO₂ atmosphere, case of the water gas shift reaction.

Figure 5.9 also describes changes of the Conversion of the Biomass Contained Carbon with both temperature and feedstock. One can notice the consistent capacity of the chemical equilibrium model to predict the Conversion of the Biomass Contained Carbon biomass gasification at 550°C and 600°C.

■ Wood pellets Equilibrium ■ Wood pellets Experimental ■ Broza Equilibrium ■ Broza Experimental ■ Bark Equilibrium ■ Bark Experimental

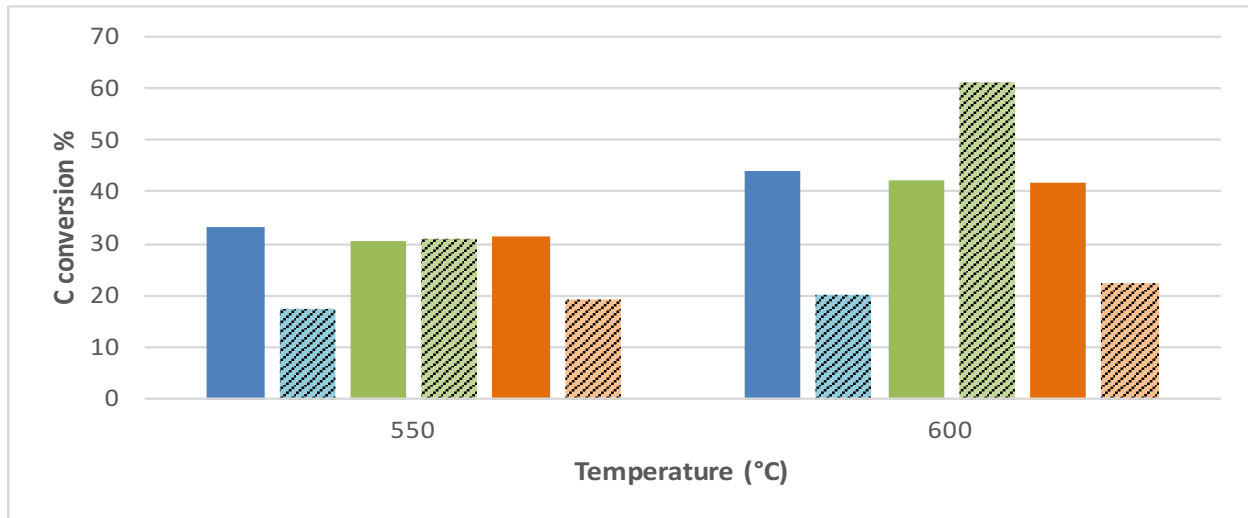


Figure 5.9. Changes of the Conversion of Biomass Contained Carbon into Synthesis Gas as Predicted by Chemical Equilibrium and as a Result of Experimental Runs in the CREC Riser Simulator. Three feedstocks are considered (wood pellets, broza and bark) with darker colors representing chemical equilibrium. Lighter-dashed colors describe data from experimental runs. Selected Gasifying atmosphere: CO₂.

5.9. Conclusions

- A chemical equilibrium model based on simultaneously solving a set of 4 independent reactions, was implemented in order to predict various biomass gasification product yields from both steam-helium and steam-CO₂ atmospheres.
- The chemical equilibrium model was solved using an Hysis-Aspen software in which stoichiometries are considered and various required formation Gibbs Free Energies are calculated automatically by the software.
- The proposed chemical equilibrium model displayed different ability for the prediction of various product yields with this being a function of the feedstock studied.
- In the case of gasification of wood pellets and bark, it was found the chemical equilibrium model was adequate for water-helium atmospheres, being fair only for water-CO₂ atmospheres. This demonstrates that the nature of the biomass feedstock can strongly affect the applicability of a chemical equilibrium model for product distribution calculations.
- In the case of broza gasification, the chemical equilibrium model showed better reliability for predicting species yields, H₂/CO ratios and CBCC conversions (Conversion of Biomass Contained Carbon). This was the case for both water-helium as well water-CO₂ atmospheres. Regarding the

observed findings for broza, this can be attributed to high mineral matter content of the broza and its potential catalytic effect.

CHAPTER 6

6. Conclusions and Recommendations

This research work studied the influence of operational parameters such as temperature, reaction atmosphere and feedstock type on biomass gasification. In particular, gasification of wood pellets, broza and bark at 550°C to 600°C thermal levels were investigated. Gasification of biomass materials was performed in a CREC Riser Simulator Reactor Unit. A thermodynamic model was developed to help describe the various product yields. It is expected that progress with the described thermodynamic model could considerably assist in gasification unit scale up.

On this basis, the following are the major findings of the present study:

- Biomass gasification and in particular the permanent gases yields produced, were observed to be strongly dependent on biomass type, thermal level and gasification atmosphere conditions (water-helium or water-CO₂).
- Temperature increases in the 550°C-600°C range, consistently favored dry gas yields and the Conversion of Biomass Contained Carbon (CBCC), with this being true for all feedstock studied as well as for water-helium and water-CO₂ atmospheres.
- Gasifying atmosphere, either water-helium and water-CO₂ had a major influence on H₂, CO, CH₄ and CO₂ product species distribution. It was observed that water-helium atmospheres led to higher H₂ yields than the ones observed for CO₂-helium.
- Regarding the syngas obtained in the present study under water-helium, one can notice its suitability for a Fischer Tropsch process and alcohol synthesis due its H₂/CO ratio higher than 2. On the other hand, steam gasification of biomass under a CO₂ atmosphere, can be employed for electrical production (H₂/CO<2).
- From all the feedstocks studied, broza appears to be the one providing the highest H₂/CO ratios, both under water-helium and CO₂-helium atmospheres. It is speculated that this is the result of the relatively high content of ash in broza promoting the water-gas shift reaction. This was also consistent with the high H₂ and CO₂ yields obtained when using broza as a feedstock.
- For water-CO₂ gasification, it appears that (with the only exception of broza at 600°C), the various feedstocks yield an essentially zero net yield of CO₂. This is encouraging because it could help set gasification in the context of a “zero” net CO₂ production process.
- Regarding modelling, a chemical equilibrium model based on simultaneously solving

- a set of 4 independent reactions, was implemented in order to predict various biomass gasification product yields from both steam-helium and steam-CO₂ atmospheres.
- The chemical equilibrium model was solved using an Hysis-Aspen software in which stoichiometries are considered and various required species Enthalpies and Gibbs Free Energies of formation are calculated automatically by Hysis-Aspen.
 - The proposed chemical equilibrium model displayed a variable ability for the prediction of various product yields with this being a function of the feedstocks studied.
 - In the case of the gasification of wood pellets and bark, it was found that the chemical equilibrium model was adequate for water-helium atmospheres and less appropriate for water-CO₂ atmospheres. This demonstrates that the type of biomass can strongly affect the applicability of the proposed chemical equilibrium model for product distribution calculations.
 - In the case of broza gasification, the chemical equilibrium model showed better reliability for predicting species yields, H₂/CO ratios and CBCC (Conversion of Biomass Contained Carbon) conversions. This was the case for both water-helium as well water-CO₂ atmospheres. Regarding the observed findings for, they can be attributed to the high mineral matter content of the broza and its potential catalytic effect.

Recommendations

- It is recommended that future work further investigate broza gasification, reviewing in particular, the CO₂ yields for broza at 600°C. These values supersede in fact, the CO₂ yields at equilibrium in the present work.
- It is recommended to modify the chemical equilibrium model, incorporating other minor, however measurable hydrocarbon species such as ethane, ethylene, propane and propylene. It is anticipated that this will provide a closer prediction of CBCC (Conversion of Biomass Contained Carbon).

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8. Appendices

Appendix A. Mass balance

This appendix reports the mass balance for the steam biomass gasification experimental data. Calculation of the mass balance is carbon based and includes all chemical species fed in and removed of the reactor. Operational parameters such as reactor temperature and reactor pressure are also considered. An important observation from these runs was that the mass balance closures, were in the $\pm 7\%$ range.

In all types of experiments, the amount of biomass loaded in the reactor was 0.04 g and the water added was 8 μg (m_i).

The total amount of coke in the char was measured by the Toc from the Shimadzu company using the solid sample module (SSM-5000A).

The mass balance closure was defined as:

$$MB_c = \frac{m_p + m_{T,c}}{m_i} * 100 \quad \text{Eq. A.1}$$

Where

$MB_c = \text{mass balance closure \%wt/wt}$

$m_i = \text{total mass of reactants injected, g}$

$m_p = \text{total mass of reaction products, g}$

$m_{T,c} = \text{total mass of coke in the char, g}$

The total mass of carbon loaded into the reactor (m_i) was calculated as the sum of the carbon present in the gas feed (m_g) plus the carbon in the biomass sample (m_{bi}). In the first place, m_{bi} was determined using the carbon content of biomass (C_{bi}) and the initial biomass loaded in the reactor ($m_{T,bi}$). The value of m_g was estimated using the the total mole of carbon in the gas feed and ideal gas law.

$$m_i = m_{bi} + m_{gi} \quad \text{Eq.A.2}$$

$$m_{bi} = C_{bi} \cdot m_{T,bi} \quad \text{Eq.A.3}$$

$$n_r = \frac{P_{r_i} \cdot V_r}{R \cdot T_{r_f}} \quad \text{Eq.A.4}$$

$$m_g = n_r \cdot MW_C \quad \text{Eq.A.5}$$

Where

n_r = total moles of carbon fed in the reactor, moles

P_{r_i} = initial reactor pressure when the 4PV is closed, psia

V_r = reactor volume, cm³

R = ideal gas constant, 1205.91cm³psia/gmolK

T_{r_i} = initial reactor temperature, K

T_{r_f} = final reactor temperature, K

MW_C = molar mass of C, 12g/mol

To calculate the total mass of product, the system reactor + vacuum was modified to a system using only the reactor (Eq.A.6)

$$m_p = n_r \sum x_i MW_C \quad \text{Eq.A.6}$$

With x_i representing the molar fraction of each carbonaceous product specie in the syngas.

The total mass of coke in the char was calculated using the carbon content in the char (C_c) and the mass of unreacted carbon (m_c).

$$m_{T,c} = \frac{m_c C_c}{100 \%} \quad \text{Eq.A.7}$$

In Table A.1 mass balances calculated for an averaged set of non-catalytic runs of wood pellets gasified under CO₂ at 550°C and 600°C. In addition, Table A.2 is presented in order to exemplify material balances for the gasification of the same biomass material under a He atmosphere at

550°C and 600°C .

Table A.1. Mass balances of non-catalytic steam gasification of wood pellets under a CO₂ atmosphere at 550°C 600°C, reaction time 40 min.

Run name	RUN-WP-550 °C	RUN-WP-600°C
Reaction time (min)	40	40
T_{r_i} (°C)	27.714	26.150
T_{r_f} (°C)	550	600
$m_{T,bi}$ (g)	0.040	0.040
m_c (g)	0.009	0.009
m_l (g)	0.008	0.008
x_{H_2}	0.0106	0.0182
x_{CO}	0.0143	0.0158
x_{CH_4}	0.0103	0.0141
x_{CO_2}	0.8344	0.8417
$x_{C_2H_4}$	0.0006	0.0004
$x_{C_2H_6}$	0.0012	0.0019
$x_{C_3H_6}$	0.1280	0.1078
$x_{C_3H_8}$	0.0004	0.0001
n_r	0.003	0.003
C_{bi} (wt%)	46.300	46.300
m_g (g)	0.025	0.025
m_{bi} (g)	0.019	0.019
m_i (g)	0.043	0.044
m_p (g)	0.029	0.029
C_c (wt%)	81	94
$m_{T,c}$ (g)	0.008	0.009
MB_c (%)	85.375	86.350

Table A.2. Mass balances of non-catalytic steam gasification of wood pellets under a He atmosphere at 550°C and 600°C, reaction time 40 min.

Run name	RUN-WP-550 °C	RUN-WP-600°C
Reaction time (min)	40	40
T_{r_i} (°C)	25.038	26.850
T_{r_f} (°C)	550	600
$m_{T,bi}$ (g)	0.040	0.040
m_c (g)	0.009	0.008
m_l (g)	0.008	0.008
x_{H_2}	0.069	0.123
x_{CO}	0.069	0.054
x_{CH_4}	0.072	0.098
x_{CO_2}	0.153	0.185
$x_{C_2H_4}$	0.002	0.003
$x_{C_2H_6}$	0.008	0.013
$x_{C_3H_6}$	0.002	0.001
$x_{C_3H_8}$	0.001	0.001
n_r	0.003	0.003
C_{bi} (wt%)	46.300	46.300
m_{bi} (g)	0.019	0.019
m_i (g)	0.019	0.019
m_p (g)	0.002	0.002
C_c (wt%)	90	90
$m_{T,c}$ (g)	0.008	0.007
MB_c (%)	54.033	49.603

Appendix B. Calibration curves

The gas chromatograph used for the analysis of gases was coupled to a thermal conductivity detector (TCD) and a packed column for the separation of hydrocarbons. High temperature inside the TCD was required to allowed the detection of smaller amounts of hydrocarbons (1ppm) and also lower amounts of hydrogen (5ppm) in the syngas.

The gas product calibration curve that correlates the concentration of each specie with its TCD area was determined using certified standard gases and changing the quantity injected to the CREC Riser Simulator linked to the GC-TCD system.

To ensure accuracy of the detector response, a leak test was done heating up the reactor and vacuum box to 250°C, while gas was circulating. The reactor temperature was set at 550 °C to ensure entire evaporation of the sample. Once the temperature in the reactor was set, the gas flow was stopped and the reactor pressure was equilibrated to atmospheric. Then, the reactor was isolated by closing the 4PV and sub-atmospheric pressure was used in the vacuum box.

Following, samples of standard gases with known concentrations of gases were injected into the reactor using a calibrated gas syringe. After a few seconds, the 4PV was opened, with a pressure drop in the reactor until equilibrium with the vacuum box. The 6PV, allowed the sample loop fill up and then the injection of the gas to the GC/TCD system.

Gases present in the gas include mainly H₂, CO, CO₂, CH₄. Although, small quantities of C₂H₄, C₂H₆, C₃H₆ and C₃H₈ are found in this fuel. The set of calibration curves for each individual component mentioned previously are found below.

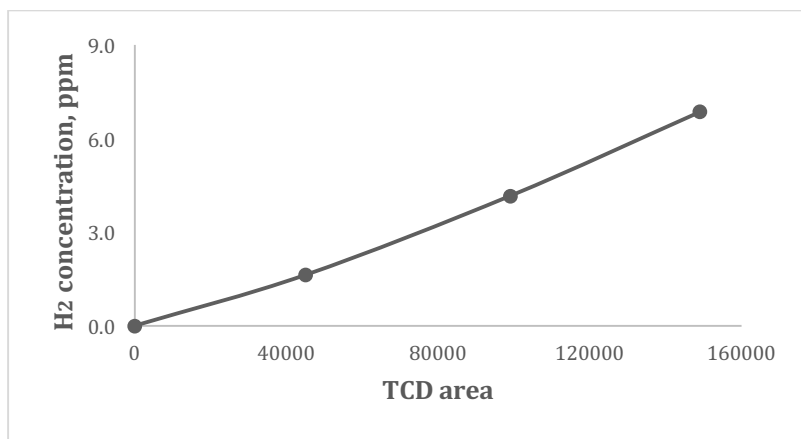


Figure B.1. TCD calibration curve for Hydrogen

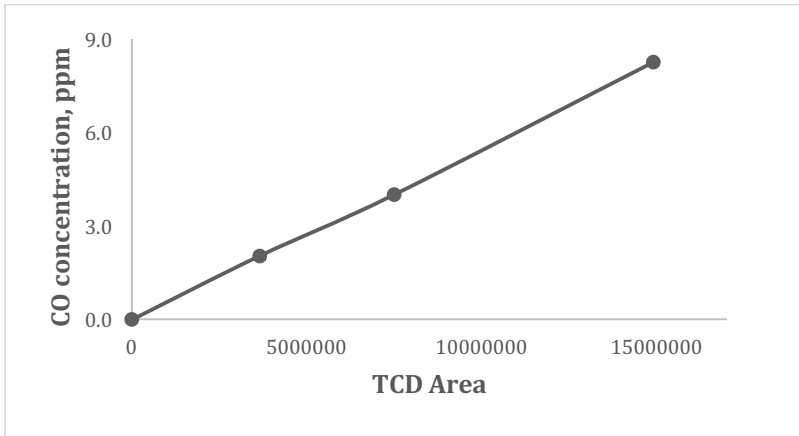


Figure B.1. TCD calibration curve for Carbon Monoxide

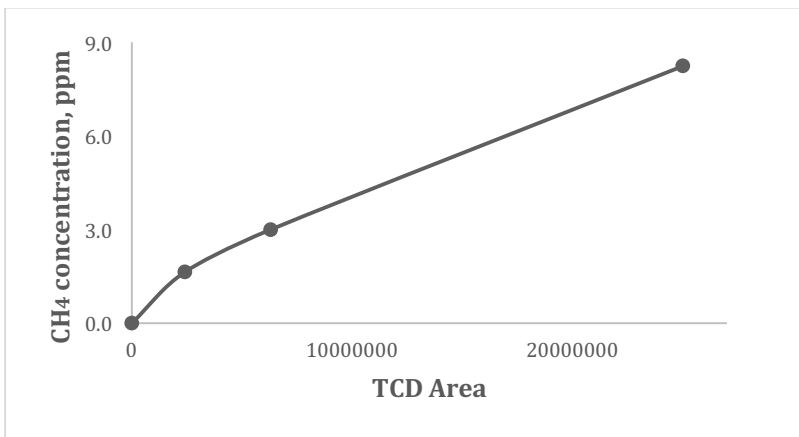


Figure B.2. TCD calibration curve for Methane

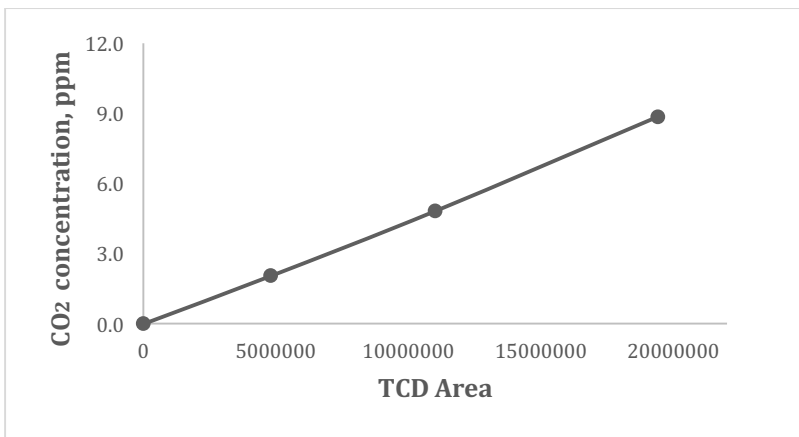


Figure B.3. TCD calibration curve for Carbon Dioxide

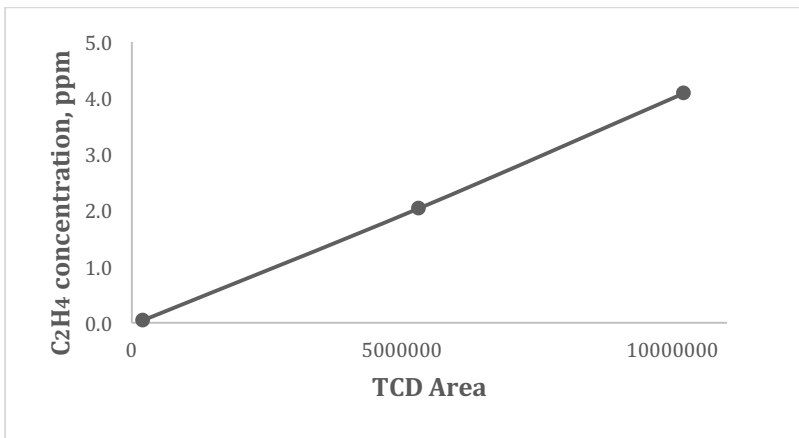


Figure B.4. TCD calibration curve for Ethylene

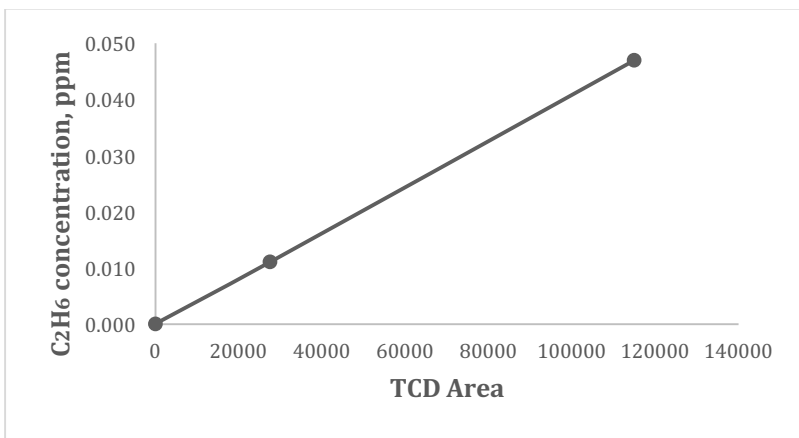


Figure B.5. TCD calibration curve for Ethane

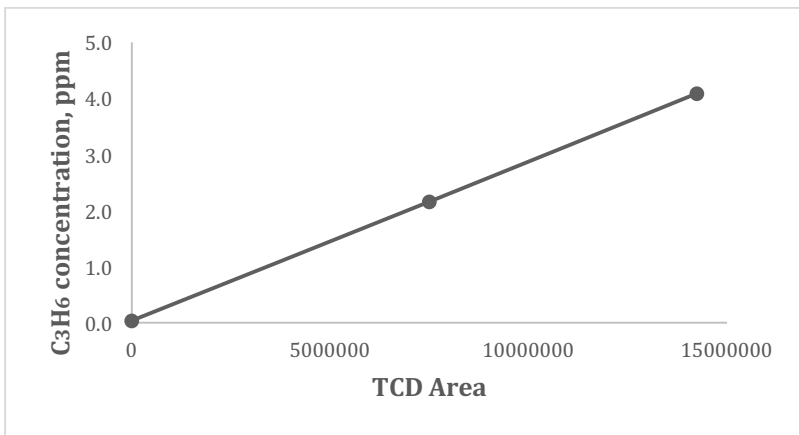


Figure B.6. TCD calibration curve for Propylene

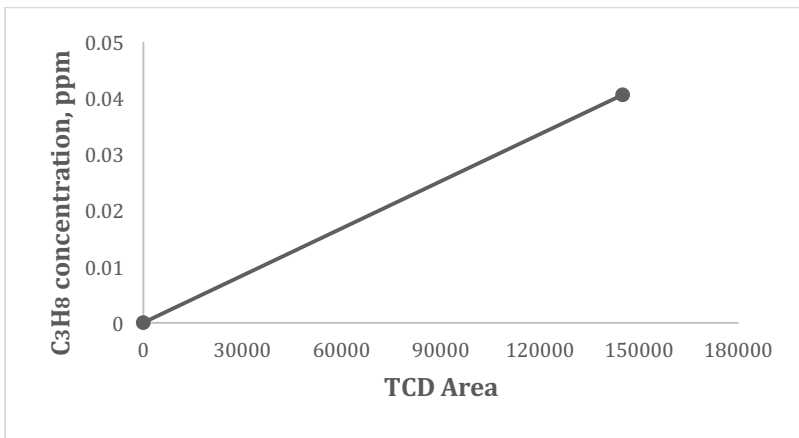


Figure B.8. TCD calibration curve for Propane

CURRICULUM VITAE

ANA M. GIRON

Skills

Solid knowledge of chemical processes, raw material transformation, regulations, standards and operational protocols in the industry and laboratory scale. Two years of experience designing, coordinating, and documenting high responsibility projects. One year of experience in the energy production field for the oil and gas industry. I am a motivated, hardworking and committed person with strong prioritization abilities and respect for others.

Education

Master in Chemical Engineering

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Experience

Research Assistant | The university of Western Ontario | Jun 2014 – Aug 2016

- Study of the effect of operational and non-operational parameters in steam biomass gasification using a novel Riser Simulator Reactor. Process optimization. Preparation and characterization of materials. Laboratory runs, process simulation and report preparation.

Teaching Assistant | The University of Western Ontario | Oct 2014 – Nov 2015

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