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Abstract

This study reports biomass gasification in a CREC Riser Simulator under thermal and catalytic conditions. Steam-CO$_2$ and steam-inert were used as gasifier agents. Biomass feedstocks and a model compound were employed to evaluate gasification performance. It was proven that catalytic steam-CO$_2$ gasification significantly reduces tar formation while improving carbon conversion to syngas.

Experimental results were compared with thermodynamic equilibrium model predictions. This model accounts for biomass composition, bed temperature and gasifying agents. The model predictions are close to experimental results for steam-CO$_2$ gasification, leading to a zero CO$_2$ gain.

2-methoxy-4-methylphenol and 20%Ni-5%CeO$_2$/γ-Al$_2$O$_3$ were selected as model compound and catalyst for the catalytic gasification. Results showed that catalytic activity reduces tars 22wt%. Furthermore, catalytic experiments under steam-CO$_2$ displays an extra 15wt% of tar reduction.

A process based on catalytic steam-CO$_2$ gasification was proposed, leading to significant tar reduction with enhanced carbon conversion to syngas. Engineering of this process benefits of the reliability of the equilibrium thermodynamic model, to predict various synthesis gas components.

Keywords

Steam-CO$_2$ Gasification of Biomass, Steam Gasification of Biomass, Catalytic Reforming of Tars, CeO$_2$ Promoted Ni/gamma-alumina, Thermodynamic Equilibrium Model, Reactivity Analysis, Tar reforming.
Dedicated to my Angel Rosa Kuhn, who happened to be my Mom.
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Nomenclature

\(C_i\) Mass Concentration of "i" species (g/cm\(^3\))

\(\text{CH}_x\text{O}_y\) Biomass Unit Formula, with "x" as H/C and "y" as O/C

\(K\) The Equilibrium Constant

\(P\) Reactor Pressure (Psi)

\(R\) The Ideal Gas Law Constant (cm\(^3\).Pa/K.mol)

\(T\) Reaction Temperature (K)

\(t\) Reaction Time (s)

\(V_t\) Total Reactor Volume (cm\(^3\))

\(\alpha\) Reaction Stoichiometric Number

\(Y_i\) Product Yield (moles)

\(y_i\) Mole Fraction of Species "i"

\(W\) Mass of Biomass or Catalyst (g)

\(\text{Wt}\%\) Weight Percentage (%)

\(\Delta G^\circ\) Standard Gibbs Energy Change of Reaction (kJ/mole)

\(\Delta H^\circ\) Standard Enthalpy Change of Reaction (kJ/mole)

Greek Symbols

\(\alpha\) Product H\(_2\)/Biomass Feed Ratio (mole/mole)

\(\beta\) Product CO/Biomass Feed Ratio (mole/mole)

\(\gamma\) Product CO\(_2\)/Biomass Feed Ratio (mole/mole)
\( \psi \)  Product \( H_2O/Biomass \) Feed Ratio (mole/mole)

\( \zeta \)  Product \( CH_4/Biomass \) Feed Ratio (mole/mole)

\( \Omega \)  Product \( C(s)/Biomass \) Feed Ratio (mole/mole)

**Acronyms**

ASTM  American Society for Testing and Material

BET  Brunauer-Emmett-Teller

CREC  Chemical Reaction Engineering Centre

GC  Gas Chromatography

GC/TCD  Gas Chromatography/ Thermal Conductivity Detector

GC/FID  Gas Chromatography/ Flame Ionization Detector

ICAFE  Instituto del Café de Costa Rica

MMP  2-Methoxy-4-Methylphenol

MS  Mass Spectrometer

SGS  Société Générale de Surveillance

SSM  Solid Sample Module

Syngas  Synthesis Gas

TOC  Total Organic Carbon Analyzer

UWO  University of Western Ontario

XRD  X-ray Diffraction

WGS  Water-gas Shift Reaction
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Chapter 1: Introduction

Energy consumption nowadays is rapidly depleting the planet’s finite fossil fuel resources. As a result, replacing fossil fuels with renewable and clean fuels will be of critical importance in coming years.\(^1\)

Energy is of importance in key areas such as the environment, health and economy. It is used in almost every daily activity, such as in transportation, cooling/heating, industrial production as well as in providing heating and air conditioning at home and in the workplace. Therefore, it is necessary to ensure that the energy supply that supports all those activities, will reduce the negative harm to the environment.

Unfortunately, we are still strongly dependent on limited and non-renewable resources like petroleum, coal and natural gas, as main sources of energy. Their overconsumption can cause serious issues, affecting our lives directly and that of future generations.\(^2\)

Examples of problems caused from fossil fuel overconsumption may be global warming. This is the case given that fossil fuels are a major CO\(_2\) emitter. The increase of CO\(_2\) in the atmosphere can lead to impaired lung function, asthma attacks and premature death from toxic smoke.\(^3\) Another issue is that some countries are still dependent on foreign sources of fossil fuel supply. This can be a danger to both economic and military security, causing sudden price variations in fossil fuels and being a catalyst for armed conflicts.

According to The US Energy Information Administration\(^4\), the total energy consumption has remained relatively flat since 2010. However, and as reported in Figure 1, a 5% rise is anticipated from 2016 to 2040. In this scenario, 35% of energy consumption will come from petroleum sources, 33% from natural gas and 11% from coal. Only 11% of this energy will be from nuclear, hydroelectric power and liquid biofuels, as well as 10% from other renewable sources, including biomass.
Another issue at play, is the intense growth of urban centres. Due to this, there is an always increasing production of municipal solid waste. While some of treatments for solid wastes are already available, such as landfill and incineration, the implementation of these processes can lead to other major issues, such as lack of available land and methane emissions. Therefore, waste disposal can be expensive and cause air pollution.

To address the energy shortage and achieve better solutions to supply energy worldwide, research is being developed to find efficient alternative technologies to convert renewable sources into energy. Renewable energy can be derived from natural resources, such as the sun, wind, rain, geothermal and biomass. Sources of biomass are much more evenly distributed around the world compared to non-renewable energy sources, such as fossil fuels.

Composed mostly of carbon (C), oxygen (O), and hydrogen (H), with traces of sulfur and nitrogen, biomass has the potential to become the largest energy supply in the world due to its abundance. Biomasses feedstock can be derivate from agricultural and forestry crops, from municipal and industrial waste, as well as from animal residues and sewage (Figure 2).
Biomass fuels have a low sulfur content and are close to CO$_2$ neutral, which makes their use very promising. Carbon present in the air and in the soil, can be absorbed by plants through photosynthesis. It can be further converted into biomass fuel, turning into carbon later, to be reused by plants. As a result, when using biomass as a fuel, no additional CO$_2$ is added to the atmosphere\textsuperscript{5}.

Biomass is abundantly and readily available in the ecosystem. Thus, its price may be less affected by the world energy prices and price fluctuations, making its supply much more stable than that of fossil fuels.

However, to utilize biomass as a fuel, it is necessary to fully develop efficient and clean biomass conversion technologies. There are several processes to produce heat and electricity from biomass, as well as various chemicals. This includes biochemical processes, to produce ethanol and methane, and thermochemical processes, to produce heat, gaseous, liquid and solid fuels.

The most common thermochemical technologies for biomass conversion are combustion, pyrolysis, liquefaction and gasification. Among them, the gasification
of biomass stands as one of the most efficient processes, given its low emission and high quality of syngas produced.

Gasification is a process that involves a series of heterogeneous reactions converting carbonaceous feedstock into gaseous, solid and liquid products. The resulting synthesis gas comprised of Hydrogen (H₂), Carbon Monoxide (CO), Carbon Dioxide (CO₂), and Water vapor (H₂O), can be used as a fuel. On the other hand, the remaining solid product, referred to as char or biochar, is a solid carbon that can be used as fertilizer. Finally, there is a liquid fraction, also known as tars or heavy hydrocarbons. Tars have limited applications, confined to paving of roads and highways, and can condense in gasifier pipe outlets and process particle filters. Thus, tars have a negative impact on the overall gasification process performance. For this reason, it is still very important to develop effective ways for reducing tar formation during gasification, as much as possible.

Biomass gasification is aided by gasifier agents, such as air, steam and/or CO₂. Steam gasification of biomass has recently attracted the interest of researchers and scientists, as it offers a synthesis gas with high heating value, high hydrogen production, and as consequence, a high H₂/CO ratio. Moreover, the use of CO₂ as a gasifying agent helps to improve the performance of the steam gasification of biomass. This is the case as CO₂ acts on tar reforming, reducing its amount and enhancing synthesis gas formation. CO₂ usage also leads to an overall CO₂ consumption reducing the footprint of the gasification process.

1.1 Scope of the Research

The present study focuses on reducing tar formation, while producing a high-quality synthesis gas, during biomass fluidized steam gasification. On this basis, an evaluation of different parameters, such as bed temperature, gasifying agent, biomass composition and catalyst application were proposed. Process temperatures below 650°C were considered. Selected operating conditions led to a more efficient gasification with limited ash agglomeration.
Steam-inert and Steam-CO\textsubscript{2} were proposed as gasifying agents in the first part of the present study. Three biomasses were involved: Costa Rica broza or coffee pulp, provided by ICAFE, followed by two other wood waste biomasses feedstock: wood pellets, provided by CANMET Energy, and bark, provided by KMW Energy.

The approach considered includes both a thermodynamic analysis, as well as reactivity studies, in a CREC Riser Simulator unit. This is a twin fluidized bed gasifier unit, which operates very close to the conditions found in the industrial riser unit. This study shows that a thermodynamic equilibrium model is valuable for performance gasifier predictions while co-feeding CO\textsubscript{2}. This study also shows the importance of co-feeding CO\textsubscript{2} in biomass gasification in order to reduce tar formation, resulting in a process with a zero CO\textsubscript{2} footprint. The developed model is also validated using the experimental results obtained: a) biomass conversion to synthesis gas, b) various synthesis gas molar fractions, b) H\textsubscript{2}/CO ratios and d) CO\textsubscript{2} yield.

As well, this research establishes the importance of using a catalyst to reduce tar formation while promoting efficient biomass gasification. To establish the catalytic gasification approach, a biomass surrogate species (2-methoxy-4-methylphenol) was used to represent the biomass feedstock. Two gasifying agents (steam-inert and steam-10%CO\textsubscript{2} in inert) and two bed temperatures (550\degree C and 600\degree C) were selected. Moreover, four reaction times were used (10, 15, 20 and 30 seconds). Finally, the efficiency of tar reduction with the catalyst developed in the present study was analyzed.

1.2 Thesis Structure

This study adds value to the steam-CO\textsubscript{2} gasification of biomass and tar reforming. Thesis chapters are organized as follow:

- Chapter 2: Review of the background of gasification processes, as well as a review of biomass feedstock properties, gasifier design and operational parameters.
• Chapter 3: Description of the materials, methods and conditions chosen in the present study for the steam-CO$_2$ and steam-inert gasification of biomass. This chapter also illustrates the reaction and analytical systems used to carry out experiments.

• Chapter 4: Reports the non-stoichiometric thermodynamic equilibrium model developed in the present study for steam-inert and steam-CO$_2$ gasification of biomasses feedstock in a CREC Riser Simulator.

• Chapter 5: Compares the experimental gasification results obtained in the CREC Riser Simulator with the yield equilibrium predictions obtained from the thermodynamic equilibrium model. This chapter also demonstrates the impact of different operation variables, as well as feedstock properties, on final product and gasification performance.

• Chapter 6: Demonstrates the effect of catalyst usage on tar reforming and biomass conversion to synthesis gas. Experimental methods and conditions, as well as the analytical system chosen are described. This chapter also highlights the importance of catalyst preparation on the physiochemical properties of the prepared catalyst.

• Chapter 7: Describes the characterization of the 20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$ catalyst developed. This chapter also reports the results of the catalytic experimental runs obtained in the CREC Riser Simulator while varying operational parameters, such as bed temperature, gasifying agent and residence time. Moreover, it compares the experimental results with equilibrium predictions.

• Chapter 8: Concludes with statements and recommendations for future work.
Chapter 2 : Literature Review

2 Gasification Process

Among other conversion processes, which employ biomasses feedstock, gasification is considered one of the most economical and efficient technologies\textsuperscript{11, 12}. Biomass can be converted into a synthesis gas product mainly composed of hydrogen (H\textsubscript{2}), carbon monoxide (CO), carbon dioxide (CO\textsubscript{2}), methane (CH\textsubscript{4})\textsuperscript{13}, and water vapor, along with char, ash and tars, in the presence of controlled amounts of a gasifying oxidant.

Final products obtained from biomass gasification are strongly dependent on operational process variables, the gasifying medium and feedstock properties\textsuperscript{14}. A large number of oxidants have been used as gasifying agents, such as air, oxygen, steam, CO\textsubscript{2} or their mixtures. However, there are different advantages and disadvantages for each of these gasifying agents\textsuperscript{15, 16, 17}.

The use of a catalyst in the gasification process helps in limiting the tar yield, while promoting a synthesis gas product with high hydrogen content\textsuperscript{13, 18, 19}. Likewise, gasifier configuration, feedstock properties, catalyst activity and stability have a significant influence on the synthesis gas quality, as well as on the amount of tar yield during steam biomass gasification processes. Therefore, it is essential to understand the thermodynamic equilibrium and chemical reactivity of gasification reactions, as will be reviewed in the following sections.

2.1 Biomass

The discovery of biomass and its relevant properties for use in various technologies represent a significant breakthrough in the history of humankind. The use of wood as a fuel source for cooking and heating is as old as civilization itself. Biomass utilization was again reintroduced throughout the nineteenth century, when the fossil fuel era began\textsuperscript{20}. Moreover, it has been used worldwide as a
principal source of food and feed, as well as for energy, materials and chemicals production.

The use of biomass as energy source is extremely important for the environment, the economy and society. It can replace fossil fuels, providing a reliable, affordable and clean energy supply. The usage of biomass as a renewable energy source has become very promising in recent years. This is justified as biomass: (i) provides a renewable and CO$_2$ neutral feedstock; (ii) can replace fossil fuels not only in the energy production aspect, but also as a supply source of important chemical compounds; (iii) enables energy storage; and finally (iv) provides a wide range of feedstock, being found almost everywhere in the world$^{21}$.

Even though biomass has the potential to be one of the world’s largest energy source, today only 14% of the global primary energy consumption comes from biomass feedstocks$^{22}$. However, studies show that the bioenergy demand may potentially grow soon, despite the fact that there are several problems to be addressed before biomass utilization increases$^{23}$.

Biomass is a complex hydrocarbon material mainly composed of carbon, hydrogen, and oxygen. These elements are structured into organic chemical species as cellulose, hemicellulose and lignin, which results in very diverse biomass feedstock materials. The final product from biomass gasification depends strongly on the biomass structural composition$^{24,25}$.

Cellulose is a saturated linear polysaccharide formed by long-chain natural polymers. Hemicellulose however, is defined as a complex mixture of heterogeneous and branched-chain polysaccharides. Finally, lignin is described as a regular polymer of four or more substituted phenyl propane units$^{26}$. Possible structures of cellulose, hemicellulose and lignin are described in Figures 3, 4 and 5.
On this basis, biomasses feedstock can be classified based on their structural composition, into six different structural types such as: a) CHL (cellulose>hemicellulose>lignin), b) CLH (cellulose>lignin>hemicellulose), c) HCL (hemicellulose>cellulose>lignin), d) HLC (hemicellulose>lignin>cellulose>, e) LCH (lignin>cellulose>hemicellulose>, f) LHC (lignin>hemicellulose>cellulose). Figure 6 demonstrates a triangular representation of feedstocks structural type.
It is important to comment that biomasses can vary significantly according to their dominant organic structural components. This structure plays an important role in carbon conversion, as well as quality of synthesis gas and biochar produced. Thus, biomasses feedstock must be characterized to determine their properties, quality, environmental issues and most suitable applications.

Various fractions of biomass can be quantified using both ultimate and proximate analyses. The ultimate analysis provides the amounts of carbon, hydrogen, oxygen, sulfur and nitrogen present along with the amount of ash. On the other hand, proximate analysis establishes fixed carbon and moisture content, volatile matter and ash yield.

On this basis, biomasses feedstock must be adequately analyzed. This is important to establish their effects on the gasification products. To accomplish this, the various analyses described in the upcoming sections must be considered.

2.1.1 Moisture Content

Moisture content in biomass feedstocks is determined by its type and origin. While water enhances gasification, it is desirable to use biomasses with low moisture content. This is the case given the inherent enthalpy losses which occur when
water contained in biomass is evaporated. Because of this, lower temperatures may lead to incomplete cracking of hydrocarbons in the pyrolysis zone. Furthermore, high moisture content yields a synthesis gas with lower heating value\textsuperscript{28}. Thus, limiting water content in the biomass feedstock is required for efficient gasification.

### 2.1.2 Ash Content

The mineral matter that remains after biomass complete combustion is designated as ash. Problems caused by ash agglomeration are: (i) clinkering/ slagging problems followed by feed blockages, and (ii) reduction of the available energy of the fuel\textsuperscript{6}. These can lead to economical and operational problems in the biomass conversion processes\textsuperscript{29, 30}. In this regard, many studies have been performed to analyze the ash contribution towards tar conversion, given the fact that ash can act as a catalyst\textsuperscript{31, 32}.

### 2.1.3 Biomass Size

Heat transfer efficiency can be enhanced with smaller particles. Gasification becomes more uniform with reactions taking place throughout the entire particle bed. As well, gasification rates can increase exponentially with temperature, following the Arrhenius’ rate law. This is due to the influence of intrinsic gasification kinetics on the overall process\textsuperscript{17}. On the other hand, larger particles can form bridges in the gasifier leading to a high-pressure drop and to the subsequent shutdown of the gasifier unit\textsuperscript{12}.

### 2.1.4 Biomass Structure

Biomass porous structure is of critical importance as well. Biomass specific surface area and pore sizes contribute to gasification, affecting diffusion of products and reactants. Thus, small biomass particles with high surface area, together with a gasifier operating at uniform temperature, yields a final product of stable and predictable composition.
However, if the biomass has a modest porosity, temperature variation between the pellet outer surface and the center of the biomass pellet may occur. As a result, biomass pellet surface may shrink with drying, pyrolysis and gasification, taking place simultaneously and yielding a final product of non-uniform composition.12

2.1.5 Volatile Matter and Fixed Carbon

Volatile matter refers to the biomass components liberated at high temperature in the absence of air. This is usually a mixture of short- and long-chain hydrocarbons and aromatic hydrocarbons. Volatile matter provides a valuable indicator of biomass reactivity and can be established using the ASTM D3175-17 Method. Fixed carbon on the other hand, is the solid combustible residue that remains after a biomass particle is heated and the volatile matter expelled. Fixed carbon is determined by subtracting the percentages of moisture, volatile matter, and ash from a sample, and can be calculated using the ASTM D3172-13 Method. Fixed carbon value observed reflect the conversion efficiency of biomass into synthesis gas.20

2.2 Chemistry of Gasification

Gasification was progressively developed over 180 years ago. The main objective was to produce combustible fuels from organic feed in blast furnaces. After World War II, the lack of cheap fossil fuels opened space to new research focusing on finding new alternatives to fossil fuels. Therefore, the gasification of biomass was reintroduced as a potential, environmental friendly and sustainable energy source technology.28

Biomass can be combusted and concurrently gasified. Having these factors in mind, a gasifier must be designed as to reduce or eliminate heavy hydrocarbon content and tar after the pyrolysis step, as this can damage the system.6,9

Gasification is a main biomass conversion alternative between thermal degradation with excess oxygen (combustion) and thermal degradation in the
absence of oxygen (pyrolysis). It usually converts 60 to 90% of the initial feedstock into fuels. Gasification is a process that is comprised of a complex network of heterogeneous reactions with controlled partial oxidation. It is applied to convert solid carbon into a gaseous and liquid fuel. Gasification process occurs supplying oxygen below the required stoichiometric amounts for complete combustion.

Gasification technology is considered one of the most flexible and efficient processes, being widely used to produce a range of commercial chemicals and clean burning fuels. Another advantage of this technology is its ability to work with different gaseous, liquid and solid feedstocks, to produce a reliable and high-quality synthesis gas product that can be further converted.

Conventional fuels, such as petroleum, coal and oil, among others have been widely used in gasification processes. There is however, growing interest on the gasification of crop residues from forest and agriculture, municipal sewage sludge, and this as a result of its lower CO₂ emissions.

The energy required in a gasification process, can be obtained via partial combustion of fed biomass, generating heat or indirectly transferring the generated heat as steam to a separate unit. Thus, gasification frequently take place in a gasifier unit in the presence of air, oxygen, steam, CO₂ or a mixture of them.

Inside of a gasifier, a series of endothermic and exothermic reactions occur between the gaseous, liquid and the solid phases. This yields a synthesis gas mostly composed of hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂), water vapour (H₂O), and methane (CH₄). However, a serious issue for the implementation of this technology is the generation of undesired contaminants, such as carbon particles and heavy hydrocarbons, designated as tars.

Regarding the products obtained and their yields, they strongly depend on the chemical reactions occurring in the gasifier unit. These reactions can progress to different reaction extents, as a function of the operating conditions selected, for instance bed temperature and gasifying agent. Biomass feedstock properties,
such as moisture and carbon content are also very relevant. They can influence dominant reaction pathways, leading to synthesis gases of different heating values.\(^\text{35}\)

Gasification involves drying, devolatilization, oxidation and reduction steps. These processes are developed in specific zones of the gasifier. The chemical composition of the feedstock, such as moisture content and particle size, as well as the flow rate of gasifying agent and the bed temperature, all have an impact on each zone.\(^\text{34}\) The position of these zones varies however, with the gasifier type, as will be discussed in this chapter.

### 2.2.1 Drying Zone

The gasifier entry section involves biomass drying. It is in this “drying zone”, where biomass moisture is removed from biomass. The drying zone and the extent of biomass drying is a major feature in a gasifier, as it can influence synthesis gas quality.\(^\text{36}\) As untreated biomass moves through the drying zone, its temperature increases progressively, accompanied by a slightly shrinking and reduction of the biomass pellets. Regarding the required energy for drying, it can be provided by dry gases evolving form other gasification zones, with temperature, velocity and moisture content of these gases affecting biomass drying.

### 2.2.2 Pyrolysis or Devolatilization Zone

Following drying, dried biomass encounters hot gases, with this leading to devolatilization and pyrolysis. These biomass conversion steps lead to the break down of large biomass molecules into permanent gases, char and tars.\(^\text{38}\)

\[
\text{C}_x\text{H}_y\text{O}_z + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} + \text{CO}_2 + \text{H}_2\text{O} + \text{C}_n\text{H}_{2m} + \text{C(s)} + \text{Tars}
\]  

Pyrolysis is crucial to produce a clean high-quality synthesis gas, minimizing the formation of undesirable products, like tars. Tars can condense in the gasifier pipe outlets, causing blockages, as well as reducing the quality of syngas product.\(^\text{9}\) As stated, the formation of undesirable compounds is one of the biggest challenges...
in the gasification process. It is known however, that temperature, rate of heating, biomass structure and composition affect biomass conversion in the pyrolysis/devolatilization zone.

It is important to highlight the influence of devolatilization on the oxidation step. The high temperature achieved in the devolatilization zone converts the large biomass molecules, yielding a synthesis gas.

### 2.2.3 Oxidation Zones

Together with pyrolysis, there are oxidation reactions, with steam or air being the oxidation agent. Because of these heterogeneous reactions taking place in the oxidation zone, portions of the carbon from the initial feedstock is burned. Thus, in the oxidation section, the oxygen content in the biomass feedstock decreases sharply, while the amount of CO₂ increases proportionally.

Oxygen driven combustion reactions are exothermic. They provide the needed enthalpy for drying biomass as well as for the endothermic biomass gasification.

Main reactions occurring in this zone can be summarized as follows:

\[ C + \frac{1}{2} O_2 \leftrightarrow CO \]  
\[ C + O_2 \leftrightarrow CO_2 \]  
\[ H_2 + \frac{1}{2} O_2 \leftrightarrow H_2O \]

### 2.2.4 Reduction Zone

In the reduction section, steam and CO₂ contribute to the formation of hydrogen, carbon monoxide and methane. Unconverted biomass remains as a solid residue, ash and char. The main reactions taking place in the reduction zone are listed in Table 1.
Table 1: Chemical Reactions in the Steam Gasification of Biomass.

<table>
<thead>
<tr>
<th>Name of Reaction</th>
<th>Chemical Equation</th>
<th>(Reaction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Gas-Shift</td>
<td>$CO + H_2O \leftrightarrow H_2 + CO_2$</td>
<td>1</td>
</tr>
<tr>
<td>Heterogeneous Water Gas-Shift</td>
<td>$C + H_2O \leftrightarrow H_2 + CO$</td>
<td>2</td>
</tr>
<tr>
<td>Steam Methane-Reforming</td>
<td>$CH_4 + H_2O \leftrightarrow CO + 3H_2$</td>
<td>3</td>
</tr>
<tr>
<td>Dry Methane-Reforming</td>
<td>$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$</td>
<td>4</td>
</tr>
<tr>
<td>Boudouard Reaction</td>
<td>$C + CO_2 \leftrightarrow 2CO$</td>
<td>5</td>
</tr>
<tr>
<td>Hydrogenating Gasification</td>
<td>$C + 2H_2 \leftrightarrow CH_4$</td>
<td>6</td>
</tr>
</tbody>
</table>

The use of steam as gasifier agent has become more popular, due to the reaction between steam and carbon monoxide to produce hydrogen and carbon dioxide (water gas-shift reaction)\textsuperscript{38}.

Reactions 1 and 2, the water-gas shift, are very important reactions in gasification processes to produce hydrogen and carbon monoxide. Reactions 3 and 4 are endothermic, and therefore, enhanced by high temperatures and low pressures. Reactions 3 and 4 can proceed very slowly, without the use of a catalyst, at low temperatures. Reaction 5, Boudouard, is endothermic and follows the same pattern of reactions 3 and 4 with an enhancement by increasing temperature. Hydrogenating gasification, reaction 6, is slow while comparing to reactions 1 and 2, unless enhanced with a catalyst or higher pressures\textsuperscript{47}.

2.3 Design of Gasifiers

Gasifier equipment can be classified in two major types: fixed bed and fluidized bed. Fixed bed devices are the oldest and simplest types of gasifiers due to their simplicity in construction and operation\textsuperscript{44}. Depending on the airflow direction, fixed bed reactors are classified as updraft, downdraft and cross-flow. Fluidized bed
devices, however, are very promising because of their higher flexibility and efficiency. Two main types of fluidized bed gasifiers are: a) bubbling bed and b) circulating fluidized bed.

2.3.1 Updraft Gasifier

The updraft gasifier is the first and simplest design of fixed bed developed. In this unit as described in Figure 7, biomass is fed at the top of the gasifier section, while the gasifying agent, for instance oxygen, steam or air, is feed countercurrent to it, through the bottom section of the unit.

![Figure 7: Updraft Gasifier](image)

In an updraft gasifier, biomass fed at the top of the unit, is dried by the upflow of hot gas. This downflow of solids reaches the devolutilization zone, where the biomass particles are pyrolyzed, releasing volatile species, and forming tars. Tars inside the gasifier can be condensed in the gasifier pipe outlet and filters, leading to blockages. As well, tars can be carried out of the reactor together with gaseous product. Following this, volatile species can be reformed in the reduction zone yielding permanent gases. Volatiles species and char can be combusted in the oxidation zone with heat being released. It is this heat that sustains the enthalpy required for pyrolysis and reactions. Since the produced gas from an updraft gasifier contains high yields of char and tar, a cleanup process is required for further processing.
Regarding the updraft gasifiers, a major challenge is the non-uniform flow with excessive pressure drop: preferential flow close to the walls with stagnant regions in the gasifier\textsuperscript{46}.

2.3.2 Downdraft Gasifier

In the downdraft gasifier, biomass moves downwards and in the same direction as the gasifying agent (Figure 8).

![Figure 8: Downdraft Gasifier\textsuperscript{45}.](image)

The downdraft reactor is composed by 4 sections: a) an upper drying zone, b) an upper middle pyrolysis zone, c) an lower middle oxidation zone and d) a lower reduction zone. In this case, the gasifying agents are fed in the lower middle zone, with gaseous products evolving towards the reactor bottom\textsuperscript{44}.

A major advantage of downdraft over updraft gasifiers is the tars content in synthesis gas product. In downdraft gasifiers, tar and char moves through a high temperature zone, where further reactions occur, leading to cleaner synthesis gas\textsuperscript{48}. However, due to the potential slagging, biomasses with high moisture and ash content are not suitable for downdraft gasifier units\textsuperscript{38}.

2.3.3 Cross-Flow Gasifier

Cross-flow gasifiers were originally designed for the use of charcoal as feedstock. In this unit, the biomass is fed at the top of the unit, moving downwards, while the gasifying agent is fed from the unit side. Synthesis gas is withdrawn from the upper
side of the unit, close to the location where the biomass is being fed. Charcoal gasification takes place at a very high temperature in the oxidation zone, due to a hot combustion/gasification zone formed around the gasifying agent entrance. This may lead to gasifier material problems. Cross-flow gasifiers show lower overall energy efficiency and high tar yields.

2.3.4 Bubbling Fluidized Bed

Fluidized bed gasifiers can provide uniform temperature in the gasification zone. This temperature uniformity is in contrast with the significant temperature variation in fixed bed gasifiers. In fluidized beds temperature uniformity is facilitated by using fine granular materials, case of sand. In a fluidized bed, gas is circulated in the form of bubbles, promoting contacting between hot combustion gases, the bed material and the biomass feedstock.

In a bubbling fluidized bed, the biomass feedstock is fed into the fine fluidized granular material bed, via a screw feeder (Figure 10). On the other hand, the gasifying agent is introduced at the gasifier bottom through a grate. The gas moves then through the bed upwards as bubbles. Bubbles may grow along the gasifier length. Temperature of the fluidized bed is established by controlling the air/biomass ratio. The gasifier is provided with an enlarged diameter in the upper section and this to minimize small particle transport in the freeboard region section. Gas velocity becomes lower in this section to reduce particle transport of suspended particles towards the cyclones. Thus, a good fraction of ejected
particles to the freeboard fall back into the dense bed zone\textsuperscript{49}. Furthermore, and due to the hot particles bed, tars or heavy hydrocarbons may crack, leading to a syngas with a low tar content\textsuperscript{15}.

![Figure 10: Bubbling Fluidized Bed\textsuperscript{44}.](image)

Figure 10, shows the various sections and relative dimensions of a bubbling fluidized bed.

2.3.5 Circulating Fluidized Bed

As an alternative, other types of fluidized beds can be used. This is the case of a circulating fluidized bed, that is able to process large amounts of biomass, however being subject to the significant challenges of attrition and ash collection\textsuperscript{45}.

In circulating fluidized bed gasifiers, the bed material circulates between the vessel and a cyclone separator. This configuration allows the removal of ash from the bed, while char and the bed material can return to the reaction vessel (Figure 11)\textsuperscript{38}.

![Figure 11: Circulating Fluidized Bed Gasifier\textsuperscript{44}.](image)
This type of reactor yields high biomass conversion, elevated conversion rates, as well as products with a low tar content. This is accomplished due to the high heat capacity of the fluidized bed material. Circulating fluidized beds have been widely used in the paper industry, for the gasification of bark and forestry crops, given that they are able to process high biomass throughputs.\textsuperscript{50}

One should note however, that the selection of a gasifier type and its design have to be dictated by capital cost, operation and maintenance, biomass feedstock, and quality of product syngas required, among other parameters.\textsuperscript{51}

Syngas products from fluidized bed reactors can be used for a wide variety of fuels. This flexibility is one of the most important advantages of fluidized beds over fixed bed reactors. On the other hand, ash agglomeration and tar content in the syngas product are still areas that require improvement when using this type of gasifier design configuration.\textsuperscript{52}

As of today, fixed bed reactors appear to be the most adaptable to produce low calorific value syngas, due to their simplicity in construction and operation. However, the deviations from equilibrium, caused by the effect of channelling and dead zones are major disadvantages in this design.\textsuperscript{46}

\subsection*{2.4 Operational Conditions of Gasification Processes}

Carbon conversion, synthesis gas quality and yield, and tar formation among other factors are strongly affected by the operational process conditions. On this basis, it is crucial to understand how each parameter influences the gasification efficiency. Temperature, pressure and gasifying agent, as well as catalyst selectivity and reaction time, are considered the most important factors in the process. The selection of each condition should also be dependent on the type of gasifier used.
2.4.1 Temperature

The bed temperature has the greatest effect on synthesis gas conversion and composition, regardless feedstock composition\(^53\). Therefore, it is very important to control this variable. Moreover, several studies have been performed, reviewing its influence on the final products\(^54, 55, 56, 57\).

Previous studies have demonstrated that high temperature is favourable for biomass gasification. To obtain a high carbon conversion from the feedstock, as well as a synthesis gas with a low tar content, an optimal temperature above 800°C is recommended\(^58\). An increase in bed temperature results in high yields of synthesis gas, rich in hydrogen, as well as in a sharp decrease in tars. As well, the low heating value (LHV) of the syngas is reduced considerably\(^59, 60\).

Besides an enhancement in gasification efficiency and a reduction of tar formation, temperature also affects tar and char chemical compositions. This due to its influence on the various chemical reactions involved in the gasification process\(^61, 62\).

A very important limitation in the operation of a gasifier is the ash melting point temperature, around 750°C. In this regard, high temperatures may lead to ash melting and particle agglomeration in the reactor, resulting in operational problems. This can reduce the efficiency of the gasification process, creating an extra cost associated to cleaning and maintenance. Several methods have been proposed to mitigate ash melting and agglomeration issues, such as (i) utilization of additives, (ii) fuel mixing, and (iii) leaching out of problematic elements from feedstock fuels before starting the process\(^63, 64\).

2.4.2 Pressure

R. A. Knight\(^65\) reported that the amount of oxygenate components, especially phenols, dropped dramatically, and were largely eliminated, when the pressure was increased.
However, T. G. Madenoglu et al.\textsuperscript{66}, illustrated the simultaneous effect of temperature and pressure on the catalytic hydrothermal gasification of glucose components. It was concluded that hydrogen yield, among other gaseous fuel products, increased with temperature rise and decreased with pressure drop.

### 2.4.3 Gasifying Agent

The use of different gasifier agents, such as air, steam, carbon dioxide, inert gas or a mix of them, during biomass gasification processes have been extensively reported in the literature. The atmosphere medium is an important parameter for gasification technology efficiency, as it provides the necessary reactants (oxygen, steam, CO\textsubscript{2}) for the various gasification reactions. As a result, the gasifying agent strongly affects the quality and composition, as well as the overall calorific value of synthesis gas products\textsuperscript{51}.

Selectivity of the gasification reactions varies with each different gasifying agent, determining the overall calorific value of the synthesis gas\textsuperscript{38}. With this being true, several studies have been performed concluding that: (i) using air as a gasifying agent results in a synthesis gas with low heating value and little amount of hydrogen. This is the result of having synthesis gas diluted in the nitrogen from air\textsuperscript{67, 68}; (ii) using steam or a combination of steam, air and CO\textsubscript{2}, a medium heating value is achieved\textsuperscript{69, 70}. In general, steam increases syngas quality and heating value, given it enhances devolatilization and reforming reactions\textsuperscript{51, 71}.

In addition, there is evidence that a higher hydrogen yield may be achieved by combining steam and air/CO\textsubscript{2} as a gasifying agent\textsuperscript{73}. This also helps to provide the required energy for the system, which is normally supplied by the exothermic nature of burning biomass\textsuperscript{72, 73}.

### 2.4.4 Residence Time

A very important parameter for the gasification process is the reaction or residence time. The residence time has a significant impact on the yield and composition of
the liquid product (tars) formed. It has been proven that the fraction of oxygenate compounds tends to drop by increasing the residence time. Moreover, the fractions of one/two aromatic ring components, excluding benzene and naphthalene, decrease linearly with residence time, whereas the fractions of three/four aromatic ring components increase linearly with residence time.

2.4.5 Catalyst

Catalysts have been extensively used in biomass gasification to improve carbon conversion and the quality of products. Catalytic reforming of biomass feedstock can be used to convert tar components into gaseous fuel products. The main criteria for an effective catalyst should include: a) the effectiveness of reducing tar content, b) the ability to reform methane, c) assistance with obtaining desirable H₂/CO ratios, d) the stability with respect to deactivation and e) the ability to be regenerated.

Several studies have shown that using a catalyst is one of the most promising methods for the tar reduction. Moreover, catalysts promote char gasification, increase the synthesis gas heating value and product yield. They also contribute to tar cracking and tar reforming at lower temperatures. Based on this, valuable prospects for new catalysts or improving existing ones are being developed in recent years. The challenge is to produce a high quality and tar-free synthesis gas and/or hydrogen.

2.5 Steam-CO₂ Gasification of Biomass

A considerable number of studies have been developed to understand how different operating parameters affect gasification processes. However, the role of CO₂ as a gasifying agent has only been addressed in a limited number of studies. CO₂ is one of the main components in greenhouse gas composition, contributing for global warming. It may also lead to serious health issues. On this basis, the
use of CO₂ as a gasifying agent may have the combined advantage of reducing CO₂ emissions to the atmosphere, promoting better gasification efficiency\textsuperscript{82}. 

As mentioned before, the reaction of carbon with CO₂ (Boudouard Reaction) is a very endothermic reaction, and as a result, highly energy-demanding\textsuperscript{47}. Thus, a mixture of CO₂ with steam and/or air is recommended in biomass gasification. T. Renganathat et al.\textsuperscript{83} developed a thermodynamic analysis for CO₂-gasification, using the Gibbs minimization approach. Authors concluded that when CO₂ is combined with steam or oxygen as a gasifying agent, the gasification energy needed, and carbon dioxide emissions is reduced. Moreover, the H₂/CO ratio for synthesis gas can be modified and this according to the amount of CO₂ fed in the system\textsuperscript{83}.

M. F. Irfan et al\textsuperscript{84} also studied different operating parameters, such as pressure, temperature, gas composition, catalyst, particle size, among others, and the influence of these parameters on gasification rates. Moreover, they also considered the kinetics and reaction rate equations for coal-char gasification under low and high temperatures and low and high pressures. Likewise, L. Garcia et al\textsuperscript{85} reviewed the influence of the catalyst weight/biomass flow rate ratio on the synthesis gas composition at low temperatures and atmospheric pressure (e.g. 700°C).

In summary, the CO₂ produced in biomass gasification under CO₂ atmosphere can be recovered and recycled back to the gasifier. Thus, CO₂ gasification can continue with minimum extra CO₂ requirements and improved carbon conversion rates.

A drawback in the application of this technology is the dilution of the synthesis gas in a CO₂ by-product. Thus, the removal of CO₂ is a downstream process requirement. This is needed to enhance synthesis gas quality and reduce CO₂ emissions. Different companies have addressed this issue. For instance, MTR’s Polaris™ membrane, as shown in Figure 12, considers a permeable CO₂ membrane that can separate 80% of feed CO₂ from other products, with a purity
up to 95 vol%. The recovered CO$_2$ can be returned to the gasification process as a gasifying agent, or be used in greenhouses, as well as in chemical and industrial applications.$^{86}$

Figure 12: CO$_2$ Removal from Syngas using MTR's Polaris$^{TM}$ Membrane.$^{86}$

2.5.1 Gasification Technology and State-of-the-Art

Based on the present review, we forecast significant opportunities for biomass gasification in fluidized beds under CO$_2$ atmospheres. It appears that various goals and objectives for biomass gasification could be accomplished including: a) production of a synthesis gas of medium heating value, b) reduction of tar, c) minimization of ash agglomeration, d) production of valuable biochar, e) gasification process with negligible CO$_2$ formation and carbon footprint. It is with these interesting prospects and goals in mind that we initiated the present study, with findings and results being reported in the upcoming chapters.

2.6 Product Utilization

One of the most attractive features of biomass gasification is its flexibility and wide range of product utilization and application, including the synthesis of fuels and chemicals, hydrogen production, and thermal power generation, as illustrated in Figure 13. This allows the planning of gasification-based energy refineries to produce a mix of energy and chemical products, allowing the staged introduction of technologies as they reach commercial viability.$^{97}$
As mentioned before, syngas or synthesis gas is mainly composed of carbon monoxide (CO) and hydrogen (H\textsubscript{2}). Synthesis gas from biomass provides the necessary building blocks to develop an environmentally friendly fuel technology\textsuperscript{97,98}.

The most common syngas application is the production of heat for boilers and turbines\textsuperscript{103}. However, the synthesis of hydrocarbons from CO hydrogenation is the oldest syngas application\textsuperscript{114}. It was discovered by Sabatier and Sanderens in 1902, who produced methane by passing CO and H\textsubscript{2} over nickel, iron, and cobalt catalysts. This was followed by methanol production. The first hydrogen produced from syngas was commercialized at around the same time. In 1910, Haber and Bosch discovered the synthesis of ammonia from H\textsubscript{2} and N\textsubscript{2}, and in 1913, the first industrial ammonia synthesis plant was built\textsuperscript{114}. Franz Fischer and Hans Tropsch discovered the production of liquid hydrocarbons and oxygenates from syngas conversion in 1923. Furthermore, variations of this synthesis gas reaction pathways allowed production of methanol, mixed alcohols, iso-synthesis products, and the hydroformylation of olefins through Fischer-Tropsch Synthesis\textsuperscript{114,115}.

Another valuable product from biomass gasification processes is the biochar, a solid residue of fine-grained charcoal, produced by burning a wide variety of biomass feedstocks. Biochar has the potential to combat climate change by
removing harmful carbon from the atmosphere. Although biochar is a new term, the use of this substance as solid amendment or as fertilizer, is not a new concept. In fact, since the discovery of "terra preta" ("black earth" in Portuguese), the highly fertile soil, used to enhance soil fertility in the Amazon region, has emerged as a viable option to sequester carbon in soil. Another important aspect is that biochar is significantly affected by the feedstock source and operational conditions.

By now, it is widely acknowledged that carbon dioxide contributes to climate change, being considered both a waste and a costly chemical specie. For this reason, many scientists have been studying different methods for CO₂ capture and utilization. It is expected that carbon dioxide conversion will be at the core of the future energy industry. Some possibilities in this field are: (i) The CO₂ circular economy and its impact on the chemical and energy value chain; (ii) New routes for CO₂ application and chemical utilization; (iii) CO₂ utilization in greenhouses; and (iv) CO₂ as a suitable C-source to move to a low-carbon chemical industry, for instance syngas production. Hence, the motivation for new studies focused on CO₂ utilization is a key strategy for future chemical processes.

Given the variety of syngas conversions processes available to produce fuels, chemicals and fertilizers, it is imperative research and development be focused on process efficiency and valuable contribution of CO₂, as in the present study. Implementation and potential improvements will be benefit by new catalysts development, with high activity and selectivity.
2.7 Conclusions

a) Biomass gasification yields gaseous, liquid and solid products. The gas product, synthesis gas, is mostly composed by hydrogen, carbon monoxide, methane, carbon dioxide and water vapour.

b) Biomass is composed by carbon, hydrogen and oxygen elements structured into cellulose, hemicellulose and lignin. Biomass elemental and chemical composition plays an important role in final gasification product composition.

c) Gasifying agents (steam, CO$_2$, air) used in biomass gasification processes must be carefully selected to provide the required energy and as well to yield the required syngas composition.

d) Biomass properties, such as moisture and ash content, size of pellets, structure, and fixed carbon, affect the gasification process. Likewise, operational parameters, such as temperature, pressure, gasifying agent, residence time and catalyst, have a strong influence on the gasification of biomass technology.

e) Undesired components, like tars, are yielded in biomass gasification. Tars can have a negative impact on the process efficiency. Operational parameters can influence tar and char product yields.

f) Biomass gasification using new catalysts can improve biomass conversion and synthesis gas quality, while reducing tar formation.

g) Biomass steam gasification processes yield a syngas with a high heating value compared to air gasification processes. On the other hand, large amounts of steam can lower gasification temperature and affect the synthesis gas quality.

h) Fluidized bed biomass gasifiers are more suitable for larger scale units, offering uniform bed temperature for gasification, as well as better conversion and product yield.
i) Biomass gasification under CO₂ atmospheres may offer special features for reducing the carbon footprint of the gasification process.
Chapter 3 : Experimental Methods

3 Experimental Materials and Methods

Chapter 3 provides details related to materials, equipment, methods and conditions involved in the experimental runs for biomass gasification assisted by steam-inert and steam-CO$_2$. Section 3.1 reports feedstock characterization for both wood and coffee wastes. Following this, a description of the operational conditions employed in the experimental program is reported. These include gasifying agent, feedstock sample, temperature and reaction times selected, among other parameters.

A detailed description of the fluidized bed reactor system, called the CREC Riser Simulator unit, used in the experimental runs is reviewed in section 3.3. Typical total pressure profiles from experimental runs are reported. This is followed by a review of the analytical equipment employed. This section also describes the methods used to analyze gasification products.

3.1 Biomasses Feedstock

In this present study, three different biomass feedstocks were considered for the steam-inert and steam-CO$_2$ gasification processes. They are a) Costa Rica broza, which is a coffee or pulp waste, and b) wood pellets and bark, which are wood waste. The coffee waste was provided by ICAFE in Costa Rica. The wood pellets were provided by CANMET Energy, and the wood bark was supplied by KMW Energy, both Canadian companies.

As mentioned before, feedstock composition may significantly affect gasification processes. In this respect, Elemental and Ultimate analyses, together with a moisture and ash contents, provide valuable biomass characterization. This data must be complemented with biomass heating value, volatile matter and fixed carbon. All these parameters are important for biomass conversion, mass and carbon balance calculations, as well as for thermodynamic models.
Elemental analyses were effected in this project by sending approximately 1 kilogram of each one of the biomasses studied to the SGS certified laboratory. Table 2 reports the values for ultimate analysis for the various feedstocks as reported by the SGS laboratory. It can be observed that biomasses feedstock composition mostly includes carbon, hydrogen and oxygen, with very little amounts of nitrogen and sulfur.

Table 2: Ultimate Analysis of Costa Rica broza, Wood Pellets and Wood Bark.

<table>
<thead>
<tr>
<th>Ultimate Analysis (wt%)</th>
<th>Costa Rica Broza</th>
<th>Wood bark</th>
<th>Wood Pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>49.9</td>
<td>46.3</td>
<td>37.78</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.05</td>
<td>5.7</td>
<td>4.26</td>
</tr>
<tr>
<td>Oxygen</td>
<td>28.1</td>
<td>41</td>
<td>30.2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.37</td>
<td>0.1</td>
<td>2.05</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.04</td>
<td>&lt;0.05</td>
<td>0.12</td>
</tr>
</tbody>
</table>

One can consider biomass using the CHxOy formula, with “x”, and “y” coefficients representing the H and O element fractions with respect to C. Thus, using Table 2 data, one can calculate the biomass unit formula and biomass unit molecular weight as reported in Table 3.

Table 3: Molecular formula and Weight of Broza, Wood Pellets and Bark.

<table>
<thead>
<tr>
<th>Biomass Feedstock</th>
<th>Costa Rica broza</th>
<th>CANMET pellets</th>
<th>Bark</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>H (x)</td>
<td>1.34</td>
<td>1.48</td>
<td>1.4</td>
</tr>
<tr>
<td>O (y)</td>
<td>0.6</td>
<td>0.66</td>
<td>0.61</td>
</tr>
<tr>
<td>Mol. Weight</td>
<td>22.94</td>
<td>24.04</td>
<td>23.16</td>
</tr>
</tbody>
</table>
Moisture, ash content, as well as fixed carbon and volatile matter in biomass, are all important parameters influencing the gasification technology. Table 4 illustrates the value of these parameters for the three biomasses of the present study.

<table>
<thead>
<tr>
<th>Proximate Analysis (wt%)</th>
<th>Costa Rica broza</th>
<th>CANMET pellets</th>
<th>Bark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture Content</td>
<td>17.54</td>
<td>6.56</td>
<td>29.8</td>
</tr>
<tr>
<td>Ash Content</td>
<td>9.76</td>
<td>0.42</td>
<td>2.92</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>8.84</td>
<td>14.83</td>
<td>19.8</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>79.16</td>
<td>84.76</td>
<td>54.7</td>
</tr>
</tbody>
</table>

Regarding Tables 2 and 4, one should notice that the data reported is given on a water free basis. In this way, it is possible to compare various biomasses on the same basis.

Moisture content in the feed favorably affects gas yields and carbon utilization efficiency. In addition, water can also help decreasing tar formation. Thus, the addition of water appears to enhance both, water-gas shift and methane steam reforming. The feeding of high excessive water however, may also decrease bed temperature and have a negative impact on the process efficiency.

Thus, for a successful biomass gasification, an optimum moisture content of 20wt% or the equivalent, $8\mu$L of water, were added to a dry biomass sample of 0.04g in this present study.

3.2 Reaction System

Gasification of biomass experiments were carried out using the CREC Riser Simulator, a novel bench scale reactor. This novel device allows us to reproduce
experiments occurring in industrial riser units. This is done on a small laboratory scale and with similar conditions as those at play in industrial riser units. The CREC Riser Simulator has been used in studies dealing with biomass gasification, catalyst evaluation and development, catalytic cracking of tars, steam and dry methane reforming, FCC studies, among others\textsuperscript{46}.

A schematic diagram of the CREC Riser Simulator and its operation is provided in Figure 14. As one can see, the CREC Riser Simulator consists of a lower section and an upper shell section, sealed by a metallic gasket. This design allows a quick and easy loading and unloading of both catalyst and/or biomass in the basket. The reactor basket, which has a half-moon shape hole, is placed in the lower shell section between two porous grids. These two grids, with one placed at the top and another one at the bottom of the basket, constrain the solid motion inside the basket\textsuperscript{15}.

The CREC Riser Simulator is a bench-scale unit, with a 50.7cm\textsuperscript{3} volume. It operates as a fluidized batch reactor. This fluidized state is achieved because of an impeller rotation located in the upper shell section of the CREC Riser Simulator. The impeller is supported by a packing gland and a cooling jacket that surrounds the shaft\textsuperscript{38}.

The impeller rotation at high speed provides both gas suction and gas compression, moving the fluid upwards in the basket central section and downwards in the outer basket section. This fluid motion provides fluidized bed conditions and creates the driving force for high gas recirculation\textsuperscript{46, 89}.
On this basis, chemical species changes can be described by the species balance equation below:

\[ V_T \frac{dC_i}{dt} = \tau_i W \]  

(5)

where \( V_T \) represents the total reactor volume in cm\(^3\), \( C_i \) stands for the mass concentration of “i” species in g/cm\(^3\), \( t \) denotes the reaction time in seconds, \( \tau_i \) is the reaction rate of “i” and \( W \) stands for the mass of catalyst or the mass of biomass in grams.

The CREC Riser Simulator unit operates in connection with a series of sampling valves, a vacuum box, two pressure transducers, two thermocouples and a gas analysis system. A schematic of the entire CREC Riser Simulator system, including reactor and auxiliary equipment, is provided in Figure 15.
The CREC Riser Simulator reactor is linked to a four-port valve (4PV). This 4PV connects the reactor to a vacuum box, with a 1205.9 cm$^3$ volume. It also allows the withdrawal of gasification products towards a vacuum box in shorts periods of time (e.g. 1 s). As well, an auxiliary six-port valve (6PV) and a carrier gas permit directing the product samples to a GC. Details about the analytical system will be provided in the next session of this chapter.

The reaction time in the CREC Riser Simulator can be set through a timer. This timer is connected to an actuator operating a 4-port valve (4PV). As a result, the total reaction time can be easily changed. Once a set reaction time is reached, products are evacuated from the reactor to the vacuum box through the 4PV. The evacuation process is almost instantaneous due to the significant pressure difference between the reactor and the vacuum box$^{15}$. As a result, the experiment is terminated when chemical species are evacuated to the vacuum box.

The CREC Riser Simulator unit is also connected with other three-way valves called V1, V2 and V3. V1 and V2 valves help selecting the gas feeding the reactor
and vacuum system. This gas acts as a gasifying agent. The V3 valve connects the vacuum box to the vacuum pump and is responsible to either vent or create a vacuum in the reactor and auxiliary system.

While the 4PV is in the “open” position, gas flows inside the reactor, through the inlet and outlet ports, reaching the vacuum box. On the other hand, in the “closed” position, the 4PV completely isolates the reactor from the rest of the system. Therefore, while in “closed” position, all gases going to the 4PV bypass the reactor and go directly to the vacuum box.

In the specific case of biomass gasification, the vacuum box collects a synthesis gas product sample. Following this, an aliquot of the synthesis gas product sample is transferred to a 6PV sampling loop in the “load position”. Once this operation is complete, the 6PV is switched to the “inject position”, and the gas product sample is transported by the helium carrier to the gas chromatograph (GC) for analysis.

Both the 4PV and 6PV valves are located inside of a heated box. Thermocouples are used to measure and control the temperatures of the transportation lines, reactor and vacuum box. The vacuum box is always kept at 195ºC and the line that connects the 6PV with the GC at 220ºC. These temperatures are important to avoid tar formation and product condensation in the lines and filters, leading to blockages and further deviations from equilibrium. The temperature inside of the reactor can be controlled by a ramp, to obtain the desired temperature.

Two pressure transducers are used in the CREC Riser Simulator system, one to monitor the reactor pressure and a second one to check the vacuum box pressure. As a result, it is possible to observe the progress of the reaction during the experimental runs.

During the first part of this study, a temperature ramp was implemented, increasing the temperature gradually for 30 minutes. This was the case until a desired temperature level was reached. Figure 16 shows both the temperature and the
total pressure increase. One can notice that when the desired thermal level was achieved, temperature and pressure remained constant for an extra 10 minutes.

![Pressure and Temperature Profiles](image)

**Figure 16: Pressure and Temperature Profiles during the Thermal Biomass Gasification Process.**

Regarding reactor operation, the following can be achieved from the unit control panel: (i) the activation of all solenoids valves; (ii) the establishment of the reaction time, initiated at reactant injection and concluded after an electronically set time; (iii) the evacuation of chemical species contained in the unit (iv) the “on-line” product analysis via gas chromatography.

### 3.3 Analytical System

As already described, once the gasification process time elapsed, gasification products were evacuated towards the vacuum box. At this time and after intense mixing of the vacuum box contents, a sample was transferred to the sampling loop of the 6PV, in loading position. Once this operation is completed, the gas sample was transferred to a Shimadzu GC/MS-2010 for analysis. This GC/MS unit was equipped with both a Thermal Conductivity Detector (TDC), and a Flame Conductivity Detector (FID). The selected GC column configuration involved a packed column connected to the TCD, and a capillary column connected to the FID. This allowed proper separation of various chemicals species. Table 5 reports the main features of both the packed and capillary columns employed.
Table 5: TCD and FID columns features.

<table>
<thead>
<tr>
<th>Detector</th>
<th>TCD</th>
<th>FID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Altech</td>
<td>SGE</td>
<td></td>
</tr>
<tr>
<td>HaveSep D</td>
<td>BPX5</td>
<td></td>
</tr>
<tr>
<td>Initial Temperature</td>
<td>35°C</td>
<td>250°C</td>
</tr>
<tr>
<td>Final Temperature</td>
<td>250°C</td>
<td>250°C</td>
</tr>
<tr>
<td>Film Thickness</td>
<td>2.0µm</td>
<td>0.25 µm</td>
</tr>
<tr>
<td>Length</td>
<td>9.1m</td>
<td>30m</td>
</tr>
<tr>
<td>Inner Diameter</td>
<td>2.0mm</td>
<td>0.25mm</td>
</tr>
</tbody>
</table>

The GC/TCD-FID analytical system was operated using a Mandel GC Solution software, which performs various tasks associated with GC/MS data acquisition, data processing and reporting. There were three programs available to program the GC oven thermal ramp. They were: (i) “blank”, employed to analyze impurities and other components inside the column; (ii) “GC Run”, used to analyze and quantify synthesis gas; and (iii) “idle”, employed to clean the column overnight.

Figure 17 reports a GC-TCD chromatogram with typical species detected, such as hydrogen (H₂), carbon monoxide (CO), methane (CH₄), carbon dioxide (CO₂) and water. The concentration of permanent gases and light hydrocarbons (C1-C2) were measured using the TCD. To accomplish this, a temperature ramp steps for the GC run program were selected as follows: a) The initial oven temperature was set to 35°C, b) After 3 minutes, the temperature was increased to 250°C, using a ramp of 25°C/min during 8.40min, c) To end, the temperature was kept constant at 250°C for 9 min.
For the quantification of permanent gases including methane, TCD calibrations are required. Calibration curves for various chemical species are reported in Appendix A.

Coke deposited on the solid biomass feedstock surface was measured as CO$_2$, after every run, using a total organic carbon analyzer (TOC-V) with a solid sample module (SSM-5000) from Mandel.

### 3.4 Experiment Conditions

This MESc thesis considers the validation of a non-stoichiometric thermodynamic equilibrium model. A detailed description of the chemical model can be found in Chapter 4. To accomplish this, experiments were carried out in a CREC Riser Simulator, as described previously. Three different biomasses feedstock were gasified: Costa Rica broza, CANMET pellets and bark, coffee and wood waste respectively, by varying the gasifying agent and temperature inside of the reactor.

All experiments were carried out close to atmospheric pressure. The rotation of the impeller, as well as total reaction time, did not vary during the runs. Steam/biomass
ratio was also kept constant. A set temperature ramp was used to gradually increase the temperature until desired thermal level was reached. Following this, temperature and pressure were kept constant for extra 10 minutes.

The conditions selected for this study were:

Table 6: Experimental Conditions Selected for this Study.

<table>
<thead>
<tr>
<th>Operational Parameters</th>
<th>Experimental Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass Feedstock</td>
<td>Costa Rica broza, CANMET Pellets and Bark</td>
</tr>
<tr>
<td>Temperature</td>
<td>550°C and 600°C</td>
</tr>
<tr>
<td>Gasifying agent</td>
<td>Steam-inert and Steam-CO₂</td>
</tr>
</tbody>
</table>

The temperature range for the study was selected by considering the energy efficiency of gasification, the ash agglomeration and the chemical reactions involved in the process. In this respect, it was highly desirable to keep the reactor temperature below 700°C. This was important to prevent ash agglomeration leading to grid blockages and corrosion.

3.5 Experimental Procedure

The goal of the present study is to understand how bed temperature, gasifier medium and feedstock composition affect the synthesis gas produced, as well as tar formation and biochar, during biomass gasification.

To accomplish this, thermal runs were developed as follows: (i) All experiments were run under close to atmospheric pressure; (ii) Impeller rotation was kept constant at 600rpm; (iii) Total reaction time was kept at 40 minutes; (iv) A steam/biomass ratio of 20% was employed; and (v) Gasifying agent/biomass ratio was set at 0.6.

Furthermore, thermal runs were implemented as follows:
a) A 0.04g of solid dry biomass was loaded in the reactor basket, along with 8µl of water, to achieve the desired steam/biomass ratio. The solid feedstock was kept inside of the basket between two grids.

b) The basket was then placed into the lower shell section of the unit. The lower and upper shell sections were sealed by using a metallic gasket and six tightening bolts.

c) Temperature and pressure were set to 24°C and 24 psi, with the selected specified gasifying agent flowing for 10 min. This was done to ensure that any remaining chemical species or contaminants from previous experiments be completely removed. This step was designated a “purging” step.

d) The reactor pressure was reduced to atmospheric with the reactor isolated from the vacuum box using the 4PV valve.

e) The vacuum bottle at 195°C, was evacuated until the total pressure reached approximately 2.9 psi. This difference between the vacuum box pressure and the reactor is required for a quick evacuation of product species in the reactor.

f) The progressive increase of the gasification temperature was set by using a selected temperature ramp, using CREC Riser Simulator temperature controllers.

g) The impeller was then started, at 600rpm, mixing all chemical species inside the basket.

h) Pressure and temperature in the reactor were continuously monitored from the beginning of run until its end. At this point, reactor contents were evacuated towards the vacuum box.

i) Product species were transferred from the reactor to the vacuum box, until the pressure in both reactor and vacuum were similar. After that, the 4PV was closed again, and the vacuum box was isolated from the reactor.
j) An aliquot of gas products was collected in the 6PV sampling loop and sent to the gas chromatograph. For the first part of this study, a Thermal Conductivity Detector (TCD) was used for product quantification.

k) Once the run was complete, the reactor was cooled down under inert gas flow. The solid residue, biochar, was collected from the catalyst basket and kept for further analysis.

3.6 Conclusions

a) The CREC Riser Simulator unit is a mini fluidized batch reactor suitable for reproducing reaction conditions in a gasifier.

b) An experimental protocol can be established for biomass gasification of biomasses covering a diversity of gasification conditions.

c) Various auxiliary devices connected to the CREC Riser Simulator allow one to unload successfully gasification product species, and to subsequently send them to a GC analytical system for quantification.

d) The coke formed as a biochar product can be analyzed successfully using TOC analysis and BET measurements.
Chapter 4 : Thermodynamic Equilibrium Model

4 Introduction

Thermodynamic equilibrium models are valuable research tools to predict the maximum achievable yield of synthesis gas. A series of studies have been previously performed to develop biomass gasification thermodynamic equilibrium models, that could be used to evaluate the feasibility of the gasification process before attempting experimental investigations\(^91, 92, 93, 94\).

In this present study, a chemical thermodynamic equilibrium model was developed based on the main components present in biomass (carbon, hydrogen and oxygen) and various product species (H\(_2\), CO, CO\(_2\), CH\(_4\) and H\(_2\)O). This model is helpful to validate the effect of biomass composition and operational parameters, such as bed temperature and gasifier agent, on the molar fractions of various synthesis gas products.

In this research, the chemical thermodynamic equilibrium model was developed using the process simulation software Aspen-Hysys. The main objective was to compare equilibrium predictions with experimental data obtained in the runs using the CREC Riser Simulator. This is significant in order to identify operating conditions that lead to decreased tar formation and higher biomass conversion and product yields.

4.1 Thermodynamic Equilibrium Model

It is very difficult to measure the thermodynamic properties of feed material, such as those of various biomasses, due to their complexity and heterogeneous nature. For this reason, biomass feedstocks are usually defined as non-conventional species, formed by the addition of their elements. Their properties are thus, estimated by incorporating both, proximate and ultimate analysis described in Chapter 3, into the Aspen Hysys program.
While developing a thermodynamic equilibrium model, chemical reactions at equilibrium can be determined by the Gibbs Free Energy minimization using 2 different approaches: stoichiometric or non-stoichiometric. The main difference between these two approaches is as follows: a) The stoichiometric model is based on equilibrium constants for all reactions involved in the gasification process, b) The non-stoichiometric model, in contrast, does not require the equilibrium constants. Instead its approach involves the minimization of the system Gibbs Free Energy for all equilibrium reactions involved in the gasification process.

This MESc thesis aims to develop a non-stoichiometric chemical equilibrium model to predict the maximum achievable species yields obtained during steam-inert and/or steam-CO$_2$ biomass gasification. As mentioned before, all experiments for this study were carried out using a CREC Riser Simulator, which is a mini batch fluidized reactor, with a constant volume. Pressure in a constant volume batch reactor, as in the case of CREC Riser Simulator unit, depends on the total moles of gas produced. Therefore, while calculating thermodynamic equilibrium pressure rise, by using a continuous unit module in Aspen-Hysys, the total pressure was changed until a volumetric flow target was attained. Details about this Aspen-Hysis simulation can be found in the upcoming sections.

### 4.2 Thermodynamic Model Assumptions

In the present study, a non-stoichiometric thermodynamic equilibrium model is developed using the process simulation software, Aspen-Hysys. Inputs to the model are based on sound assumptions:

a) The gasifier operates isothermally under steady state conditions. These are the conditions anticipated in a fluidized bed gasifier;

b) Biomass$^{17}$ can be split up into carbon, hydrogen and oxygen constitutive elements, in accordance with its elemental analyses;
c) Other elements present in biomass, such as sulfur and nitrogen can be neglected given they are present in small quantities;

d) Main gasification products are hydrogen, carbon monoxide, carbon dioxide, methane and water vapour;

e) Char can be considered as 100% carbon and does not react or act as a catalyst;

f) Char and tar are accounted for as unconverted carbon;

g) Biomass particles are assumed to be small enough, such that mass and heat transport limitations can be neglected.

4.3 Steam Biomass Gasification Equilibrium Model

Biomass gasification can be considered to be the result of a “primary reaction”, where biomass is broken down into permanent gases and char as follows:

\[ C_{x}H_{y}O_{z} + H_{2}O \rightarrow \alpha H_{2} + \beta CO + \gamma CO_{2} + \psi CH_{4} + \zeta H_{2}O + \Omega C(s) \]  

with \( \alpha, \beta, \gamma, \psi, \zeta \) and \( \Omega \) being the stoichiometric coefficients in Equation 6.

Furthermore, this “primary reaction” can be followed by “secondary reactions”, where the permanent gases and the formed char are interconverted and react between each other altering the final product, as reported Table 1.

However, and to describe chemical equilibrium for the secondary reactions, a set of four independent chemical reactions were selected as described below:\textsuperscript{91}:

\[ C + O_{2} \rightarrow CO_{2} \]  

\[ CO + H_{2}O \leftrightarrow CO_{2} + H_{2} \]  

\[ CH_{4} + H_{2}O \leftrightarrow CO + 3H_{2} \]  

\[ C + H_{2}O \leftrightarrow CO + H_{2} \]
Furthermore, and to develop equilibrium calculations using Aspen-Hysys, one can consider a process flowsheet involving four modules as described in Figure 18.

Figure 18: Thermodynamic Equilibrium Model using the Aspen Hysys Module and Four Modules for Biomass Gasification.

Figure 18 reports a “Mixer Module 1”, called the Biomass Assembler Unit. This unit allows the numerical blending of dry biomass elemental constituents, which are (i) the C molar flow, (ii) the H\textsubscript{2} molar flow and (iii) the O\textsubscript{2} molar flow. This resulting combined stream gives the “dry biomass”. The dry biomass stream is blended in the “Mixer Module 2”, which is called the Biomass Humidifier Unit. In this unit, a water stream represents the moisture included in the raw biomass. This wet biomass emerging from the “Mixer Module 2” is fed into the “Conversion Reactor Module”, together with CO\textsubscript{2} or an inert gas. It is in the “Conversion Reactor Module” where Reaction (7) takes place. Given the very high equilibrium constant for Reaction (7), a full consumption of the biomass contained oxygen is hypothesized in the “Conversion Reactor Module”.

Following this step, the residual carbon, the CO\textsubscript{2}, H\textsubscript{2}O, and the H element molar flows are fed to a “Gibbs Equilibrium Reactor Module” where Reactions (8), (9) and (10) take place under chemical equilibrium constraints. It is important to mention that the “Gibbs Equilibrium Reactor Module” is an important component in the
Aspen-Hysys model where thermochemical gasification reactions take place at thermodynamic equilibrium, as mentioned previously. In addition, solid carbon was used to represent char and tars.

Following these conditions, equilibrium synthesis gas compositions were calculated as a function of temperature.

4.4 Equilibrium Constant Calculation to Chemical Reactions

The “Gibbs Equilibrium Reactor Module”, involves the $\Delta G^0$ and $\Delta H^0$ calculations for each one of the 3 reactions considered (reactions (8), (9) and (10)), at 298K and chemical equilibrium as follows:

$$K_j = \exp\left(-\frac{\Delta G^0_j}{RT_0}\right)$$  \hspace{1cm} (11)

with $T_0=298K$ and $\Delta G^0_j = \sum \gamma_{i,j} G^0_{i,j}$ in kJ/mole being the Gibbs Free Energy change for reaction “$j$” at 298K.$^{95}$

Furthermore, the changes of the $K_j(T)$ chemical equilibrium constant with temperature can be accounted for using the van’t Hoff equation.$^{95}$:

$$\frac{\partial (\ln K_j(T))}{\partial T} = \frac{\Delta H^0_j}{RT^2}$$  \hspace{1cm} (12)

once the $K_j$ equilibrium constants for every “$j$” are evaluated, they can be related to the $y_j$ species molar fractions as follows:

$$K_j(T) = \sum \gamma_{i,j} P^{\Delta u_{i,j}}$$  \hspace{1cm} (13)

with $P$ being the total system pressure, $\Delta u_{i,j} = \sum u_{i,j}$ representing the molar change, $u_{i,j}$ representing the various stoichiometric coefficients for “$i$” species and “$j$” reaction.

Finally, the “Gibbs Equilibrium Reactor Module” yields the $y_i$ fractions, and the corresponding reaction extents via the simultaneous solution of equation (13) for
reactions (8), (9) and (10). Results of these calculations are adequate when using a continuous fluidized bed gasifier unit operating at close to constant pressure, as described in Figure 18.

In constant volume batch reactors, as in the case of CREC Riser Simulator unit, it is important to emphasize that variations in the total molar flow yield, changes in the total reactor pressure. Thus, and to develop “equivalent” equilibrium calculations using Aspen-Hysys, one must allow the total pressure changes to compensate for the total molar flow variations, keeping the total volumetric flow constant. To accomplish this, an extra “Adjust Module” was implemented, as described in Figure 18. This "Adjust Module" function operates by having the total reactor pressure as an “Adjust Variable” and the volumetric flow as “Target Variable”. The total pressure thus varies until the volumetric flow becomes constant.

A validation of the equilibrium thermodynamic model was developed by comparing predicted species synthesis gas molar fractions, with the ones experimentally observed in a CREC Riser Simulator unit.
4.5 Conclusions

a) A non-stoichiometric thermodynamic chemical equilibrium model was implemented using the Aspen-Hysys software. The model developed involved a Conversion Reactor and a Gibbs Equilibrium Reactor Module.

b) The equilibrium model, as considered in the Gibbs Equilibrium Reactor, solved simultaneously a set of three independent reactions.

c) The Aspen-Hysys based equilibrium model, developed for a continuous unit, was adapted to the constant volume batch CREC Riser Simulator operation, using an Adjust function.
Chapter 5: Thermal Gasification of Biomass

5 Experimental Results

The validation of a model, such as in the case of the chemical equilibrium model of the present study, is of major importance to progress in the successful implementation of gasification of biomass. To achieve this, predicted chemical equilibrium model results were compared with experimental data obtained in the CREC Riser Simulator unit.

This thesis aims to study the effects of bed temperature, gasifying agent gas and biomass feedstock on biomass conversion and syngas composition. The selected bed temperatures were 550°C and 600°C. These temperatures were chosen to establish the impact of the thermal level on gasification and ash agglomeration. Selected gasifier agents were steam-inert and steam-CO$_2$. As mentioned before, coffee waste (Costa Rica broza) and two wood wastes (wood pellets and wood bark) were used as feedstocks in this study. In addition, 20wt% (wet basis) of external water was added to the 0.04g of biomass sample inside of the reactor basket.

Total pressures during the runs, for both the reactor and the vacuum box, were monitored using a Personal Daq connected to two pressure transducers (Omega Engineering, Model PX603). The synthesis gas produced from the gasification was analyzed using a Shimadzu GC connected to a TCD (Thermal Conductivity Detector). Likewise, coke deposited on the char surface was measured using a Total Organic Carbon Analyzer (TOC-V) and a Solid Sample Module (SSM-5000A) from Shimadzu.

5.1 Experimental Calculations

For every experimental condition, 15 experiments were developed to have statistically representative results. The relatively large number of repeats was required given the intrinsic heterogeneity in biomass samples, and the relatively
small amount of biomass used in every experiment. On this basis, average and standard deviations were calculated for each experimental condition. Data reported include product yields and product molar fractions.

Overall mass balances and overall carbon balances involved all chemical species fed and products removed from the reactor, as described in Chapter 4.

More specifically, mass balance closure was defined as:

\[ MB = 100 \times \left( \frac{m_p + m_c}{m_i} \right) \] (14)

where \( MB \) is the mass balance closure (%), \( m_p \) represents the mass of synthesis gas products (g), \( m_c \) stands for the mass of coke found in the solid biochar (g), and \( m_i \) denotes the mass of reactants injected in the reaction system (g). Appendix B reports further information about mass balance closures as per equation 14.

\[ CB = 100 \times \left( \frac{N_{Cp} + N_{Cc}}{N_i} \right) \] (15)

where \( CB \) is the carbon balance closure (%), \( N_{Cp} \) represents the moles of carbon in synthesis gas products (g), \( N_{Cc} \) stands for the mass of coke found in the solid biochar (g), and \( m_i \) represents the total mass of carbon in the reactants injected (g). Appendix B reports further information about mass carbon balance closures as per equation 15.

The calculation of product yields was developed as:

\[ y_i = \frac{\text{Moles of product } i}{\text{Moles of C in biomass fed}} \] (16)

where \( y_i \) is the product yield (%).

The separation and quantification of product moles were performed in a Shimadzu 2010 GC with a Thermal Conductivity Detector (TCD), using calibration curves that can be found in Appendix A. The moles of carbon in the biomass fed were calculated using a total organic carbon analyzer (TOC-V) with a solid sample.
The molar fraction calculation was performed with $Y_i$ being divided by the total number of carbon moles injected in the system.

It is important to mention that for every mass balance and carbon balance closures, important deviations were observed from the expected 100%. While deviations from 100% were assigned to tar formations, these deviations remained in a ± 5% range.

As mentioned in Chapter 2, every biomass feedstock can be classified by its structural composition into six different types, based on its location in a cellulose, hemicellulose and lignin composition triangular diagram. Figure 19 illustrates the placement of the biomasses of the present study, in this cellulose-hemicellulose-lignin triangular plot.

![Figure 19: Structural Compositions for the Three Biomasses Feedstock Involved in this Study.](image)

Figure 19 shows that Costa Rica broza, or coffee waste, can be considered as HCL, a feedstock with hemicellulose>cellulose>lignin. On the other hand, CANMET pellets and wood bark can be considered as CHL feedstocks, having a cellulose>hemicellulose>lignin order.
5.2 Steam Biomass Gasification Experimental Runs

Experiments were carried out using the CREC Riser Simulator, as described in Chapter 3. The impeller rotation was kept constant at 600rpm during the entire run. The total reaction time was kept constant at 40 min, and the temperature was increased linearly for 30 min, due to a set 25°C/min temperature ramp. Once the desired thermal level was reached, the temperature was kept constant for 10 min.

Every experiment was repeated at least 15 times to secure the reproducibility of results. Char sample amounts were taken for further analysis. Black bars in all graphs represent standard deviation of repeats.

After every experiment, both mass balances and carbon balances were calculated including all experimental species observed in the runs, such as H₂, CO, CO₂, CH₄. A comparison between the non-stoichiometric thermodynamic model and the experimental results was developed using as a reference: (i) The biomass carbon conversion, (ii) The H₂ yield, (iii) The CO yield, (iv) The H₂/CO ratio and (v) The CO₂ yield. Due to the very little amounts of ethylene, ethane, propylene and propane, their molar fractions were not taken in account for the comparison with the model predictions.

5.2.1 Overall Dry Biomass Conversion

Figure 20 reports the overall dry biomass conversion into synthesis gas and char. Results are for steam-inert and steam-CO₂ as gasifying agents, at 550°C and 600°C temperatures. One should note that in Figure 20, a 100% dashed line shows the full dry biomass conversion into various products (syngas, tar and biochar).
Figure 20: Dry Biomass Conversion into Synthesis Gas and Char in the CREC Riser Simulator. Temperatures: 550°C and 600°C; Biomass feedstocks: Costa Rica broza, CANMET pellets and Bark; Gasifier Agents: steam-inert and steam-CO$_2$; Gasifying Agent/Dry Biomass Fed (mole%): 55%; Steam/Dry Biomass Fed (mole%): 20%. Total Reactor Pressure prior to sampling: 57-58psi.

It is reported in Figure 20 that at the selected operation conditions, 50-85% of the dry biomass feedstock is converted into synthesis gas and char, with the rest being assigned to liquid products, also called tars or heavy hydrocarbons.

Moreover, one can conclude that the higher thermal levels help in increasing the combined dry biomass conversion into gas and solid products, synthesis gas and char, as well as decreasing the tars. Furthermore, one can also notice that changing the gasifying agent from an inert gas to CO$_2$ helps considerably to further augment the synthesis gas plus char fraction, while reducing tar formation. These gasification enhancements are assigned to a more dominant role of CO$_2$ in hydrocarbon reforming and char gasification.

While comparing the two gasifier agents, inert and CO$_2$, one can see that steam-CO$_2$ biomass gasification processes led to conversion values in the 80-90% range, with this being true for every feedstock studied in this research. On the other hand,
Costa Rica broza for instance, shows conversion value in the 50% range for steam-inert biomass gasification at 550°C. This value is 30% less than the process under steam-CO\textsubscript{2} atmospheres at the same temperature.

Thus, the reported results confirm that carbon dioxide may act as a tar reforming agent, enhancing biomass steam gasification and improving biomass conversion to CO and CH\textsubscript{4}\textsuperscript{96}.

As well, it is possible to observe a slight reduction in the amount of char as temperature increases. Thus, one can assume that an increase in temperature leads to an increase in char microporosity, which aids in the diffusion of CO\textsubscript{2} into char particles, promoting the Boudouard reaction (Reaction 5) between CO\textsubscript{2} and char\textsuperscript{111}.

5.2.2 Biochar from Gasification

The solid residue, biochar, obtained after various gasification experiments using different biomass feedstocks, was evaluated using BET specific surface area. More details about this physicochemical technique can be found in Chapter 6. As reported in Table 7, BET specific surfaces areas, showed average results between 10-20m\textsuperscript{2}/g. These values are in the expected range for biochar as reported by others\textsuperscript{113}.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{BET}) (m\textsuperscript{2}/g) 550°C</th>
<th>(S_{BET}) (m\textsuperscript{2}/g) 600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Costa Rica Broza</td>
<td>10.2</td>
<td>10.6</td>
</tr>
<tr>
<td>Wood Pellets</td>
<td>18.5</td>
<td>19.3</td>
</tr>
<tr>
<td>Wood Bark</td>
<td>15.6</td>
<td>18.5</td>
</tr>
</tbody>
</table>

Table 7: BET Surface Areas for the Three Feedstock Analyzed in this Study. Gasifying agent: Steam-CO\textsubscript{2}. Bed temperatures: 550°C and 600°C.
Furthermore, biochars from gasification experiments were analyzed using the Total Organic Carbon (TOC). Figure 21 shows the percentage of carbon in the solid residue, after steam-CO$_2$ gasification of Costa Rica broza, CANMET pellets and Bark feedstocks, at 550°C and 600°C, respectively. As reported, carbon content in biochar varied in the 80-90% range, with the smallest values obtained for Costa Rica broza. This is consistent with its high percentage of mineral content in the raw feedstock, as illustrated in Table 4.

![Figure 21: Carbon Contained in Biochar after Experiments in a CREC Riser Simulator. Bed temperatures: 550°C and 600°C. Gasifying medium: steam-CO$_2$.](image)

On the other hand, Figure 22 illustrates the percentage of carbon in the solid residue, at two temperatures, after steam-inert runs for the three feedstocks studied. From this figure, one can notice that the amount of carbon in biochar varies in the 90-95% range. This was the case for all biomass feedstocks under steam-inert atmospheres.
5.2.3 Experiments under Steam-Inert Atmospheres

Figures 23-26 report $\text{H}_2$, CO, $\text{CH}_4$ and $\text{CO}_2$ molar fractions in synthesis gas using steam-inert as gasifying agents, at 550°C and 600°C.

Figure 23 shows hydrogen molar fractions for the three feedstocks of this study. Higher temperatures consistently increased hydrogen molar fractions. This was assumed as result of a higher influence of the water-gas-shift reaction, favoring $\text{H}_2$ production. In this respect, Costa Rica broza showed the highest hydrogen molar fraction, with this being 40% at 600°C.
Figure 23: Changes of Hydrogen Molar Fractions with Temperature, in the CREC Riser Simulator, under Steam-Inert Atmospheres. Biomass feedstocks: (Costa Rica broza, CANMET pellets and Bark). Gasifying agent/dry biomass fed (mole%): 55%; Steam/dry biomass fed (mole%): 20%. Total reactor pressure prior to sampling: 57-58psi.

Figure 24 reports CO molar fraction changes with temperature. CO yields increased from 7.6% to 9.2% for CANMET pellets and from 5.5% to 7.4% for Costa Rica broza. Therefore, it can be assumed that the reactions promoting CO formation, such as water-gas shift and Boudouard are favored at higher temperatures. This agrees with the endothermic reverse water-gas shift reaction, being promoted at higher thermal levels. On the other hand, bark reached the highest CO yields at 550°C with a 7% value. At 600°C however, CO yields were mildly reduced to 6.5%.
Moreover, when bed temperature rises during biomass gasification processes under an inert-steam atmosphere, one can observe a mild boost in methane molar fractions (Figure 25). For example, when using CANMET pellets as a feedstock, one can see an increase from 17% to 19%.
Figure 25: Changes of Methane Molar Fractions with Temperature, in the CREC Riser Simulator, under Steam-Inert Atmospheres. Biomass feedstocks: (Costa Rica broza, CANMET pellets and Bark). Gasifying agent/dry biomass fed (mole%): 55%; Steam/dry biomass fed (mole%): 20%. Total reactor pressure prior to sampling: 57-58psi.

A small increase in temperature, however, has a significant impact on the CO$_2$ molar fractions when using Costa Rica broza and CANMET pellets, as shown in Figure 26. For instance, it is possible to see a 10% decrease of Costa Rica broza CO$_2$ molar fractions, by increasing the temperature from 550°C to 600°C. Furthermore, for the bark feedstock, a minor decrease in the CO$_2$ molar fraction was observed.
Figure 26: Changes of Carbon Dioxide Molar Fractions with Temperature, in the CREC Riser Simulator, under Steam-Inert Atmospheres. Biomass Feedstocks: (Costa Rica broza, CANMET pellets and Bark). Gasifying agent/dry biomass fed (mole%): 55%; Steam/dry biomass fed (mole%): 20%. Total reactor pressure prior to sampling: 57-58psi.

5.2.4 Experiments under a Steam-CO$_2$ Atmosphere

Figures 27-30 report the H$_2$, CO, CH$_4$ and CO molar fractions for steam-CO$_2$ gasification, at 550°C and 600°C, using 3 different biomasses feedstock.

In particular, Figure 27 displays the hydrogen molar fractions. One can notice that the temperature increment, from 550°C to 600°C, favours a higher hydrogen molar fraction. This trend is in the 8-12% range for all three feedstocks involved in the study.
Figure 27: Changes of Hydrogen Molar Fractions with Temperature, in the CREC Riser Simulator, under Steam-CO$_2$ Atmospheres. Biomass Feedstocks: (Costa Rica broza, CANMET pellets and Bark). Gasifying agent/dry biomass fed (mole%): 55%; Steam/dry biomass fed (mole%): 20%. Total reactor pressure prior to sampling: 57-58psi.

Figure 28 reports CO molar fractions at 550°C and 600°C with the following CO yields: a) 6% at 550°C and 10% at 600°C for Costa Rica broza, b) 5% at 550°C and 8% at 600°C for CANMET pellets, and c) at 6% at 550°C and 9% at 600°C for bark.

These results can be explained considering that there is first a rapid biomass conversion via pyrolysis, which leads to the formation of char. Following this, steam or CO$_2$ may be adsorbed on the biochar$^{82}$. Adsorbed species may react with biochar, via dry reforming or water gas shift, contributing to the rise in CO molar fraction.
Figure 28: Changes of Carbon Monoxide Molar Fractions with Temperature, in the CREC Riser Simulator, under Steam-CO$_2$ Atmospheres. Biomass Feedstocks: (Costa Rica broza, CANMET pellets and Bark). Gasifying agent/dry biomass fed (mole%): 55%; Steam/dry biomass fed (mole%): 20%. Total reactor pressure prior to sampling: 57-58psi.

Figure 29 describes the CH$_4$ molar fractions at 550°C and 600°C, using steam-CO$_2$ as a gasifying agent. The following was observed: a) from 4% to 5% for Costa Rica broza, b) from 3% to 7% for CANMET pellets, and c) from 8% to 9% for bark. Thus, a mild increase in methane molar fractions with temperature was observed for Costa Rica broza and bark, while a bigger one was noticed for CANMET pellets. These results can be assigned to the combined contribution of the endothermic biomass thermal cracking, forming methane, and the endothermic dry and steam reforming, consuming methane. All these reactions are favored at higher temperatures.$^{56}$
Figure 29: Changes of Methane Molar Fractions with Temperature, in the CREC Riser Simulator, under Steam-CO$_2$ Atmospheres. Biomass Feedstocks: (Costa Rica broza, CANMET pellets and Bark). Gasifying agent/dry biomass fed (mole%): 55%; Steam/dry biomass fed (mole%): 20%. Total reactor pressure prior to sampling: 57-58psi.

Figure 30 describes Carbon dioxide molar fractions obtained, having steam-CO$_2$ as a gasifying agent at 550°C and 600°C. One can observed that carbon dioxide yields decrease significantly with temperatures increase. This is clearly in contrast with the observed trends for the other synthetic gas components (H$_2$, CO, CH$_4$).

It is important, nevertheless, to emphasize that the CO$_2$ molar fractions reported in Figure 30 incorporate the CO$_2$ amount initially injected in the reactor, and this before the reaction takes place. Furthermore, in Section 5.3, it is possible to compare the CO$_2$ co-fed and the CO$_2$ contained in the final product.
5.3 Thermodynamic Equilibrium Model Validation

The validation of a model, such as in the case of the chemical equilibrium model of the present study, is of major importance for the successful gasification of biomass. To achieve this, predicted chemical equilibrium model results were compared with experimental data obtained in the CREC Riser Simulator unit\textsuperscript{92}. Every experiment was repeated at least 15 times to ensure the reproducibility of results. The vertical black crossbars from Figures 31-40, represent standard deviations of repeated experiments.

From Section 5.3.1 onwards, experimental runs and chemical equilibrium predictions, developed for each type of feedstock and operational condition, have been compared. These assessments start by stating the results of gasification processes using steam-CO\textsubscript{2} as gasifying medium, followed by the ones using a steam-inert atmosphere.
These comparisons between the non-stoichiometric thermodynamic model and the experimental results were developed using the following parameters: (i) Biomass carbon conversion, (ii) H\textsubscript{2} molar fraction, (iii) CO molar fraction, (iv) H\textsubscript{2}/CO ratio and (v) CO\textsubscript{2} molar fraction. Experiments were carried out by varying the bed temperature (550°C and 600°C), the gasifying agent (steam-CO\textsubscript{2} and steam-inert gas) and the type of biomass feedstock used (coffee pulp or Costa Rica broza, CANMET pellets and bark).

5.3.1 H\textsubscript{2} Molar Fractions

Figures 31 and 32 report the hydrogen molar fractions for the two types of gasification considered. Figure 31 describes gasification under steam-CO\textsubscript{2} atmospheres while Figure 32 considers gasification under steam-inert atmospheres. These figures also compare the experimental values obtained in the CREC Riser Simulator with the values predicted by the thermodynamic equilibrium gasification model.

From Figure 31, it can be observed that there is a consistently good agreement between the hydrogen molar fractions predicted by the thermodynamic equilibrium model and those obtained in experimental runs in the CREC Riser Simulator for broza, CANMET pellets and bark gasification, performed under steam-CO\textsubscript{2} atmospheres.
Figure 31: Changes of Hydrogen Molar Fractions in Syngas Conversion with Temperature, for both, Equilibrium Conditions and Experimental Runs in the CREC Riser Simulator, under Steam-CO$_2$ Atmospheres. Biomass Feedstocks: Costa Rica broza, CANMET pellets and bark. Gasifying agent/dry biomass fed (mole%): 55%; Steam/dry biomass fed (mole%): 20%. Total reactor pressure prior to sampling: 57-58psi.

Furthermore, Figure 32 reports hydrogen yields from the gasification of several biomasses in the CREC Riser Simulator under steam-inert atmospheres. One can notice that the effect of the temperature is very similar to the one predicted by the thermodynamic equilibrium model, with hydrogen yields increasing with the thermal level. However, H$_2$ molar fractions from steam-inert gasification display values relatively far from chemical equilibrium predictions. This is more apparent for the CANMET pellets and bark feedstocks. A closer agreement between H$_2$ molar fractions under steam-inert atmospheres and thermodynamic equilibrium values was observed in the case of Costa Rica broza, with this being attributed to its high mineral content, such as calcium and iron.
The higher amount of hydrogen molar fraction, observed in the experimental runs under steam-inert atmosphere, can be assigned to the effect of both dry-steam reforming and water-gas shift reactions. The excess of CO$_2$ inside of the reaction system promotes H$_2$ and CO formation through dry reforming reaction. However, it also promotes the reverse water-gas shift reaction, consuming the CO$_2$ and H$_2$ to augment the CO molar fraction in synthesis gas composition.

5.3.2 CO Molar Fractions

Figures 33 and 34 report carbon monoxide molar fractions from both the thermodynamic equilibrium model and experimental runs in the CREC Riser Simulator.

Figure 33 shows that steam-CO$_2$ atmospheres, in the CREC Riser Simulator, yield CO molar fractions that are close to thermodynamic equilibrium predictions, with these being in the 8-15% range. This is the case for the three feedstocks and two
temperatures studied. For instance, the Costa Rica broza predicted values for the carbon monoxide molar fractions that were 8% at 550°C and 14% at 600°C, followed by values obtained in the experimental results at 6% and 11%, respectively.

Figure 33: Changes of Carbon Monoxide Molar Fractions with Temperature, in Syngas Conversion, for both Equilibrium Conditions and Experimental Runs in the CREC Riser Simulator, under Steam-CO$_2$ Atmospheres. Biomass Feedstocks: Costa Rica broza, CANMET pellets and bark. Gasifying agent/dry biomass fed (mole%): 55%; steam/dry biomass fed (mole%): 20%. Total reactor pressure prior to sampling: 57-58psi.

Figure 34 reports the CO molar fractions from biomass gasification using steam-inert atmospheres. It is shown that the observed CO molar fractions are close to thermodynamic equilibrium model predictions. A consistently positive effect is obtained by raising the temperature, for broza and CANMET pellets. Bark however, displays an important deviation.

Moreover, there is an approximate 10-15% of carbon monoxide yield for both inert-steam and CO$_2$-steam atmospheres. From that, one can assume that excess CO$_2$ co-fed into the system improves biomass gasification reactions, such as the dry reforming of methane and the reverse water-gas shift reactions, enhancing CO yield and providing a H$_2$/CO ratio in the 1-2% range$^{47}$. 
5.3.1 CH$_4$ Molar Fractions

Figures 35 and 36 report methane molar fractions from both, the thermodynamic equilibrium model and the experimental results in the CREC Riser Simulator.

Figure 35 shows that under steam-CO$_2$ atmospheres, the experimental results for CH$_4$ molar fractions are above chemical equilibrium values. This is the case for the three feedstocks and two temperatures studied. The phenomena of methane molar fractions moderately surpassing chemical equilibrium values can be explained by considering that methane is a primary gasification product, as shown in Equation 6. Thus, further transformation of this primary product, as described by the set of Reactions (1) to (6) in Chapter 2, is closely linked to the dry reforming activity reaction, which is enhanced when CO$_2$ partial pressures are augmented.
Figure 35: Changes of Methane Molar Fractions with Temperature, in Syngas Conversion, for both Equilibrium Conditions and Experimental Runs in the CREC Riser Simulator, under Steam-CO$_2$ Atmospheres. Biomass Feedstocks: Costa Rica broza, CANMET pellets and bark. Gasifying agent/dry biomass fed (mole%): 55%; steam/dry biomass fed (mole%): 20%. Total reactor pressure prior to sampling: 57-58psi.

Figure 36 reports a similar trend for CANMET pellets and Costa Rica broza feedstocks, with the experimental methane molar fractions significantly surpassing methane molar fractions predicted by chemical equilibrium model under a steam-inert atmosphere. This again, being assigned to the fact that methane is a primary product, depending on secondary reaction to convert it into syngas.
Figure 36: Changes of Methane Molar Fractions with Temperature in Syngas Conversion, for both Equilibrium Conditions and Experimental Runs in the CREC Riser Simulator, under Steam-Inert Atmospheres. Biomass feedstocks: Costa Rica broza, CANMET pellets and bark. Gasifying agent/dry biomass fed (mole%): 55%; steam/dry biomass fed (mole%): 20%. Total reactor pressure prior to sampling: 57-58psi.

5.3.1 CO \(_2\) Molar Fractions

Figures 37 and 38 show CO \(_2\) molar fractions for both the thermodynamic equilibrium model and the experimental runs in the CREC Riser Simulator.

Figure 37 shows that under a steam-CO \(_2\) atmosphere, the CO \(_2\) molar fractions are close to chemical equilibrium, with this being the case for the three feedstocks and two reaction temperatures studied.
Figure 37: Changes of Carbon Dioxide Molar Fractions with Temperature, in Syngas Conversion, for both Equilibrium Conditions and Experimental Runs in the CREC Riser Simulator, under Steam-CO$_2$ Atmospheres. Biomass Feedstocks: Costa Rica broza, CANMET pellets and bark. Gasifying agent/dry biomass fed (mole%): 55%; steam/dry biomass fed (mole%): 20%. Total reactor pressure prior to sampling: 57-58psi.

On the other hand, Figure 38 reports CO$_2$ molar fractions under steam-inert atmospheres exceeding thermodynamic equilibrium values.

Figure 38: Changes of Carbon Dioxide Molar Fractions with Temperature, in Syngas Conversion, for both Equilibrium Conditions and Experimental Runs in the CREC Riser Simulator.

These reported CO$_2$ levels determined experimentally, surpassed chemical equilibrium as in Figure 38. Furthermore, CO$_2$ molar fractions above equilibrium were also observed for methane (Figure 36). These findings provide an indication that experimental steam-inert gasification results are still significantly affected by primary reactions. This is in sharp contrast, with the carbon dioxide molar fractions observed under steam-CO$_2$ atmospheres, where dry reforming is promoted, allowing secondary reactions (Reactions (1) to (6)) to reach chemical equilibrium.

5.3.2 H$_2$/CO ratio

Figure 39 reports the H$_2$/CO ratios obtained experimentally and those predicted using the thermodynamic equilibrium model, for the three biomass feedstocks of the present study, under steam-CO$_2$ atmospheres. One can observe that in all cases, the H$_2$/CO ratio remained in the 1.5-2 range, for both experimental results and chemical equilibrium predictions.

The experimental H$_2$/CO ratios for the various biomasses under CO$_2$-steam, at 600°C, show values in the 1.8-2.2 range. On this basis, one can conclude that this H$_2$/CO ratio data agrees with thermodynamic equilibrium. It thus, appears that an excess of CO$_2$ in the reactor atmosphere contributes to the reverse water-gas shift reaction (CO+H$_2$O$\rightleftharpoons$CO$_2$+H$_2$), enhancing the production of carbon monoxide, and therefore reducing the H$_2$/CO ratio$^{112}$. 
Figure 39: H\textsubscript{2}/CO Ratios at 550°C and 600°C in the CREC Riser Simulator, under Steam-CO\textsubscript{2} Atmospheres. H\textsubscript{2}/CO ratios calculated using chemical equilibrium are reported for comparison. Biomass feedstocks: Costa Rica broza, CANMET pellets and bark.

Figure 40 reports the H\textsubscript{2}/CO ratios for experiments under a steam-inert atmosphere. One can see that this ratio for the Costa Rica broza can be as high as 6 at 550°C, with this ratio being reduced to 4 at 660°C. One can also notice that these high H\textsubscript{2}/CO ratios are not achieved with CANMET pellets and bark. In fact, broza is the only feedstock that is gasified at conditions very close to thermodynamic equilibrium. This behaviour, once again, can be attributed to the high content of mineral matter (ash) in this raw feedstock, which can act as a catalyst, promoting key gasification reactions.
Figure 40: H₂/CO Ratios at 550°C and 600°C in the CREC Riser Simulator, under Steam-Inert Atmospheres. H₂/CO ratios calculated using chemical equilibrium are reported for comparison. Biomass Feedstocks: Costa Rica broza, CANMET pellets and bark.

The H₂/CO ratio is a crucial parameter of biomass gasification processes. Syngas can be used to produce various chemicals, as showed in Figure 41. On this basis, one can argue that the syngas from this study are excellent for methanol synthesis as well as Fischer-Tropsch synthesis. Likewise, the syngas produced experimentally during biomass gasification under inert-steam conditions is excellent for ammonia synthesis and synthesis of natural gas, with a H₂/CO ratio higher than 3.

Figure 41: Syngas Utilization Routes
5.3.3 Overview of Process Advantage

As reported in Figure 39, the CO$_2$ molar fractions observed when CO$_2$ and steam were co-fed as gasifier agents, provide yields close to those obtained with the thermodynamic equilibrium model.

Furthermore, Figure 42 compares the CO$_2$ yields co-fed to the reactor and the ones obtained.

![Figure 42: Carbon Dioxide Yields at 550°C and 600°C in the CREC Riser Simulator, under Steam-CO$_2$ Atmospheres. CO$_2$ amounts co-fed into the system are reported as a reference. Biomass Feedstocks: Costa Rica broza, CANMET pellets and bark.](image)

One can notice that the CO$_2$ yield, obtained at 550°C with CANMET pellets is 1.15mol/mol of C fed. This is smaller than the 1.4mol/mol of C co-fed as CO$_2$. This same trend was observed for the other two feedstocks studied. Thus, one can conclude that steam-CO$_2$ gasification leads to an overall CO$_2$ consumption, helping to reduce CO$_2$ emissions. It is envisioned that this overall CO$_2$ consumption provides a major environmental advantage to biomass gasification operating under this principle, as carbon dioxide is a pollutant from almost every major industry.

Based on the results obtained, one can conclude that the molar fractions of various synthesis gas products are close to chemical equilibrium values, when biomass
gasification takes place under steam-CO\textsubscript{2} atmospheres. By taking advantage of the predictability of molar fractions, one can envision biomass gasification processes such as the one described in the enclosed Figure 43.

![Figure 43: Schematic Diagram of Biomass Gasification under CO\textsubscript{2} Atmospheres. The proposed process includes a biomass gasifier operating under a CO\textsubscript{2} atmosphere and a CO\textsubscript{2} membrane unit separator. CO\textsubscript{2} is recycled back to the gasifier. A small CO\textsubscript{2} makeup stream is also needed.](image)

In this process, CO\textsubscript{2} is co-fed to the biomass gasifier unit. Carbon dioxide is later separated by using a CO\textsubscript{2} membrane separation unit\textsuperscript{86}, and is recycled back to the gasifier. This yields a syngas with both, a good H\textsubscript{2}/CO ratio and an adequate heating value. This is accomplished with minimum CO\textsubscript{2} makeup process requirements.
5.4 Conclusion

a) Biomass gasification in a CREC Riser Simulator demonstrates that this process can be significantly enhanced under steam-CO\textsubscript{2} atmospheres. Under these conditions, biomass conversion is augmented, and the tar formed is reduced. These findings were assigned to the special role of CO\textsubscript{2}, favoring both char gasification and dry hydrocarbon reforming reactions.

b) Biomass gasification of three different feedstocks studied under steam-CO\textsubscript{2} atmospheres, showed that hydrogen, methane, CO and CO\textsubscript{2} molar fractions were in agreement with the thermodynamic equilibrium model predictions. Under these gasification conditions, H\textsubscript{2}/CO ratios remained in the 1.5-2 range.

c) Biomass gasification in the CREC Riser Simulator under a steam-inert gas atmosphere, yielded CO\textsubscript{2} and methane molar fractions significantly different from the ones predicted at chemical equilibrium. The closest agreement between experimental data and predictions from the thermodynamic equilibrium model was for a Costa Rica broza feedstock, with this being assigned to the high mineral content of this feedstock, for instance calcium and iron.

d) Biomass gasification in the CREC Riser Simulator under steam-CO\textsubscript{2} atmospheres showed CO\textsubscript{2} consumption. Thus, steam-CO\textsubscript{2} biomass gasification can allow the reduction of CO\textsubscript{2} emissions that can provide a major process environmental advantage while compared with steam-inert gas gasification.

e) BET specific surface areas, showed average results between 10-20m\textsuperscript{2}/g for the three biomasses studied, at 550°C and 600°C. These results were in agreement with other outcomes reported by others113.

f) Carbon content in biochar varied in the 80-90% range, for the experimental runs under steam-CO\textsubscript{2} atmospheres, and in the 90-95% range for the experiments under steam-inert atmospheres.
Chapter 6 : Catalyst Development

6 Experimental Procedure

Chapter 6 provides details of the experimental procedures and methods involved in the preparation, characterization and efficiency evaluation of a fluidizable Ni-based catalyst. This catalyst was used in the experimental runs for catalytic steam gasification of a biomass surrogate species.

Section 6.1 describes biomass catalytic gasification background information briefly, while Sections 6.2 and 6.3 report catalyst preparation and techniques used to characterize the prepared catalyst. Section 6.4 describes the model compound selected and the gasifying agents. This is followed by Section 6.5, which reports operational conditions (e.g. temperature and reaction time). A description of the fluidized bed reactor system, the CREC Riser Simulator unit, is provided in Section 6.6, followed by an explanation of the analytical system used to quantify synthesis gas products.

6.1 Catalytic Reforming of Tars

Several studies have shown the benefits of using different catalysts during biomass gasification processes\textsuperscript{15, 38, 77}. Catalytic gasification of biomass feedstocks has been widely used to break down the heavier tar molecules into lighter gaseous products. The use of an effective catalyst, which should be stable and highly active, helps to produce high quality and tar free synthesis gas, promoting char gasification, while avoiding costly tar removal and disposal\textsuperscript{9, 80, 103}. It is important to mention that catalysts are specific and have to be evaluated in terms of their efficiency in the process that they are being proposed for.

Dolomites and zeolites, have been used as catalysts in biomass gasification. However, nickel is considered a more promising catalyst, given its affordability and high reforming activity\textsuperscript{107}.
Olivares et al.\textsuperscript{108} showed that the nickel reforming catalyst was 8-10 times more reactive than calcined dolomite. Nickel catalysts promote the water-gas shift reaction, being promising for tar reforming. This results in a high synthesis gas quality and high H\textsubscript{2}/CO ratios\textsuperscript{109}.

On the other hand, while using nickel-based catalysts, the drawback is the presence of several deactivation mechanisms\textsuperscript{79, 104}. At high temperatures, gasification may also lead to Ni deactivation. This is given the carbon formation and the Ni crystallite agglomeration. Therefore, availability of a catalyst with a long-life on stream is essential for biomass gasification\textsuperscript{9}. In this context, Ni supports, and Ni promoters have been largely used to enhance catalyst mechanical strength and minimize deactivation\textsuperscript{105, 106, 110}.

The present study considers fluidizable Ni-based catalysts with high specific surface area for biomass gasification. Fluidizable γ-Al\textsubscript{2}O\textsubscript{3} is one of the most promising supports used for a Ni-based catalyst. This is mainly due to its high surface area and mechanical strength. Previous studies showed that a Ni/γ-Al\textsubscript{2}O\textsubscript{3} catalyst provides higher conversion and lower deactivation rates than the Ni/α-Al\textsubscript{2}O\textsubscript{3} catalysts\textsuperscript{123}. However, a drawback of using γ-Al\textsubscript{2}O\textsubscript{3} is the fact that this support is not stable at high temperatures, due to thermal sintering and phase transformation\textsuperscript{110}.

The use of Ni on γ-Al\textsubscript{2}O\textsubscript{3} offers challenges given its acidity, as well as low thermal stability and basicity. CeO\textsubscript{2} is one of the most suitable materials, among the rare earth oxides\textsuperscript{124, 125}. When CeO\textsubscript{2} is added to a Ni catalyst, it favours metal-support interaction, improving catalytic activity and reducing carbon formation. Previous studies found that a good loading of CeO\textsubscript{2} in a Ni catalyst is in the 1-5wt\% range\textsuperscript{126}.

For the present study, CeO\textsubscript{2} was selected as a promoter of Ni/γ-Al\textsubscript{2}O\textsubscript{3} catalysts. A final 20\%Ni-5\%CeO\textsubscript{2} γ-Al\textsubscript{2}O\textsubscript{3} was prepared and its performance was studied during the catalytic steam gasification processes of biomass surrogate species. The Ni-CeO\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} was characterized using: a) NH\textsubscript{3} Temperature Programmed Desorption and b) BET surface area. The prepared catalyst was used for
gasification of 2-methoxy-4-methylphenol. This chemical species can be considered as surrogate of biomass lignin component. Experiments were carried out in a CREC riser simulator.

6.2 Catalyst Preparation

The method of catalyst preparation may influence its structural properties, the metal-support interaction, the metal reducibility and the dispersion\textsuperscript{120, 121}. The catalyst used in this study, was prepared via an ‘incipient wetness’ technique, under vacuum conditions. Previous studies have shown that besides being simple and largely used to prepare stable supported nickel catalysts at a commercial scale, this technique provides a higher nickel reducibility, as well as a proper control of metal loading\textsuperscript{15, 77}.

The various materials used for catalyst preparation were: a) Ni(NO$_3$)$_2$·6H$_2$O (99.9\%, Sigma-Aldrich, Germany), b) γ-Al$_2$O$_3$ (Sasol North America, Sasol Catalox® SSCa5/200), and c) Ce(NO$_3$)$_3$·6H$_2$O (99.9\%, Sigma-Aldrich, Germany).

Three main steps were followed to achieve the desired result:

a) Support impregnation with Ce and Ni
b) Drying
c) Reduction of metal precursors

The first impregnation step was carried out in a quartz conical flask, containing 15g of fluidizable alumina. The flask had a lateral outlet port connected to a vacuum line. There was as well a flask inlet sealed with a rubber septum, which allowed maintaining the vacuum conditions throughout the impregnation. To remove the trapped gas inside the porous support, the support was first evacuated under vacuum for 10 minutes. At this point, an aqueous Ce nitrate solution was prepared by dissolving a set amount of Ce nitrate in water. The needed aqueous Ce nitrate solution was determined based on the available pore volume in the alumina
support. Once the Ce nitrate solution was prepared, it was added drop-by-drop to the alumina support, while mixing it continuously using a magnetic rod.

Next, a nickel nitrate solution was added, drop-by-drop, to the already Ce impregnated support, under vacuum conditions. Once the Ni solution was added, the resulting paste was stirred for an extra 30 minutes. Finally, the impregnated γ-\text{Al}_2\text{O}_3 paste was slowly dried overnight at 140°C.

The last step of the catalyst preparation was the metal precursor reduction step. This was accomplished by having the dried powder transferred to a fluidized bed reactor unit. This unit was then placed into a Thermolyne 48000 muffle furnace to reduce the metal nitrates. The temperature was raised progressively from 23°C to 700°C over 3.5 hours. After that, temperature was kept at 700°C under the constant gas flow of a 10% hydrogen in helium mixture for 8 hours.

To complete the support impregnation at the selected Ni and Ce loadings, three consecutive impregnation steps were implemented until the desired metal loading was reached. It is also important to mention that an increase in the active metal concentration implies, in principle, a higher catalytic activity. However, if in excess, metal loading can cause catalyst destabilization via metal sintering, phase transformation and particle agglomeration\textsuperscript{116,122}. On this basis, the Ni loading was set at 20wt\%\textsuperscript{15} while the Ce was set at 5wt%.

6.3 Catalyst Characterization

Catalyst characterization is important to predict the structural properties of the catalyst and the interaction between the catalyst and the metal-support. The various physicochemical techniques used in the present study are described in the upcoming sections.

6.3.1 $\text{N}_2$ Physisorption

The $\text{N}_2$ adsorption-desorption method provides the pore size distribution and pore geometry, which are important catalyst structural properties. In the case of this
thesis, the specific surface area, the average pore diameter and the pore volume of the catalyst developed were determined in a Micromeritics, ASAP 2010, by using N\textsubscript{2} adsorption at 77K. Approximately 0.25g of catalyst sample was degassed at 250\degree C for 3h, before starting the analysis. Both isotherms were measured in a $10^{-6}$ to 1 relative pressure range.

### 6.3.2 Particle Size Distribution

Particle size and particle size distribution are important properties required to secure fluidization. Small catalyst particles favour fluidization. However, small particles can lead to catalyst losses in cyclones and bag filters\textsuperscript{9}.

### 6.3.3 Temperature Programmed Studies

A Micromeritics Autochem II 2920 chemisorption analyzer was used to conduct ammonia Temperature programmed desorption (NH\textsubscript{3}-TPD), Temperature programmed reduction (TPR), temperature programmed oxidation (TPO), and H\textsubscript{2} pulse chemisorption. Approximately 0.15g of catalyst sample was loaded in a U-shape quartz tube and placed inside of the heating chamber of the analyzer.

### 6.3.4 Temperature programmed desorption (TPD)

Temperature Programmed Desorption (TPD) can be used to characterize the total acidity and basicity for the γ-Al\textsubscript{2}O\textsubscript{3} catalysts, by determining the amount and strength of acids sites on the support.

Before starting the TPD experiment, the catalyst sample was pre-treated by flowing He in the bed at 700\degree C. After that, the sample was brought to saturation by flowing a gas stream containing 5\% NH\textsubscript{3} in helium, through the bed at 50\degree C for 1 hour. When the saturation step was complete, the sample was purged, one more time, with a He stream for 1 hour, at the adsorption temperature.

Following this, the bed temperature was linearly raised (15\degree C/min), from 23\degree C to 950\degree C, while a stream of He has was flowing throughout the bed. The total acidity
in the analyzed catalyst was directly related to the amount of desorbed ammonia released from the sample surface, which was measured using a Thermal Conductivity Detector (TCD).

6.3.5 Temperature programmed reduction (TPR)

Temperature Programmed Reduction (TPR) determines the reduction properties of a prepared catalyst. In this respect, TPR was performed to establish the amount of reducible species in the $\gamma$-Al$_2$O$_3$ catalysts and the temperature range at which the reduction occurs.

Before the hydrogen TPR experiment was started, the catalyst sample was pre-oxidized by a stream containing a gas with 5% oxygen in helium, at 650°C. To remove any oxygen trapped in the catalyst, the sample was then cooled down under argon flow. Then, the reduction step was performed, using a gas with 10% hydrogen in argon at a heating rate of 10°C/min.

The total amount of hydrogen consumed during the reduction step was determined from the TCD signal. In this way the reducible species present in the catalyst sample were quantified.

6.3.6 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation (TPO) is employed to establish the extent that a catalyst can be oxidized. In this present study, the TPO runs were developed prior to the TPR runs. By doing this, the catalyst sample was brought to the fully oxidized state prior to reduction.

The TPO runs mirrored the TPR runs, with the flowing gas composed in this case, of 5% O$_2$ and 95% He. Based on the total amount of consumed oxygen, the percentage of oxidizable metal was calculated.
6.3.7 Chemisorption

H\textsubscript{2} Pulse Chemisorption is used to determine the metal dispersion and average metal crystal sizes. This was achieved based on the anticipated H\textsubscript{2} chemisorbed monolayer on the catalyst surface. In our study, Pulse Chemisorption was performed at ambient temperature and following TPR runs. To accomplish this, 50mL/min of argon was flown through a catalyst sample, previously reduced at 900°C. Following this, a series of 1.0mL consecutive pulses of hydrogen were injected, with 1.5min delay between each gas injection. Outlet hydrogen peaks were recorded by using a TCD. Considering the total amount of hydrogen chemisorbed, the metal dispersion was calculated. Based on this and given the total reducible metal established with TPR, the average metal crystallite size was obtained.

6.3.8 X-Ray Diffraction

X-Ray diffraction is a technique used to identify crystalline structures, phases and crystallite sizes. A Rigaku MiniFlex diffractometer with a Ni filtered Cu K\textsubscript{α} (\(\lambda = 0.15406\) nm) radiation was used in the present study. The catalyst sample was irradiated with a tube voltage of 40 kV and a tube current of 40 mA, being scanned every 0.02 degrees from 10 to 90 degrees, with a constant scan time of 2 \(\theta/\text{min}\)\textsuperscript{14,77}. The calculation of Ni crystallite sizes were effected using the Scherrer’s equation, below:

\[
d = \frac{0.94 + \lambda}{(\beta - \beta_0) \cdot \cos \theta}
\]

(17)

where \(d\) is the volume average diameter of the crystallite and \(\beta - \beta_0\) is the full width at half maximum intensity of the peak.

6.4 Reaction System

Catalytic steam gasification of 2-methoxy-4-methylphenol, which is a lignin surrogate, was carried out using a CREC Riser Simulator\textsuperscript{88}. A full description of
the CREC Riser Simulator can be found in Chapter 3. As mentioned before, the Riser unit operates as a bench-scale mini-fluidized bed reactor, composed of two outer shells, a lower section and an upper section, that allows a quick catalyst loading and unloading.

The simulator unit operates in connection with a series of sampling valves, a vacuum box, two pressure transducers, two thermocouples and a gas analysis system, which allows sending the reaction product sample to the analytical system. An operational scheme is illustrated in Chapter 3, Figure 14-15. Details about the analytical system will be provide in the next session of this chapter.

A manual injector switch with a syringe allows the easy injection of the biomass surrogate into the reactor (Figure 44). The reaction time, one of the operational parameters selected, is set with a timer connected to the actuator of the 4-port valves. This timer is linked to a micro-switch located in the manual injector, which is started as soon as the feedstock is placed in the reactor. When the desired reaction time is reached, the actuator opens the 4-port valve and the reaction products inside of the reactor are evacuated and transferred to the analytical system.

![Figure 44: Manual Injector Switch with Syringe](image)

The reaction temperature was measured using thermocouples (Omega Engineering, Model KM WIN-062G-6) placed at strategic reactor locations. These thermocouples display temperatures on a control panel. The reaction pressure is another important parameter. It was measured both in the annulus of the reactor and in the vacuum box with a pressure transducer (Omega Engineering, Model
PX603). An example of the pressure profile for a run using 2-methoxy-4methylphenol is provided in Figure 45. The upper curve represents the pressure changes in the reactor, while the lower curve shows pressure changes in the vacuum box.

![Pressure Profile](image)

**Figure 45: Pressure Profile during Catalytic Steam Gasification Process of Biomass Surrogate Specie. Gasifying agent: Steam-CO₂. Reaction time: 30 seconds. Bed Temperatures: 550°C and 600°C.**

Figure 45 reports the pressure profile during the catalytic runs. From that, one can observe a quick vaporization of lignin solution as soon as the sample is injected. This first step is followed by MMP gasification, which contribute to both MMP conversion as well as changing in the final product composition. One can also see an increase in the reactor pressure at higher temperatures, suggesting more efficient gasification with increased synthesis gas yields.

### 6.5 Analytical Conditions

The synthesis gas produced was directed to a Shimadzu GC/MS-2010 with both a Thermal Conductivity Detector (TDC), and a Flame Ionization Detector (FID) for product analyses. A packed bed column was connected to the TCD and a capillary column to the FID. The features for both columns can be found in Chapter 3. This
allowed the separation of various chemicals species present in the synthesis gas product.

The TCD signal was calibrated using certified standard gases. A typical gas chromatogram obtained using the TCD is illustrated in Figure 46.

![TCD Chromatogram Result of Permanent Gases for Catalytic Steam Gasification of Biomass.](image)

Regarding hydrocarbons formed and the unconverted 2-mehoxy-4-methylphenol, they were calculated using a FID chromatogram, as shown in Figure 47. Peaks areas, in the FID chromatogram, are proportional to masses. Thus, the mass fraction of tars were quantified for all species with a carbon number larger than C6.
Figure 47: FID Chromatogram Result of Permanent Gases for Catalytic Steam Gasification of Biomass\textsuperscript{77}.

The GC/TCD-FID analytical system was operated using a Mandel GC Solution software. This software performs several tasks associated with GC/MS data acquisition, data processing and reporting. There are three available programs to heat the GC oven using a thermal ramp: (i) blank, where one can analyze the impurities and other components inside the column; (ii) GC thermal run, used to analyse and quantify synthesis gas; and (iii) idle, to clean the column overnight.

The GC-TCD and GC-FID program ramp steps were as follows: a) The initial oven temperature was set to 35°C, b) After 3 minutes, the temperature was increased to 250°C, using a ramp of 25°C/min during 8.40min, c) To end, the temperature was kept constant at 250°C for 9 min.

The coke deposited on the prepared catalyst surface was measured as CO\textsubscript{2}, using a Mandel Total Organic Carbon analyzer (TOC-V) with a solid sample module (SSM-5000).
6.6 Experimental Materials and Methods

6.6.1 Biomass Surrogate Species

As mentioned before, biomass is mostly composed by cellulose, hemicellulose and lignin lumps, along with ash and moisture. Among them, cellulose is the main carbohydrate element of biomass, and usually represents 22.5 to 50.3 wt% of feedstock composition. However, lignin is known as the major non-carbohydrate, polyphenolic structural constituent of biomass. Lignin is hard to gasify, being considered the main contributor to tar formation during gasification processes\textsuperscript{38}. The lignin percentage in biomasses feedstock typically ranges from 10.9 to 28.8%.

On this basis, for this MESc study, 2-methoxy-4methylphenol was chosen to represent the lignin species in biomass, during the catalytic steam gasification performance of the 20%Ni-5%CeO\textsubscript{2} γ-Al\textsubscript{2}O\textsubscript{3} catalyst developed in this research.

6.6.2 Gasifying agent

To better understand the CO\textsubscript{2} effect on biomass gasification efficiency, as well as tar reforming, two gasifying agents were selected for this study: a) steam-inert and b) steam-10%CO\textsubscript{2} in inert. The objective was to quantify the combined effect of CO\textsubscript{2} partial pressure and of the prepared catalyst aiming to zero tar production during gasification processes.

6.7 Experiment Procedure

All experiments for catalytic steam gasification of biomasses feedstock were developed in the CREC Riser Simulator, a laboratory scale unit described before. The goal of this study is to understand how temperature, gasifier medium and residence time affects tar formation and synthesis gas quality during the conversion process.

Some variables were kept constant during the thermal experiments runs: (i) All experiments were developed under close to atmospheric pressure, 14 psi; (ii)
Impeller rotation was kept constant at 5500rpm; (iii) Steam/biomass ratio of 0.4, using 8µl of water and 20µl of 2-methoxy-4-methylphenol, and (iv) Catalyst/Biomass ratio of 12.5, using 0.25g of catalyst and 0.02g of biomass.

The steps described bellow were followed during every catalytic gasification run:

a) A 0.25g (20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$) of catalyst, already thermally treated during the preparation steps, was loaded in the reactor basket, to achieve the desired biomass/catalyst ratio. The catalyst was kept inside a basket contained by two filters (grids).

b) The basket was then placed into the lower shell section of the unit. The lower and upper shell sections were sealed by using a metallic gasket, six bolts were tightened, and the system leak tested.

c) After the reactor reached the desired temperature, the reactor pressure was reduced to atmospheric conditions and the 4PV was closed. This allowed isolating the CREC Riser Simulator from the vacuum box. For the steam-10%CO$_2$ in inert reactions, the vacuum box was filled with an inert gas. This was done to avoid high levels of CO$_2$ to be analyzed.

d) The vacuum box temperature was kept at 195°C and the pressure was set at 2.9 psi. This provides significant pressure differential with the CREC Riser Simulator total pressure allowing for rapid evacuation of products from the reactor.

e) After setting pressure and temperature in both reactor and vacuum box, the CREC Riser Simulator system was ready to start an experiment. To monitor the reaction progress, the pressure was recorded continuously.

f) The impeller rotation was started and set at 5500rpm, fluidizing the catalyst inside the basket and mixing all chemical species in the CREC Riser Simulator reaction chamber.
g) 2-methoxy-4-methylphenol and water were injected into the reactor chamber via a manual injector. As soon as the feed was injected into the reactor, an electronic timer started a countdown.

h) Once the reaction time was reached, the reactor was automatically opened, and all chemical species were evacuated from the reactor to the vacuum box. Following this, the 4PV was closed again, isolating the reactor from the vacuum box. To ensure the 6PV sample loop was filled with a representative gas product sample, the contents of the vacuum box were mixed for approximately 1 min and evacuated.

i) To finalize the run, gas products were directed from the 6PV sample loop to a gas chromatograph, connected to both Thermal Conductivity Detector (TCD) and a Flame Ionic Detector (FID). This allowed product analysis.

j) For some selected runs, an aliquot of the catalyst was recovered for TOC analysis. As a result, the coke formed was evaluated.

k) For the other runs, the catalyst was regenerated as follows: (i) Step 1: air was circulated for 10 minutes, with the temperature in the reactor set at 550°C/600°C; (ii) Step 2: 10% hydrogen in argon was flown for 10 minutes in order to load catalyst metal components (e.g. Ni) under reduced state conditions; (iii) Step 3: helium was circulated for 15 minutes.

l) Once all runs were completed, the reactor was cooled down and the used catalyst was kept for further analysis.
6.8 Conclusions

a) A Ni-based catalyst preparation method was successfully established. This catalyst preparation involved ‘incipient wetness’ technique, under three steps: support impregnation, drying, and reduction of metal precursor.

b) A 2-methoxy-4-methylphenol (MMP) was chosen as a model compound to represent lignin species in biomass feedstocks. Two agents were selected for gasification: Steam-inert and Steam-10%CO$_2$ in inert, along with two temperatures (550°C and 600°C), and four different residence time, 10, 15, 20 and 30 seconds.

c) Combined FID and TCD analytical techniques were chosen and demonstrated for the adequate analysis of various gasification products, including H$_2$, CO, CH$_4$, CO$_2$, light gases (C2-C5) and (C6+).

d) The mini-fluidized bed CREC Riser Simulator reactor was chosen as the laboratory reactor of choice for establishing the anticipated high MMP gasification efficiency of the prepared catalyst.
Chapter 7: Catalytic Gasification of Biomass

7 Experimental Results

In this present study, 2-methoxy-4-methylphenol (MMP) was selected as a model compound, to represent the lignin in biomass. Gasification experiments were developed in a CREC Riser Simulator, using different temperature levels, gasifier agents and residence times. These runs allowed to evaluate the CeO$_2$ modified Ni-$\gamma$Al$_2$O$_3$ catalyst performance.

Every experiment was repeated at least 4 times to secure the result reproducibility. Standard deviations were in the +/- 0-3% range. These deviations are shown in the various graphs of this chapter as vertical black cross bars. The products observed during the runs were permanent gases (H$_2$, CO, CO$_2$, CH$_4$), light carbonaceous components (C3-C5) and higher carbonaceous compounds (C6-C7).

Catalytic gasification was evaluated, using different gasifying agents (steam-inert and steam-CO$_2$), based on the following parameters: (i) synthesis gas molar fractions, (ii) carbon conversion to permanent gases, (iii) H$_2$/CO ratio, and (iv) tar formation. In this respect, C6+ aromatics and oxygenates species were lumped in the tar fraction. Coke was ignored in this present study, given that the Total Organic Carbon (TOC) results showed negligible amounts of coke (smaller than 0.01wt%).

Four reaction times were considered: 10, 15, 20 and 30 seconds. The chosen temperatures for gasification evaluation were 550°C and 600°C. This temperature range was selected to minimize ash agglomeration.

The total pressure during the runs for both, reactor and vacuum box, were recorded using a Personal Daq connected with two pressure transducers, as explained in Chapter 3. Synthesis gases produced from the gasification process were analyzed using a Shimadzu GC Analyzer with both a TCD (Thermal Conductivity Detector) and a FID (Flame Ionization Detector).
7.1 Catalyst Characterization Results

Table 8 reports the BET specific surface area (m$^2$/g), pore volume (cm$^3$/g) and average pore diameter (Å) for the fresh Alcan γ-Al$_2$O$_3$, as well as for the 20%Ni γ-Al$_2$O$_3$, and 20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$ catalysts. The addition of 5wt% of CeO$_2$ is considered optimum for this catalyst$^{77}$. Higher CeO$_2$ amounts can cause a decrease in the catalyst surface area, due to blocking of small pores by cerium$^{126}$.

One can observe that the surface area of the fresh support was reduced, from 193.4m$^2$/g to 128.1m$^2$/g, after Ni loading. This reduction in BET surface area shows the effect of metal loading on the γ-Al$_2$O$_3$ particles. One should notice however, that CeO$_2$ addition limits specific surface area reduction to 142.9m$^2$/g, showing limited Ni small pores blockage with good metal dispersion promoted by CeO$_2$$^{131}$.

Table 8 also reports that incorporating Ni on the Alcan γ-Al$_2$O$_3$ support yields a considerable increase in the catalyst average pore diameter, from 104.1Å to 113.6Å. This increase in pore diameter suggests a thermal sintering and blocking of the smaller support pores by the nickel metal particles$^{127}$. The addition of CeO$_2$, however, yields an essentially unchanged average pore reduction to 90.5Å.

Table 8: BET surface area, pore volume and pore diameter of the fresh Sasol γ-Al$_2$O$_3$, and the 20%Ni γ-Al$_2$O$_3$, and 20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$ catalysts$^{15,77}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Avg pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al$_2$O$_3$ (Sasol)</td>
<td>193.4</td>
<td>0.5</td>
<td>104.1</td>
</tr>
<tr>
<td>20%Ni Sasol γ-Al$_2$O$_3$</td>
<td>128.1</td>
<td>0.4</td>
<td>113.6</td>
</tr>
<tr>
<td>20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$</td>
<td>142.9</td>
<td>0.3</td>
<td>90.5</td>
</tr>
</tbody>
</table>
In summary, the 20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$ provides a catalyst more resistant to thermal sintering, with a higher surface area and lower average pore diameter than the 20%Ni Sasol γ-Al$_2$O$_3$ catalyst.$^{77, 78, 131}$

The acidity and the basicity of the support play an important role in the catalytic activity and the resistance to coke deposition of catalysts. Mazumder and de Lasa$^{130}$ showed that there are no Brønsted acid sites on the γ-Al$_2$O$_3$ surface, strong enough to form pyridinium ions. On the other hand, weak to moderate Lewis acid sites are expected$^{78}$. Furthermore, investigation of catalyst acidity and basicity was performed by NH$_3$-Temperature Programmed Desorption (TPD) in the present study. This allowed the absence of Brønsted acid sites to be confirmed and the presence of Lewis acid sites at different strengths to be detected$^{77}$.

The addition of 5wt% CeO$_2$ to the Ni/γ-Al$_2$O$_3$ catalyst caused a drop in the total acidity from 511µmol NH$_3$/g γ-Al$_2$O$_3$ to 150µmol NH$_3$/g γ-Al$_2$O$_3$. Thus, 5wt% CeO$_2$ on the Ni/γ-Al$_2$O$_3$ catalyst, reduces acidity effectively. However, once the Ni was incorporated into the catalyst, the 20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$ increased to 342µmolNH$_3$/g γ-Al$_2$O$_3$ acidity, as reported in Table 9. This resulting acidity is however, still lower than the 511-547µmolNH$_3$/g γ-Al$_2$O$_3$ values, observed for the 20%Ni-Al$_2$O$_3$ catalyst free of CeO$_2$, as reported by Mazumder and de Lasa$^{78}$.

Table 9: Total Acidity of the fresh Sasol γ-Al$_2$O$_3$, 20%Ni γ-Al$_2$O$_3$, 5%CeO$_2$ γ-Al$_2$O$_3$, and 20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$ catalysts.$^{15, 77}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Acidity (µmolNH$_3$/g γ-Al$_2$O$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al$_2$O$_3$ (Sasol)</td>
<td>511</td>
</tr>
<tr>
<td>20%Ni Sasol γ-Al$_2$O$_3$</td>
<td>547</td>
</tr>
<tr>
<td>5%CeO$_2$ γ-Al$_2$O$_3$</td>
<td>150</td>
</tr>
<tr>
<td>20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$</td>
<td>342</td>
</tr>
</tbody>
</table>
Metal dispersion on a support may depend on several factors, such as: i) type of metal/support used, ii) specific surface area of the selected support, and iii) catalyst preparation methods\textsuperscript{15, 78, 130}. When comparing the TPR for 20\%Ni/\(\gamma\)-Al\(_2\)O\(_3\) catalyst, developed by Mazumder and de Lasa\textsuperscript{78}, with the one of the present study, TPR profiles show that CeO\(_2\) addition reduces NiAl\(_2\)O\(_4\) formation. This is attested in Figure 48, which shows a smaller TPR peak at 700°C\textsuperscript{77}. Furthermore, the CeO\(_2\) addition also facilitates Ni reducibility. The TPR maximum peak is at 480°C, with metal reducibility and metal dispersion being 76.7\% and 5.51\%, respectively\textsuperscript{77, 78}.

![Figure 48: TPR profile of the CeO\(_2\) modified Ni/\(\gamma\)-Al\(_2\)O\(_3\)\textsuperscript{77}.](image)

Figure 49 reports the XRD diffractogram for the fresh and used 20\%Ni-5\%CeO\(_2\) \(\gamma\)-Al\(_2\)O\(_3\). Regarding these catalyst, Mazunder\textsuperscript{15} and Van Geenhoven\textsuperscript{77} observed a XRD pattern with low intensity peaks at 37.6°, 45.8° and 67.1° in the 2\(\theta\) scale. These XRD peaks are characteristic of \(\gamma\)-Al\(_2\)O\(_3\). In agreement with this, the XRD diffractograms of the present study show XRD peaks at 37.6° and 67.1° diffraction angles.

As well, XRD peaks were observed in this study, at 44.4°, 51.8° and 76.4°. These XRD peaks were assigned to Ni crystallites. On this basis, Ni crystallite sizes were assessed by applying the Scherrer’s equation (eq. 17). The thickness at half maximum of the largest Ni intensity, found at 44.4°, was used to calculate the particle size. By doing that, the average crystal size of Ni, in the 20\%Ni-5\%CeO\(_2\)
γ-Al₂O₃, was calculated as 6.2nm. Moreover, the average size for the used catalyst showed similar results with an average crystallite size of 6.7nm. This demonstrates that the 20%Ni-5%CeO₂ γ-Al₂O₃ catalyst is stable for biomass gasification with little crystallite agglomeration¹⁵, ⁷⁷, ¹²⁸.

Chen and Ren¹²⁸ also noticed the presence of NiAl₂O₄ peaks in the XRD diffractogram at 37.4-37.7°, 45.9-46° and 66.8-66.9°, while Wong et al¹²⁹ reported CeO₂ peaks at 28.8°, 33.4°, 47.8°, 56.7°, 59.4°, 69.8°, 77.0° and 79.4°. In line with this, in the present study, XRD peaks were observed at 37.6°, 44.4° and 67.1° and 77.0° in the 2θ scale, for nickel and cerium, respectively⁷⁷. There was also a peak at 66.8° assigned to NiAl₂O₄.

![XRD patterns of the (a) fresh and (b) used 20%Ni-5%CeO₂ γ-Al₂O₃ catalyst.](image)

**Figure 49:** XRD patterns of the (a) fresh and (b) used 20%Ni-5%CeO₂ γ-Al₂O₃ catalyst. Model Compound: 2-methoxy-4-methylphenol. Steam/Biomass Ratio: 0.4g/g. Bed temperature: 600 °C. Reaction Time: 20 seconds.

### 7.2 Catalytic Gasification of 2-methoxy-4-methylphenol

Gasification experiments were carried out in a CREC Riser Simulator unit, as described in Chapter 3, under the following conditions: a) thermal runs, b) catalytic runs under steam-inert atmospheres, and b) catalytic runs under steam-CO₂ in inert atmospheres. For the steam-CO₂ catalytic runs, a gas stream containing 10%CO₂ in an inert gas was used.
The impeller rotation was kept constant at 5500rpm during every run. In this present study, gasification runs involved a biomass surrogate species, which was 2-methoxy-4-methylphenol (MMP). This was as a representative of the lignin biomass fraction.

Table 10 reports the main experimental parameters studied, by varying the reaction time, bed temperature and gasifier atmosphere. Product species observed during the experiments included H$_2$, CO, CO$_2$, CH$_4$ as well as C3-C7 hydrocarbons. A detailed description of C molar balance calculation for a typical experiment is reported in the Appendix C.

<table>
<thead>
<tr>
<th>Operational Parameters</th>
<th>Experimental Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model Compound</td>
<td>2-methoxy-4-methylphenol (MMP)</td>
</tr>
<tr>
<td>Catalyst</td>
<td>20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$</td>
</tr>
<tr>
<td>Temperature</td>
<td>550°C and 600°C</td>
</tr>
<tr>
<td>Gasifying agent</td>
<td>Steam-inert and Steam-CO$_2$</td>
</tr>
<tr>
<td>Reaction Time</td>
<td>10, 15, 20 and 30 seconds</td>
</tr>
</tbody>
</table>

A comparison of catalytic gasification runs under different operational conditions were evaluated based on: (i) synthesis gas molar fraction, (ii) carbon conversion to permanent gases, (iii) H$_2$/CO ratio, and (iv) tar formation. It is important to mention that aromatics and oxygenates of a C6+ structure, identified in product composition, were considered as tars.

### 7.2.1 Synthesis Gas Composition

Figure 50 reports the overall MMP conversion into synthesis gas and tars, for the thermal experimental runs at 600°C and 30 seconds. As well, catalytic runs using
both gasifying agents, steam-inert and steam-10%CO$_2$ in inert, at 600°C and 30 seconds were reported for comparison. It is quite apparent from Figure 50 that the use of a catalyst, as the one considered in the present study, reduces the amount of tar formed considerably. For instance, the amount of tars from the thermal experiments was reduced from 42 to 20% by employing catalytic steam-inert gasification.

![Figure 50: Gas and Tar Molar Fractions in the final product for Non-Catalytic and Catalytic gasification. Biomass surrogate: 2-methoxy-4-methylphenol. Temperature: 600°C. Reaction Time: 30 seconds.](image)

One can also notice that gasification under steam-10%CO$_2$ in inert atmosphere led to 15% higher product conversion to synthesis gas, with a significant tar reduction from 20 to 5%. These gasification enhancements can be assigned to the dominant CO$_2$ hydrocarbon reforming.

Figures 51 and 52 show product molar fractions in light gases and tars, respectively. One this basis, once can compare products from thermal and catalytic runs under steam-inert gasification. A 33% increase in the hydrogen molar fraction can be observed.
As well, Figure 51 confirms an enhanced CO formation when CO\textsubscript{2} is used as gasifying agent. This is in line with the role assigned to CO\textsubscript{2}, which acts as tar-reforming agent, enhancing the reverse water-gas shift reaction, improving the MMP conversion to CO, from 8 to 19\%\textsuperscript{96}.

Figure 52 reports the major influence of CO\textsubscript{2} on the formed tar. Catalytic runs under steam-10\%CO\textsubscript{2} in inert reduce tars significantly to 3\%. This is an improvement compared to the 34\% and 16\% observed tar formation for thermal and catalytic runs under steam-inert, respectively.
Figure 52: Breakdown of Tar Molar Fractions into C6 and C7 species, Present in the Final Product for Non-Catalytic and Catalytic gasification. Biomass surrogate: 2-methoxy-4-methylphenol. Temperature: 600°C. Reaction Time: 30 seconds.

7.2.2 Hydrogen Yields

Figures 53(a) and 53(b) report the hydrogen molar fractions for the experimental runs at 550°C and 600°C, using MMP and a 20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$ catalyst. Figure 53 (a) describes gasification under steam-CO$_2$ while Figure 53 (b) describes gasification under a steam-inert atmosphere. Four reaction times of 10, 15, 20 and 30 seconds were considered. Reported chemical equilibrium values, shown as dashed lines, were calculated using the approach reported in Chapter 3.

Figures 53(a) and 53(b) show a hydrogen yields in the 35-40% range for steam-10%CO$_2$ in inert and in the 45-50% range when using a steam-inert atmosphere. It can be observed that hydrogen yields increase both with temperature and contact time. The influence of contact time is especially important for the steam-inert gasification.
Figure 53: Changes of Hydrogen Molar Fractions in Syngas Conversion with Temperature and Reaction Time. Catalyst used: 20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$. Gasifying agents: (a) steam-10%CO$_2$ in inert and (b) steam-inert. Biomass Surrogate Specie: 2-methoxy-4-methylphenol. Hydrogen molar fractions at chemical equilibrium are reported for comparison.

Furthermore, it can also be noticed that hydrogen yields for the MMP catalytic gasification, under steam-10%CO$_2$ in inert atmospheres, shows H$_2$ values very close to chemical equilibrium. This applies for all runs developed. In the case of steam-inert catalytic gasification, values are slightly above chemical predictions at 550°C.

7.2.3 Carbon Monoxide Yields

Figures 54(a) and 54(b) report carbon monoxide molar fractions for steam-10%CO$_2$ in inert and steam-inert atmospheres, at 550°C and 660°C, and four reaction times. Chemical equilibrium yields are also reported with broken lines as a reference.
One can notice that the observed CO yields fall in the 20-30% range for steam-10%CO$_2$ in inert and in the 10-20% range for steam-inert gasification. For both reaction atmospheres, CO molar fractions are not close to the equilibrium predictions. This is true with values being above equilibrium for steam-10%CO$_2$ in inert experiments and below equilibrium for steam-inert experiments.

### 7.2.4 Methane Yields

Figures 55(a) and 55(b) report methane molar fractions under steam-10%CO$_2$ in inert and steam-inert, at 550°C and 600°C, and four reaction times. The dashed lines represent the methane molar fractions at chemical equilibrium.

The methane molar fractions reported a similar pattern, being in the same range, 10-15%, for different operational conditions. Experimental results for the steam-10%CO$_2$ in inert catalytic gasification agree with equilibrium predictions. On the other hand, catalytic runs under steam-inert resulted in methane fractions being far from equilibrium for the runs at 550°C, but closer for the experiments at 600°C.
agents: (a) steam-10%CO$_2$ in inert and (b) steam-inert. Biomass Surrogate Specie: 2-methoxy-4-methylphenol. Carbon Monoxide molar fractions at chemical equilibrium are reported for comparison.

One can notice in Figures 55 (a) and (b) that methane reaches the 10% molar fraction composition at all contact times, for both temperatures selected. This is true for experimental runs under steam-10%CO$_2$ in inert and steam-inert atmosphere. This certainly represents an advantage for the process, given the expected increase of heating value of the synthesis gas produced.

7.2.5 Carbon Dioxide Yields

Figure 56(a) and (b) report CO$_2$ molar fractions for the catalytic gasification reaction of MMP under steam-10%CO$_2$ in inert and steam-inert, four reaction times and 550°C and 600°C. It is important to mention that the CO$_2$ molar fractions reported in Figures 56 (a) and (b) discounts the amount of CO$_2$ co-fed in the system for both experimental results and equilibrium predictions.

![Figure 56: Changes of Carbon Dioxide Molar Fractions in Syngas Conversion with Temperature and Reaction Time. Catalyst used: 20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$. Gasifying agents: (a) steam-10%CO$_2$ in inert and (b) steam-inert. Biomass Surrogate Specie: 2-methoxy-4-methylphenol. Carbon Dioxide molar fractions at chemical equilibrium are reported for comparison.](image)

Figure 56(a) and (b) show that under steam-10%CO$_2$ in inert, CO$_2$ molar fractions tend to decrease linearly. However, experiment results appear to be far from chemical equilibrium, with reported values being below than the predicted ones.
On the other hand, for steam-inert gasification, CO$_2$ molar fractions agree with chemical equilibrium predictions for the experiments at 600°C, while at 550°C, CO$_2$ molar fractions are slightly below the equilibrium predictions.

Figure 57 compares the CO$_2$ yield in the synthesis gas produced with the ones predicted by the chemical equilibrium and co-fed in the reaction system (10% CO$_2$ and 90% Inert). The dashed lines represent the chemical equilibrium predictions, while the continuous line the amount of CO$_2$ co-fed in the reactor in moles.

From that, one can see that the CO$_2$ yield in the products is slightly higher than the one co-fed in the system. This is an encouraging result, given it shows the very limited CO$_2$ production for this type of gasification. This CO$_2$ yield however, is below than what can be predicted by the chemical equilibrium.

![Figure 57: Comparison Between CO$_2$ yields in the Produced Synthesis Gas, Predicted by the Chemical Equilibrium Model and co-fed in the Reaction System.](image)

Thus, the obtained results with a very limited net CO$_2$ formation, can be assigned to the low CO$_2$ levels in the gasifying agent: 10% CO$_2$ and 90% Inert. It is anticipated that increased carbon dioxide molar fractions in the gasifying agent composition, may lead to an overall CO$_2$ consumption, as observed in Chapter 5 using three biomass feedstocks and CO$_2$ streams feeds.
7.2.6 H₂/CO Ratios

Figure 58 reports the H₂/CO ratios obtained using the steam-10%CO₂ in inert agent. One can observe that in all cases, the H₂/CO ratio remains in the 1.5-2 range, with these ratios being in line with chemical equilibrium predictions.

One should note that H₂/CO ratios for the various biomasses studied under steam-CO₂ at 550°C and as reported in Chapter 2, show values in the 2.0 range. This ratio is very good for the Fischer-Tropsch hydrocarbon synthesis. These results confirm the beneficial effect of CO₂ as gasifying agent, contributing to the reverse water-gas shift reaction (CO+H₂O↔CO₂+H₂) and to CO₂ dry reforming. All this enhances the carbon monoxide yields.

Figure 58: H₂/CO Ratios at 550°C and 600°C in the CREC Riser Simulator, under Steam-10%CO₂ in inert Atmospheres. Catalyst: 20%Ni-5%CeO₂/γ-Al₂O₃. Reaction Times: 10, 15, 20 and 30 seconds. Biomass Surrogate: 2-methoxy-4-methylphenol.

Figure 59 reports the H₂/CO ratio for runs under steam-inert atmospheres. The H₂/CO observed ratios in this case, are suitable for ammonia synthesis. One can notice that higher H₂/CO ratios are achieved in this scenario with these values being in all cases below H₂/CO ratios anticipated by chemical equilibrium thermodynamics.
Figure 59: H$_2$/CO Ratios at 550°C and 600°C in the CREC Riser Simulator, under Steam-Inert Atmospheres. Catalyst: 20%Ni-5%CeO$_2$/γ-Al$_2$O$_3$. Reaction Times: 10, 15, 20 and 30 seconds. Biomass Surrogate: 2-methoxy-4-methylphenol.
7.3 Conclusions

a) It was proven that the prepared 20%Ni-5%CeO₂ γ-Al₂O₃ catalyst can gasify MMP model compounds, a chemical species representing the lignin fraction in biomass. This is the case for both steam-inert and steam-10%CO₂ in inert gasification.

b) It was observed that the prepared catalyst enhances MMP gasification with higher MMP conversion and with a significant reduction of tars formed.

c) It was also proven that MMP gasification under a steam-10%CO₂ in inert atmosphere leads to higher yields of H₂, CO, CO₂ and CH₄, with the observed product yields remaining very close to chemical equilibrium predictions, with CO₂ molar fractions being the exception.

d) It was also shown that steam-10%CO₂ in inert MMP gasification gives a H₂/CO ratio in the range of 1.5-2. Therefore, it can be concluded that the 20%Ni-5%CeO₂ γ-Al₂O₃ catalyst is adequate to produce syngas suitable for Fischer-Tropsch hydrocarbon synthesis.

e) It was also anticipated that the steam-10%CO₂ in inert catalytic gasification provides a most valuable operating condition, with yields close to net zero-CO₂ gasification process emissions.
Chapter 8

8 Conclusions and Recommendations

This MESc thesis studied the suitability of thermal and catalytic biomass gasification using steam-CO$_2$ and steam-inert gasifying agents. All gasification experiments were developed in a CREC Riser Simulator. The analytical Gas Chromatography (TCD/FID-MS) unit, which operates in conjunction with the CREC Riser Simulator, allowed quantification of synthesis gas components produced. As well, biochar and coke-on-catalyst were determined with the help of a Total Organic Carbon (TOC) analyzer.

In the first section of the thesis, the gasification of Costa Rica broza, CANMET pellets, and bark were achieved by varying the bed temperature from 550°C to 600°C and the steam-CO$_2$ and steam-inert gasifying agents, until 40min reaction time had elapsed. A thermodynamic model was developed, showing agreement of product yields with those from steam-CO$_2$ gasification.

In the second section of this thesis, a 2-methoxy-4-methylphenol (MMP) gasification was achieved by using a fluidizable Ni-CeO$_2$/γ-Al$_2$O$_3$ catalyst. This catalyst was characterized using XRD, TPR, TPD and H$_2$ chemisorption. The MMP model compound was selected to represent the lignin fraction of biomass. Catalytic gasification experiments were carried out at 550°C to 600°C, using steam-10%CO$_2$ in inert and steam-inert gasifying agents. The 10, 15, 20, and 30 seconds reaction times were chosen for the catalytic runs. The thermodynamic model developed, exhibited agreement of various product yields with those from steam-inert and steam-10%CO$_2$ in inert gasification, with CO$_2$ molar fractions being an exception.

8.1 Conclusions

The main findings of this MESc study can be concluded as follows:
a) Thermal biomass gasification was observed to be strongly dependent on biomass composition, temperature and gasifying agent.

b) Thermal biomass gasification can be significantly enhanced under steam-CO$_2$ atmospheres. Under these conditions, biomass conversion is augmented, tar formed is reduced, with the biochar formed displaying a 10-20m$^2$/g specific surface area.

c) Thermal biomass gasification of the three different feedstocks studied, under steam-CO$_2$ atmospheres, showed that hydrogen, methane, carbon monoxide and carbon dioxide molar fractions were in close agreement with those of thermodynamic equilibrium. This led to a H$_2$/CO ratio in the 1.5-2 range.

d) Thermal biomass gasification under steam-CO$_2$ atmospheres showed CO$_2$ consumption. This type of biomass gasification with CO$_2$ consumption sets the stage for a process with reduced CO$_2$ emissions.

e) Catalytic MMP gasification using a 20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$ catalyst under a steam-10%CO$_2$ in inert atmosphere, showed both increased MMP conversion and augmented synthesis gas yields. MMP conversions were at 98.5% at 600°C with a very significant reduction in tars.

f) Catalytic MMP gasification with a 20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$ catalyst under a steam-10%CO$_2$ in inert atmosphere also yielded a synthesis gas with a valuable 1.5-2 H$_2$/CO ratio. This is likely the result of enhanced reverse water-gas-shift and improved dry reforming.

g) Catalytic MMP gasification with a 20%Ni-5%CeO$_2$ γ-Al$_2$O$_3$ catalyst under a steam-10%CO$_2$ in inert atmosphere provided a CO$_2$ yield approximately equal to the CO$_2$ co-fed, with a CO$_2$ net production close to zero.
8.2 Recommendation for Future Work

Based on the results obtained in this study, recommendations for future work are as follows:

a) To further investigate formed biochar physochemical properties, considering the effects of both temperatures and gasification agents. Moreover, the role of ash acting as a catalyst is an opportunity of improvement.

b) To consider the effects of CeO$_2$ loading on the Ni-based catalyst, in terms of synthesis gas yields and tar yields.

c) To further study the effect of CO$_2$ partial pressures on both thermal and catalytic gasification. This would be important to run the gasification process using optimized steam-CO$_2$ gasification mixtures. In these processes, one could forecast negative CO$_2$ emissions (consumption of CO$_2$), very high biomass conversion and negligible tars formation.
Appendices

Appendix A: Calibration curve for Gas Chromatography TCD analysis.

The synthesis gas produced after the gasification runs were analyzed using a Gas Chromatography (GC) connected to a Thermal Conductivity Detector (TCD) and a Flame Conductivity Detector (FID). High temperature was required inside both columns, in order to detect small amounts of light hydrocarbons (1ppm), as well as low amounts of hydrogen (5ppm) in the produced synthesis gas.

Calibration curves for permanent gases, Hydrogen (H\(_2\)), Carbon Monoxide (CO), Carbon Dioxide (CO\(_2\)), Methane (CH\(_4\)), were carried out using the Shimazu GC/TCD configuration. Although these are the main components in the synthesis gas, small quantities of Ethylene (C\(_2\)H\(_4\)), Ethane (C\(_2\)H\(_6\)), Propylene (C\(_3\)H\(_6\)), Propane (C\(_3\)H\(_8\)), and Water (H\(_2\)O), were also found in the products.

The use of certified standard gases was necessary to succeed in the calibration. 1ml sample of the certified standard gas was injected into the CREC Riser Simulator, connected to a Shimatzu GC/TCD, at different concentrations (dilutions with Helium), to obtain the linear graph. At the end, the synthesis gas calibration curves correlate the number of moles of each specie detected, with its TCD area. To ensure reproducibility, injections were repeated at least 8 times\(^{38}\).

The set of calibration curves for all synthesis gas components can be found as follow:

a) Hydrogen (H\(_2\)):

Figure A.1 illustrates the correlation between the area, measured by the TCD, and its corresponding number of moles. The molar concentration of H\(_2\) in the certified standard gas varied from 4.0wt\% to 16.8wt\%.
b) Carbon Monoxide (CO):

The correlation between CO TCD area and its number of moles is illustrated in Figure A.2. In this case, the CO molar concentration in the certified standard gas varied from 5.0wt% to 20.2wt%.

![CO Calibration Curve](image)

Figure A. 2: TCD Calibration Curve for Different CO Molar Concentrations.

c) Methane (CH₄):

The Methane TCD area correlated to its number of moles can be found in Figure A.3. Methane molar concentration varied from 0.1wt% to 20.2wt%.

![Methane Calibration Curve](image)

Figure A. 3: TCD Calibration Curve for Different CH₄ Molar Concentrations.
d) Carbon Dioxide (CO$_2$):

Figure A.4 illustrates the correlation between the area, measured by the TCD, and its corresponding number of moles. The molar concentration of Carbon Dioxide in the certified standard gas varied from 5.0wt% to 21.6wt%.

![CO$_2$ Calibration Curve](image)

Figure A. 4: TCD Calibration Curve for Different CO$_2$ Molar Concentrations.

e) Ethylene (C$_2$H$_4$):

The correlation between Ethylene TCD area and its number of moles is illustrated in Figure A.5. In this case, the C$_2$H$_4$ molar concentration in the certified standard gas varied from 0.1wt% to 10.0wt%.

![C$_2$H$_4$ Calibration Curve](image)
Figure A. 5: TCD Calibration Curve for Different C$_2$H$_4$ Molar Concentrations.

f) Ethane (C$_2$H$_6$):

Figure A.6 illustrates the correlation between the area, measured by the TCD, and its corresponding number of moles. The molar concentration of Ethane in the certified standard gas varied from 0.1wt% to 15.6wt%.

Figure A. 6: TCD Calibration Curve for Different C$_2$H$_6$ Molar Concentrations.

g) Propylene (C$_3$H$_6$):

The Propylene TCD area correlated to its number of in moles can be found in Figure A.7. Propylene molar concentration varied from 0.1wt% to 10.0wt%.
h) Propane (C₃H₈):

The correlation between Propane TCD area and its number of moles is illustrated in Figure A.8. In this case, the C₃H₈ molar concentration in the certified standard gas varied from 0.1wt% to 10.0wt%.

i) Water (H₂O):

Figure A.9 illustrates the Water correlation between TCD area and number of moles. Differently from the other components, for the water calibration curve the CREC Riser Simulator unit was heated up to 150°C, over its boiling point temperature, assuring that the water sample injected was evaporated. After that,
a known amount of water was injected into the reactor using a calibrated syringe. The concentration of water varied from $5.59 \times 10^{-7}$ to $1.23 \times 10^{-6}$.

Figure A. 9: TCD Calibration Curve for Different C$_3$H$_8$ Molar Concentrations.
Appendix B: Mass Balance Calculations for Steam Gasification of Different Biomasses Feedstock.

Appendix B reports the mass balance calculation for the steam biomass gasification of three different biomasses feedstock. It is important to mention that for every mass balance closure and carbon balance closure important deviations were observed from the expected 100%. While deviations from 100% were assigned to tar formations, these deviations remained in a ± 5% range.

Experimental steam gasification runs for different biomasses feedstock were developed by varying operational conditions, such as temperature and gasifying agent. On the other hand, some parameters were kept constant in all experimental runs. They were: the amount of biomass loaded in the reactor (0.04g), the amount of water added to the biomass sample (8µl), and the reaction time (40 minutes).

The Shimadzu Total Organic Carbon analyzer (TOC), with a solid sample module (SSM-5000) from Mandel, measured the total amount of coke deposited onto the surface area of the solid biomass feedstock.

The mass balance closure was defined as follow:

\[
MB = 100 \times \left( \frac{m_p + m_c}{m_i} \right)
\]

(Eq B.1)

Where we have:

- MB = Mass Balance Closure (%);
- \(m_p\) = Total Mass of Synthesis Gas Product (g);
- \(m_c\) = Total Mass of Coke in the Solid Biochar (g); and
- \(m_i\) = Total Mass of Reactants Injected in the Reaction System (g).

To measure the total mass of reaction products (\(m_p\)), first it was necessary to calculate the total number of moles in the reaction system, adapted to consider only the moles into the reactor, using the ideal gas law.
\[ n_r = \frac{P_R V_R}{R_R T_R} \]  
\hspace{1cm} \text{(Eq B.2)}

Where:

- \( n_r \) = Total Number of Moles in the Reaction System (moles);
- \( P_R \) = Reactor Pressure After Reaching Equilibrium (psia);
- \( V_R \) = Reactor Volume \((\text{m}^3)\);
- \( R_R \) = Ideal Gas Constant \((1,205.91 \text{ cm}^3\cdot\text{psia}/\text{gmol.K})\); and
- \( T_R \) = Final Reactor Temperature (K).

Then, the total number of moles in the reaction system was multiplied by the average molecular weight of synthesis gas product mixture, in an argon free basis, aiming to calculate the total mass of reaction products \((m_p)\).

\[ m_p = n_r \times MW_p \]  
\hspace{1cm} \text{(Eq B.3)}

Where:

- \( n_r \) = Total Number of Moles in the Reaction System (moles); and
- \( MW_p \) = Average Molecular Weight of Synthesis gas Product Mixture \((\text{g/gmol})\).

The average molecular weight of the synthesis gas product mixture \((MW_p)\) was calculated using the molecular weight of the individual species and the weight fractions, as follow:

\[ MW_p = \frac{1}{\sum \frac{x_i}{MW_i}} \]  
\hspace{1cm} \text{(Eq B.4)}

Where we have:

- \( MW_p \) = Average Molecular Weight of Synthesis gas Product Mixture \((\text{g/gmol})\);
- \( x_i \) = Mass Fraction of each product species in the Synthesis gas Mixture \((\text{g/g})\); and
- \( MW_i \) = Molar Mass of Synthesis gas Product Mixture \((\text{gmol/g})\).
The separation and quantification of permanent gases (H$_2$, CO, CO$_2$, H$_2$O and CH$_4$), water and light hydrocarbons were performed using a gas chromatography (GC) connected to a thermal conductivity detector (TCD), using their specific calibration curves.

Following the mass balance components, the total mass of coke deposit in the solid biochar ($m_c$) after experimental runs was calculated using the carbon content in char ($C_c$), measured in a Total Organic Carbon Analyzer (TOC), and the mass of unreacted carbon ($m_{uc}$).

$$m_c = \frac{C_c \times m_{uc}}{100\%}$$  \hspace{1cm} (Eq B.5)

To finish, the total mass of reactants injected in the reaction system ($m_i$) was calculated as the sum of the amount of biomass sample and added water inserted in the system, plus the total grams of gasifying agent fed in the reactor.

$$m_i = m_{bi} + m_w + m_{gi}$$  \hspace{1cm} (Eq B.6)

With $m_{bi}$ representing the amount of biomass samples (g), $m_w$ representing the amount of added water in the feedstock (g), and $m_{gi}$ the amount of gasifying agent fed into the reactor (g).

The carbon balance closure was defined as follow:

$$CB = 100 \times \left( \frac{N_{Cp} + N_{Cc}}{N_i} \right)$$  \hspace{1cm} (15)

where CB is the carbon balance closure (%), $N_{Cp}$ represents the moles of carbon in synthesis gas products (g), $N_{Cc}$ stands for the mass of coke found in the solid biochar (g), and $m_i$ represents the total mass of carbon in the reactants injected (g). The steps followed to calculate the variables were the same as mass balance calculation. However, in this case only number of carbons were taken in account.

It is possible to find more details about the experimental method and system, as well as operational conditions selected for this study in Chapter 3.
Appendix C : Calculations for Catalytic Steam Gasification of Different Biomasses Feedstock.

The separation and quantification of permanent gases (H₂, CO, CO₂, H₂O and CH₄), water and light hydrocarbons were performed using a gas chromatography (GC) connected to a Thermal Conductivity Detector (TCD), using their specific calibration curves. On the other hand, the components present in the tar fraction were quantified using the Shimadzu 2010 GC connected with a Flame Ionization Detector (FID). The Shimadzu Total Organic Carbon analyzer (TOC), with a Solid Sample Module (SSM-5000) from Mandel, measured the total amount of coke deposited onto the catalyst surface area.

Calculation for the catalytic steam gasification runs of a biomass surrogate specie in a CREC Riser Simulator is demonstrated in Appendix C. 2-methoxy-4-methylphenol was chosen as model compound to represent the lignin percentage in biomass feedstock. Two reaction mediums were selected for this study, steam-10%CO₂ in inert and steam-inert. Along with it, two bed temperatures, 550°C and 600°C, and four reaction times, 10, 15, 20 and 30 seconds. For the catalytic runs, calculations were oscillating in a 0-3% range.

The number of moles for all permanent gases, water and light hydrocarbons were quantified by the gas chromatography connected to a TCD. However, the FID results give the area of every carbon compound present in the tar fraction. Because methane is present in both results, GC-TCD and GC-FID, it was possible to correlate the number of moles given by TCD with the area given by FID and calculate the total number of moles present in tars.
Figure C. 1: GC-TCD Result of Permanent Gases for Catalytic Steam Gasification.

Figure C. 2: GC-FID Result of Carbonaceous Components for Catalytic Steam Gasification.

A correction factor was calculated for each component present in the FID result as follow:

\[ MW_t = \frac{1}{\sum MW_i} \]  \hspace{1cm} (Eq C.1)

\[ C_f = \frac{MW_i}{MW_T} \]  \hspace{1cm} (Eq C.2)
Where:

\[ MW_i = \text{Average Molecular Weight of Product Mixture (g/gmol)}; \]

\[ A_i = \text{Area Fraction of Each Specie in the Product Mixture (%)}; \]

\[ MW_i = \text{Molar Mass of Synthesis gas Product Mixture (g/mol/g)}; \]

\[ C_f = \text{Correction Factor}. \]

After that, it was possible to calculate the total number of moles in the reaction system, followed by the molar fraction of every component.

\[ mols_i = \frac{mols_{CH_4} \cdot MW_i}{MW_{CH}} \]  

(Eq C.4)
Appendix D : Thermal results for the 2-methoxy-4-methylphenol Experimental Runs in a CREC Riser Simulator.

Appendix D reports the thermal experimental results of 2-methoxy-4-methylphenol steam gasification in a CREC Riser Simulator that are not shown in Chapter 7. Figures D.1-D.6 illustrates the thermal gasification results for the experiments under steam-inert atmosphere, with bed temperature at 550⁰C and varying the reaction time as 10, 15, 20 and 30 seconds.

As one can notice from Figure D.1, an increase in reaction time results in a slight rise of gas fraction in synthesis gas biomass conversion. However, while compare with the catalytic runs reported in Chapter 7, this number is still very low, being assigned to the catalyst activity in the gasification results.

![Figure D. 1: Gas Fraction in Biomass Conversion for the Thermal Gasification of 2-methoxy-4-methylphenol Thermal Runs. Bed Temperature: 550⁰C. Gasifying agent: Steam-Inert. Reaction Time: 10, 15, 20 and 30 seconds.](image)

On the other hand, longer reaction times promote a small reduction in tar formation.

Figure D.3-D.6 report the molar fraction composition for the permanent gases (H₂, CO, CH₄, CO₂) in the synthesis gas fraction. Every synthesis component demonstrated a positive effect at longer reaction times, but unfortunately, this number is very small.

Figure D. 3: Changes of Hydrogen Molar Fraction in Syngas Conversion at Different Reaction Times, for the Experimental Thermal Runs in the CREC Riser Simulator.


Figure D. 5: Changes of Methane Molar Fraction in Syngas Conversion at Different Reaction Times, for the Experimental Thermal Runs in the CREC Riser Simulator.

Appendix E: Pressure Profile for Different Operational Conditions.

Appendix E reports the Pressure profile for the catalytic steam gasification runs of 2-methoxy-4-methylphenol in a CREC Riser Simulator. Two bed temperatures were selected for this study, 550⁰C and 600⁰C. Moreover, two gasifying agents were used as reaction medium, steam-10%CO₂ in inert and steam-inert. In order to evaluate the reaction time impact in the final result, four reaction times were selected, 10, 15, 20 and 30 seconds.

Figure E.1 shows the pressure profiles for the runs under steam-10%CO₂ in inert at 550⁰C, for the 4 reaction times selected to this study. The maximum pressure found under these conditions was 38.1psi, with 30 seconds reaction time.

Likewise previous graph, Figure E.2 report the pressure profiles for the catalytic experimental runs under steam-10%CO₂ in inert conditions. However, for those experiments, the bed temperature selected was 600⁰C. Reaction time remained same as before. In this case, the maximum pressure achieved was under 30 seconds reaction, as well, at 40.2psi.
Figure E. 2: Pressure Profile for the Catalytic Steam gasification of 2-methoxy-4-methylphenol. Gasifying agent: steam-10%CO₂ in inert. Bed temperature: 600°C.

Reaction time: 10, 15, 20 and 30 seconds.

Figures E.3 and E.4 illustrated the pressure profiles for the catalytic experimental runs under a steam-inert atmosphere. As, one can observe in Figure E.3, four reaction times were used: 10, 15, 20 and 30 seconds. The bed temperature selected in the graph bellow is 550°C. Under these conditions, the maximum pressure value achieved was 38.6psi, with 30 seconds of reaction time.
Figure E. 3: Pressure Profile for the Catalytic Steam gasification of 2-methoxy-4-methylphenol. Gasifying agent: Steam-Inert. Bed temperature: 550°C. Reaction time: 10, 15, 20 and 30 seconds.

Figure E.4 however shows the pressure profiles for the catalytic experimental runs, under a steam-inert atmosphere, at 600°C. Between all reaction times selected, the maximum temperature was achieved with 30 seconds, 40.1psi.

Figure E. 4: Pressure Profile for the Catalytic Steam gasification of 2-methoxy-4-methylphenol. Gasifying agent: Steam-Inert. Bed temperature: 600°C. Reaction time: 10, 15, 20 and 30 seconds.
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