Mild Wet Torrefaction and Characterization of Woody Biomass from Mozambique for Thermal Applications

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Doctoral Dissertation

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Abstract

Mozambique has vast forestry resources and also considerable biomass waste material such as bagasse, rice husks, sawdust, coconut husks and shells, cashew nut shell and lump charcoal waste. The potential of the total residues from the agricultural sector and the forest industry is estimated to be approximately 13 PJ. This amount of energy covers totally the production of charcoal which amounted to approximately 12.7 PJ in 2006. Although biomass is an attractive renewable source of energy, it is generally difficult to handle, transport, storage and use due to its lower homogeneity, its lower energy density and the presence of non-combustible inorganic constituents, which leads to different problems in energy conversion units such as deposition, sintering, agglomeration, fouling and corrosion. Therefore, a pretreatment of the biomass to solve these problems could lead to a change of current biomass utilization situation. The aim of this study is to convert Mozambican woody biomass residue into a solid biochar that resembles low-grade coal.

In this work the current energy situation in Mozambique has been reviewed, and the available and potential renewable sources including residues from agricultural crops and forest industry as energy have been assessed. It was found that the country is endowed with great potential for biofuel, solar, hydro and wind energy production. However, the production today is still far from fulfilling the energy needs of the country, and the majority of people are still not benefiting from these resources. Charcoal and firewood are still the main sources of energy and will continue to play a very important role in the near future. Additionally, enormous amounts of energy resources are wasted, especially in the agricultural sector. These residues are not visible on national energy statistics. The chemical composition and the fuelwood value index (FVI) showed that by failing to efficiently utilise residues from *Afzelia quanzensis*, *Millettia stuhlmannii* and *Pterocarpus angolensis*, an opportunity to reduce some of the energy related problems is missed. An evaluation of effect of a mild wet torrefaction pretreatment showed that the chemical composition of the biochar is substantially different than the feedstock. The use of diluted acid as catalysts improves the biochar quality, namely in terms of the energy density and ash characteristics; however, the increment of the S content in the final product should be considered for market acceptance (because the fuels have a maximum allowance for S concentration). The thermal behaviour of the untreated and treated biomass was also investigated. The pyrolytic products of umbila and spruce were affected by the treatment and catalyst in terms of yield and composition of the vapours.

**Keywords:** Biomass; Wet torrefaction; Fast Pyrolysis; kinetics; Catalyst
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And finally
All my friends and family for always supporting me…

Carlos Cuvilas
2014-12-20
Stockholm, Sweden
List of Papers in the Thesis


**Contribution Statement:**

In papers I, I performed all the literature review and writing;

In paper II, I performed part of the experiments data analysis and writing;

In the remaining papers, I performed the HTC, Pyro-GC-MS (non-catalytic) test, data analysis and writing.
List of Papers not in the Thesis


## Contents

**CHAPTER I**  
1. **INTRODUCTION** .................................................................................................................. 1  
1.1. Introduction .......................................................................................................................... 1  
1.2. Aim and objectives of the work .......................................................................................... 4  
1.3. Structure of the dissertation ............................................................................................... 4  

**CHAPTER 2**  
2. Biomass, Properties of hot compressed water and Wet torrefaction process and Reaction mechanism ........................................................................................................... 7  
2.1. Biomass composition .......................................................................................................... 7  
2.2. Biomass pretreatment .......................................................................................................... 9  
2.2.1. Steam explosion (SE) ..................................................................................................... 10  
2.2.2. Dry torrefaction or torrefaction ...................................................................................... 10  
2.2.3. Wet torrefaction or hydrothermal carbonization (HTC) .............................................. 11  
2.3. Properties of Hot Compressed Water ................................................................................. 12  
2.4. Wet torrefaction of biomass - reaction mechanism ............................................................. 14  

**CHAPTER 3**  
3. Experimental Procedure, Materials and Methods .................................................................. 15  
3.1. Energy situation and biomass characterization .................................................................. 15  
3.1.1. Ash characteristics ........................................................................................................ 17  
3.2. Wet Torrefaction ................................................................................................................. 18  
3.3. Crystallinity ........................................................................................................................ 19  
3.4. Mass and energy balance ................................................................................................... 19  
3.4.1. Mass balance .................................................................................................................. 19  
3.4.2. Energy balance .............................................................................................................. 20  
3.5. TGA and kinetic models ...................................................................................................... 21  
3.6. Py-GC-MS .......................................................................................................................... 22  
3.6.1. Teste of umbila ............................................................................................................... 22  
3.6.2. Teste of Spruce ............................................................................................................. 22  

**CHAPTER 4**  
4. Energy situation in Mozambique – A review ......................................................................... 25  
4.1. Introduction ....................................................................................................................... 25  
4.2. Results and Discussion ..................................................................................................... 25
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2.1. Wood fuel and residues from forest industries</td>
<td>26</td>
</tr>
<tr>
<td>4.2.2. Residues from agricultural sector</td>
<td>27</td>
</tr>
<tr>
<td>4.2.3. The Characterization of Wood Species from Mozambique as a Fuel</td>
<td>29</td>
</tr>
<tr>
<td>4.3. Conclusions</td>
<td>30</td>
</tr>
<tr>
<td>CHAPTER 5</td>
<td>33</td>
</tr>
<tr>
<td>5. The impact of mild sub-critical hydrothermal carbonization pretreatment on Umbila wood - A mass and energy balance perspective</td>
<td>33</td>
</tr>
<tr>
<td>5.1. Introduction</td>
<td>33</td>
</tr>
<tr>
<td>5.2. Results and Discussion</td>
<td>33</td>
</tr>
<tr>
<td>5.2.1. Mass balance</td>
<td>33</td>
</tr>
<tr>
<td>5.2.2. Energy Balance</td>
<td>34</td>
</tr>
<tr>
<td>5.2.3. Effect of pretreatment on elemental composition and ash characteristics</td>
<td>35</td>
</tr>
<tr>
<td>5.2.4. Change of biomass structure by pretreatment</td>
<td>36</td>
</tr>
<tr>
<td>5.2.5. Ash fusibility characteristics</td>
<td>38</td>
</tr>
<tr>
<td>5.2.6. Kinetic of thermal Decomposition of HTC-char</td>
<td>41</td>
</tr>
<tr>
<td>5.3. Conclusions</td>
<td>47</td>
</tr>
<tr>
<td>CHAPTER 6</td>
<td>49</td>
</tr>
<tr>
<td>6. Fast Pyrolysis of pretreated biomass</td>
<td>49</td>
</tr>
<tr>
<td>6.1. Introduction</td>
<td>49</td>
</tr>
<tr>
<td>6.2. Results and Discussion</td>
<td>49</td>
</tr>
<tr>
<td>6.2.1. Fast pyrolysis of umbila (hardwood) and Spruce (softwood)</td>
<td>49</td>
</tr>
<tr>
<td>6.2.2. Effect of zeolite on product yield and composition during pyrolysis of hydrothermally pretreated Spruce</td>
<td>52</td>
</tr>
<tr>
<td>6.3. Conclusions</td>
<td>56</td>
</tr>
<tr>
<td>CHAPTER 7</td>
<td>57</td>
</tr>
<tr>
<td>7.1. General Conclusions</td>
<td>57</td>
</tr>
<tr>
<td>7.2. Recommendations for Future Work</td>
<td>59</td>
</tr>
<tr>
<td>Process</td>
<td>59</td>
</tr>
<tr>
<td>Application</td>
<td>59</td>
</tr>
<tr>
<td>Bibliography</td>
<td>60</td>
</tr>
</tbody>
</table>
CHAPTER I

1. INTRODUCTION

1.1. Introduction

Mozambique is an African country with vast forestry resources, including 120 tropical wood species [1], some of them with high commercial value that is internationally recognized thus, the export of timber is a commercial option of considerable value for the country. According to Marzoli [2], only three wood species (Afzelia quanzensis Welwn, Millettia stuhlmannii Taub and Pterocarpus angolensis DC), locally known, respectively, as chanfuta, jambire and umbila, represented 78% of the total wood exploited in Mozambique in 2004, producing considerable biomass residues from logging activities and wood processing. In addition, other sources of biomass materials are available in the country, such as bagasse, rice and coconut husks, cashew nut and coconut shells, charcoal and other forms of residues from agricultural activities and processing. The potential biomass residues from forest logging and timber processing were estimated to be approximately 2.7 PJ [3]; however, utilization of such residues as a fuel is marginal. In this context, an integral and efficient use of timber including residues could reduce the depletion rate of these species and increase alternative sources of energy and therefore contribute to a certain extent to the protection of the forest, especially in country where more than 80% of the population is largely dependent on biomass fuel.

Although biomass is an attractive renewable source of energy, it is generally difficult to handle, transport, store and use [4, 5, 6], due to its low homogeneity and energy density and presence of non-combustible inorganic constituents, which leads to different problems in energy conversion units such as deposition, sintering, agglomeration, fouling and corrosion [7]. Therefore, in most cases, it is important to pretreat the biomass by physical and/or chemical means, producing a secure and affordable fuel alternative that satisfies the requirements for biochemical or thermochemical conversion processes, such as fermentation, combustion, gasification, pyrolysis and others. Thus, according to several authors [7, 8], various pretreatment methods have been investigated, such as 1. physical pretreatment (mechanical comminution and pyrolysis), 2. physicochemical pretreatment (steam explosion, ammonia fiber explosion and carbon explosion), 3. chemical pretreatment (acid hydrolysis, alkaline hydrolysis, oxidative delignification and organosolv process), 4. biological pretreatment and 5. pulse electric-field pretreatment. Pretreatment is perhaps the most crucial step as it has a large impact on the later steps of the biomass utilization processes. Despite extensive scientific and commercial efforts, the theory and applicability of the majority of pretreatments methods remains, due to several reasons,
insufficiently developed. Many of these methods were primarily devoted to panels production in pulp and paper industry and lately to production of ethanol for fuel, where the main goal is to remove lignin, hemicellulose and producing sugar, reduce the crystallinity of the cellulose and at the same time avoid the degradation or loss of carbohydrates and the formation of inhibitor of the fermentation process [9].

In the present study, a hydrothermal carbonization (HTC), also known as wet torrefaction or wet pyrolysis process, was conducted to pretreat umbila and spruce. It is a spontaneous, exothermal and relatively low temperature (175–350ºC) process which, under pressures and subcritical water, converts lignocellulosic biomass to obtain a carbon-rich solid fraction, so called biochar, biocoal, hydrochar or HTC-char [10-13]. This process has shown to first decompose hemicellulosic material, which is the most sensitive of three main components of the lignocellulosic biomass [14, 15], while retaining most of the cellulose and lignin fractions, producing, apart from char, non-condensable gases such as H2, CO, CO2, CH4 and a large variety of water-soluble organic compounds. However, due to the formation of a multitude of furan-type dehydrated intermediates from carbohydrates and the complexity of the chemistry, the formation process and the final material structures are rather complicated and a clear scheme has not been reported [16]. Although the chemistry of the process for converting biomass into biochar is not yet completely understood [17], it is known that the HTC coal formation results from hydrolysis, dehydration, decarboxylation, polymerization and aromatization reactions, which in essence are, respectively, the cleavage of ester and ether bonds, the removal of biomass water, the elimination of carboxyl groups and condensation [11, 17]. The main advantage of the hydrothermal carbonization process is that it can convert wet input materials, which include animal manures, human waste, sewage sludge, municipal solid waste, aquaculture and algal residues into carbonaceous solids at relatively high yields without the need for an energy-intensive drying before or during the process [18].

The resulting biocoal can be employed for several processes such as soil amendment or water purification. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [19]. The biocoal can also be directly combusted and/or co-combusted with mineral coal or other feedstock to produce heat that can be used for electricity production or other processes.

As a response to the depletion of fossil fuel, the increased demand in transportation fuels and chemicals and environmental concerns, HTC-biomass has also been used in new alternatives to biofuel conversion technologies, such as gasification, liquefaction and fast pyrolysis. The first two technologies (gasification and liquefaction) will not be discussed in detail in this work.

Gasification is a thermo-chemical conversion process of gaseous fuel production by the partial oxidation of a solid fuel [20]. It simultaneously produces gases, such as H2, CO, CO2 and CH4, a complex of organic vapours that under ambient condense are known as
tar and a solid residue consisting of char and ash. It is an endothermic and high-temperature process [21], while hydrothermal liquefaction is a technique that uses water as an important reactant and catalyst to convert biomass into liquid fuel without an energy-consuming drying step [22]. It is generally carried out at 280-370°C and between 10 and 25 MPa [23]. The composition and yield of liquid fuel depends upon on feedstock and operating parameters [24]. The main disadvantage of this technique is the expensive alloys required due to corrosion [25].

Fast pyrolysis is one of the most promising technologies to convert biomass into liquid fuel. It occurs in the temperature range of 300–750°C, at high heating rate (10-200°C/s to above 1000°C/s), and with a very short residence time (~1–2 s). During this process, biomass decomposes to generate vapours, aerosols and some char. After condensation of the vapours, 70–80% of a brown mobile liquid is obtained (bio-oil) [26], which has been regarded as promising candidate to replace petroleum fuels. However, due to its high oxygen content (40-50%), water content (20-50%), acidity, corrosiveness to common metals, thermochemical instability and immiscibility with petroleum fuels, it is considered a low-grade liquid fuel [27-29]. This has made direct bio oil utilization almost impossible in most cases. Thus, to overcome such difficulties, a catalytic conversion is needed, with the main objective to remove oxygen in the form of H₂O, CO₂ and CO through deoxygenation. Different types of catalysts have been used, including metal oxides, zeolites, transition metal-based catalysts, etc. Zeolite catalysts have been shown to be more effective in the selective deoxygenation of pyrolytic vapours, resulting in the formation of decreased O/C bio-oil [30].

Several zeolite structures have been widely tested in catalytic biomass pyrolysis, such as HZSM-5, Al-MCM-41, Beta and SBA-15. Generally, zeolites with stronger acidity promote the decomposition of the lignin fraction, but according to Adjaye et al. [31] and Vitolo et al. [32] the main problems are fast deactivation of the catalysts by coke deposition, low organic liquid yield and the formation of polycyclic aromatic hydrocarbons. The inherent nature of a one-step catalytic pyrolysis of biomass for the synthesis of hydrocarbons is very attractive and offers much potential for fuels and chemicals. The significant processing and economic advantages of catalytic pyrolysis/upgrading compared for instance with hydrotreating is that: no H₂ is required; treatment takes place at atmospheric pressure, which reduces operating and capital cost; temperatures employed are similar to those used in the production of bio-oil [33]; and aromatic compounds obtained have a potentially higher market value as fuel additives and chemical feedstock [34]. The catalytic properties of zeolite ZSM-5 are attributed to both its strong acid sites and the three-dimensional system of intersecting channels, which is made up of elliptical straight channels (0.51 x 0.55 nm) and near circular zigzag channels [31].
1.2. Aim and objectives of the work

The aim of this study is to convert Mozambican woody biomass residue into a solid biochar that resembles low-grade coal.

To achieve this aim, the following objectives were considered:

- Review the current energy situation in Mozambique and assess the available and potential renewable sources, including residues from agricultural crops and forest industry as energy.

- Determine the main physical and chemical characteristics of common and less-used hardwood species growing in Mozambique and evaluate their quality as a fuel.

- Investigate the impact of the mild wet torrefaction process using water and diluted H₂SO₄ as catalyst, on physical and chemical biomass characteristics.

- Investigate the effect of the mild wet torrefaction process on fast pyrolysis.

1.3. Structure of the dissertation

This dissertation is organised into seven chapters; each chapter provides and discusses the main results of several aspects of hydrothermal carbonization biomass and further conversion processes and includes the respective conclusions.

First it provides, in chapters 1 and 2, brief information about Mozambique (wood and residue) and review of basic concepts of the hydrothermal and other conversion processes of biomass, including the structure of the work. Chapter 3 describes the experimental procedure, material used and analytical methods. Chapter 4 summarizes the energy situation in Mozambique and assesses the potential for energy production from renewable sources, including residues from the agricultural crops and forest industries and an evaluation of physical, chemical and quality as fuel characteristics of locally common hardwood species. Chapters 5 and 6 present results and discussion on the mild wet torrefaction process and its impact on thermal conversion of biomass. Chapter 7 presents the general conclusions and recommendations for future work.
The research work is schematically shown below (Figure 1).

Figure 1: Structure of the work
An overview of the supplements and the corresponding objectives are listed in Table 1.

<table>
<thead>
<tr>
<th>Supplements</th>
<th>Event</th>
<th>Objective</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Energy Situation in Mozambique – A Review</td>
<td>• Analyse the energy situation; • Assess the potential for energy production.</td>
</tr>
<tr>
<td>II</td>
<td>The Characterization of Wood Species from Mozambique as Fuels</td>
<td>• Determine the physical and chemical characteristics of common hardwood species; • Evaluate their quality as a fuel.</td>
</tr>
<tr>
<td>III</td>
<td>The Impact of a Mild Sub-Critical Hydrothermal Carbonization Pretreatment on Umbila Wood – A Mass and Energy Balance Perspective</td>
<td>• Investigate the impact of a mild subcritical HTC pretreatment on umbila (hardwood) • Determine the mass and energy balance of the process.</td>
</tr>
<tr>
<td>IV</td>
<td>Spruce Pretreatment for Thermal Application: Water, Alkaline and Diluted Acid Hydrolysis</td>
<td>• Investigate the impact of a mild subcritical HTC pretreatment on spruce (softwood)</td>
</tr>
<tr>
<td>V</td>
<td>Effect of Mild Hydrothermal Pretreatment on Biomass Pyrolysis Characteristics and Vapour Composition</td>
<td>• Investigate the impact of HTC process on fast pyrolysis products; • Investigate the impact of treatment on relative reaction rates.</td>
</tr>
<tr>
<td>VI</td>
<td>Effect of Zeolite on Product Yield and Composition during Pyrolysis of Hydrothermally Pretreated Spruce</td>
<td>• Investigate the effect of acidic wet torrefaction and catalyst (HZSM-5) in composition and yield of pyrolytic vapours.</td>
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</tbody>
</table>
CHAPTER 2

2. Biomass, Properties of hot compressed water and Wet torrefaction process and Reaction mechanism

2.1. Biomass composition

Lignocellulosic biomass consists of mainly three types of polymers with extensive chains connected with each other, namely cellulose, hemicellulose and lignin [35, 15], (Figure 2).

Cellulose is formed in long linear chains from glucose molecules that are linked in the form of D-anhydroglucopyranose units (Figure 3) with (1 ~ 4)-/3-D-glycosidic ether bridges [36]
Hemicelluloses are high polymers built from sugar units with side chains. The backbone chain frequently consists of pentoses (e.g., xylans), alternating units of mannose and glucose (mannans or glucomannans) or galactose units (galactans) (Figure 4).

![Hemicellulose Compounds](image)

**Figure 4** Main compounds of hemicellulose

Lignin is an amorphous cross-linked resin and accounts for 23%-33% of the mass of softwoods and 16%-25% of the mass of hardwoods [37]. It is the main binder for the agglomeration of fibrous cellulose components while also providing a shield against the rapid microbial or fungal destruction of the cellulosic fibres. Lignin is a three-dimensional, highly branched, polyphenolic substance that consists of an irregular array of variously bonded “hydroxy-” and “methoxy-” substituted phenylpropane units [38]. These three general monomeric phenylpropane units exhibit the $p$-coumaryl, coniferyl and sinapyl structures (Figure 5).

![Lignin Monomers](image)

**Figure 5** Lignin monomers
In softwoods predominantly guaiacyl lignin, which results from the polymerization of coniferyl phenylpropane units, is present, whereas in many hardwoods, guaiacyl-syringyl lignin, a copolymer of both the coniferyl and sinapyl phenylpropane units is found [26, 39].

2.2. Biomass pretreatment

Biomass pretreatment is an important step that produces an affordable alternative fuel satisfying the requirements for a biochemical or thermochemical conversion processes, such as fermentation, combustion, gasification or pyrolysis. Depending on the objective of the treatment, generally, the main goal is to remove alkali metals and other undesirable minerals, reduce the moisture content, increase the energy density, homogeneity, grindability and hydrophobicity, promote the accessibility of enzymes to the cellulose, produce sugars, etc. Thus, several pretreatment technologies were developed, such as:

- Physical pretreatment:
  - Mechanical comminution and pyrolysis;
  - Thermochemical pre-treatment
- Torrefaction:
  - Dry Torrefaction or simply torrefaction
  - Wet Torrefaction or Hydrothermal carbonization
- Lime pretreatment
- Steam explosion (SE)
- Biological pretreatment
- Pulse-electric-field pretreatment
2.2.1. Steam explosion (SE)

Steam explosion (SE) is a process in which biomass is subjected to 180 - 240°C hot steam under pressure (1 to 3.5 MPa) followed by a quick decompression, resulting in the rupture of the biomass wood cell walls. A dark brown and hydrophobic feedstock is produced as a result of the disruption of the carbohydrate structure by releasing hemicelluloses into the solution, changing both cellulose and lignin [40]. SE was first used for bio-ethanol production and the main objective was to preserve the sugars as much as possible and promote better accessibility of the enzymes to the substrate. Currently, SE is also used as pretreatment for the production of dark brown pellets. During this process, lignin, which is used as binder, is released from the cell wall to the surface of the substrate, resulting in stiff, hydrophobic pellets. The severity of the treatment, temperature, biomass particle size and moisture content are the governing parameters of the process. Thus, according to Ramos [41], when the pretreatment severity is low, the partial conversion of acid-labile polysaccharides into sugars governs the process. With a further increase in the severity (milder condition), the dehydration reaction becomes dominant, causing a loss of soluble sugars from plant polysaccharides. A severe pretreatment condition tends to initiate a condensation reaction involving lignin, hemicellulose and cellulose-derived product. Additionally, lignin produced after severe pretreated condition is extensively modified.

2.2.2. Dry torrefaction or torrefaction

Torrefaction is a thermochemical method that uses heat at 200 - 300°C to essentially roast the biomass under atmospheric conditions in the absence of oxygen. It consists typically of pre-drying, roasting, product cooling and an optional step, which is the combustion of the torrefaction gas to generate heat for further drying and torrefaction. During the process, the decomposition reactions affect mostly the hemicellulose and lignin, with a slight effect on the cellulose [42]. From a chemical point of view, the principle of the torrefaction process is the removal of oxygen from the feedstock to produce torrefied biomass with a lower O/C ratio and, consequently, a higher energy density, good grindability, higher flowability and uniformity in product quality [43, 44, 45, 42]. In terms of yield, torrefied biomass contains 70% of its initial weight and 90% of its original energy content [46]. The major disadvantage is the increment of alkali metals and other minerals, and consequently the ash content of the torrefied biomass.
2.2.3. Wet torrefaction or hydrothermal carbonization (HTC)

Hydrothermal carbonization (Figure 6) also known as the wet torrefaction or wet pyrolysis process, is a spontaneous, exothermal and relatively low-temperature (175 – 350°C) process which, under pressures and subcritical water, converts lignocellulosic biomass to obtain a carbon-rich solid fraction, so called biochar, biocoal, hydrochar or HTC-biomass [11-12]. It has been shown that hemicellulose, which is the most susceptible to thermal decomposition of three main components of the lignocellulosic biomass [36, 15], is decomposed first, and most of the cellulose is retained; the lignin fraction produces, apart from char, non-condensable gases such as H₂, CO, CO₂, CH₄ and a large variety of water-soluble organic compounds. However, due to the formation of a multitude of furan-type dehydrated intermediates from carbohydrates and the complexity of the chemistry, the formation process and the final material structures are rather complicated and a clear scheme has not been reported [16].

The degree of carbonization \( f_{HTC} \) can be estimated by the equation below suggested by Ruyter [47].

\[
f_{HTC} = 50t^{0.2}e^{-\frac{3500}{T}} 
\]  
(Eq 1)

Where

\( T \) - temperature in [K]; and

\( t \) - residence time in [s].
From this equation it can be observed that the coalification process can be affected by manipulating the residence time and the temperature. According to Erlach [48], by increasing the temperature approximately 10°C, it is possible to reach the same degree of carbonization in half of the time. However, he recognizes the weakness of this equation because important parameters such as feedstock, solvent and the effect of temperature on the reactions are not taken in consideration in the equation.

2.3. Properties of Hot Compressed Water

Pressurized hot water extraction, also called subcritical water extraction, can be defined as an extraction process in which the temperature is above 100°C but below the critical temperature of water (374°C). Water is kept in liquid form by keeping the system under sufficiently high pressure [49]. In such conditions water behaves very differently not only from water at room temperature but in some aspects also from supercritical water (Figure 7).
Subcritical water can catalyse both acidic and basic reactions by enhanced self-dissociation of H₂O to H⁺ and OH⁻ [50]. The ionic product (Kw) of water at room temperature is approximately 10⁻¹⁴, which increases to 10⁻¹¹ at 200–300°C [51]. In addition, the dielectric constant of water used to describe the polarity of a liquid [50], changes from approximately 80 at room temperature to 6 at 400°C (Table 2), promoting some organic reactions that usually occur in non-polar solvents.

In the opposite side, some salts reduce their solubility, with exception of sodium chlorine, which reduces its solubility with an increment of temperature and forms fine crystalline slime [52]. These unique properties of water at high temperatures and pressures play a significant role in subcritical hydrothermal carbonization process.

![Figure 7 The triple point phase diagram of water [17]](image-url)

**Table 2** Properties of water at various conditions [25]

<table>
<thead>
<tr>
<th>Property</th>
<th>Normal water</th>
<th>Subcritical water</th>
<th>Super critical water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. (°C)</td>
<td>25</td>
<td>250</td>
<td>350</td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td>0.1</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>Density, ρ (g cm⁻³)</td>
<td>1</td>
<td>0.80</td>
<td>0.6</td>
</tr>
<tr>
<td>Dielectric constant, ε (Fm⁻¹)</td>
<td>78.5</td>
<td>27.1</td>
<td>14.07</td>
</tr>
<tr>
<td>Ionic product, pKw</td>
<td>14.0</td>
<td>11.2</td>
<td>12</td>
</tr>
<tr>
<td>Heat capacity, Cₚ (kJ kg⁻¹K⁻¹)</td>
<td>4.22</td>
<td>4.86</td>
<td>10.1</td>
</tr>
<tr>
<td>Viscosity, η (mPa s)</td>
<td>0.89</td>
<td>0.11</td>
<td>0.06</td>
</tr>
</tbody>
</table>

In the opposite side, some salts reduce their solubility, with exception of sodium chlorine, which reduces its solubility with an increment of temperature and forms fine crystalline slime [52]. These unique properties of water at high temperatures and pressures play a significant role in subcritical hydrothermal carbonization process.
2.4. Wet torrefaction of biomass - reaction mechanism

The detailed reaction mechanism of HTC, including hydrolysis, dehydration, decarboxylation, condensation-polymerization and aromatization, is extremely complex and still far from being well understood [14, 12]. First the biomass goes through hydrolysis, cleavage of esters and ether bonds of hemicellulose and cellulose, producing monomers that are soluble in water [53, 54]. Then, the biomass is subjected simultaneously to dehydration and decarboxylation reactions. Due to the removal of extractives and hemicellulose, the biomass becomes hydrophobic, and then, the remaining water is injected (physical process) while hydroxyl groups are removed (chemical reaction). Carboxyl and carbonyl groups rapidly degrade above 150°C, yielding CO₂ and CO, respectively [55], and reducing the H/C and O/C ratios of the HTC-biomass. Intermediate products such as hydroxymethylfurfural (HMF) and furfural polymerize form char according to the path suggested by Titirici et al. [56]:

\[
\text{Cellulose} \rightarrow \text{Hexoses (glucose, sacrose)} \xrightarrow{\text{H}_2\text{O} \atop T=180^\circ\text{C}} \text{HMF} \rightarrow \text{Char}
\]

\[
\text{Hemicellulose} \rightarrow \text{Pentoses (xyloses)} \xrightarrow{\text{H}_2\text{O} \atop T=180^\circ\text{C}} \text{Furfural} \rightarrow \text{Char}
\]
CHAPTER 3

3. Experimental Procedure, Materials and Methods

For the present work, the following experimental procedure, materials and methods were applied.

3.1. Energy situation and biomass characterization

The energy situation assessment was based on reviewing and evaluating the available literature on the energy situation in Mozambique. The potential quantities of residues were calculated via estimated ratio of by-product by multiplying the crop production of a particular period by the residue ratio.

For characterization of some woody biomass from Mozambique, samples were collected from three provinces - Cabo Delgado and Nampula in the northern part and Sofala in the central parts of the country. Samples of *Afzelia quanzensis* (chanfuta), *Millettia stuhlmannii* (Jambire), *Pterocarpus angolensis* (umbila), *Sterculia appendiculata* (muanga), *Pericopsis angolensis* (metil), *Acacia nigrescens* (namuno), *Pseudolachnostylis maprouneifolia* (ntholo) and *Icuria dunensis* (icuria), taken at breast height (1.3 m), were dried and milled before analysing for lignin, cellulose and hemicellulose, high heating value, density, volatiles and ash content; the mineral constituents in ash were also determined. Standard methods were used by the accredited commercial laboratories that performed the analyses (Table 3). The ranking of the studied species as fuel was performed using the fuelwood value index (FVI), which characterizes the overall quality of the fuel by accounting for several important parameters such as higher heating value, density, ash content and moisture content. Some or all of these parameters have been used for FVI calculation [57, 58, 59]. In this study, the FVI was calculated using the following formula:

$$FVI = \frac{HHV (kJ/g) \times \text{Density (g/cm}^3\text{)}}{\text{Ash (g/g)}}$$

(Eq 2)

Moisture content (MC), which can vary amongst different species, negatively influences the energy obtained from the fuel wood. However, due to logistical difficulties during sample collection in Mozambique, the exact initial MC was difficult to determine and was therefore excluded from the formula.
Table 3 Methods and standards used for the determination of wood properties and ash analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>High heating value</td>
<td>Combustion in a bomb calorimeter (Parr 6300).</td>
<td>SS 187182</td>
</tr>
<tr>
<td>Ash content</td>
<td>Incinerated at 550°C ± 25°C.</td>
<td>SS 187171:1</td>
</tr>
<tr>
<td>Pb</td>
<td>Inductively coupled plasma mass spectroscopy (ICP-MS).</td>
<td>ALC208:902</td>
</tr>
<tr>
<td>Cd, As, Co, Cu, Cr</td>
<td>ICP-MS after pressure digestion.</td>
<td>NMKL161</td>
</tr>
<tr>
<td>Ni, V, Zn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>AAS after microwave digestion</td>
<td>NMKL170</td>
</tr>
<tr>
<td>Mn</td>
<td>ICP-AES.</td>
<td>NMKL161</td>
</tr>
<tr>
<td>Si</td>
<td>AAS</td>
<td>ALC208:201</td>
</tr>
<tr>
<td>C, H, N</td>
<td>Combustion at 1050°C (LECO CHN 1000)</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>Calculated as difference between 100 and the sum of C and H.</td>
<td></td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>Acid hydrolysis</td>
<td>T 249 cm-00</td>
</tr>
<tr>
<td>Lignin</td>
<td>Klason lignin*</td>
<td>T 222 om-0</td>
</tr>
<tr>
<td>S</td>
<td>Furnace combustion in oxygen at 1350°C with infrared detection procedure.</td>
<td>SS187177:1</td>
</tr>
<tr>
<td>Cl</td>
<td>Using Eschka mixture, titration by Mohr procedure.</td>
<td>SS187154:1</td>
</tr>
<tr>
<td>Volatiles</td>
<td>Heating at 900 °C without contact with air during 7 minutes.</td>
<td>SS-ISO 562:1</td>
</tr>
<tr>
<td>Extractives</td>
<td>Acetone soluble</td>
<td>Scan-CM 9:03</td>
</tr>
<tr>
<td>Density</td>
<td>Mass/displacement (12% moisture content)</td>
<td>ISO 3131</td>
</tr>
</tbody>
</table>

* The gravimetric values were not corrected for acid-soluble lignin
3.1.1. Ash characteristics

In biomass combustion, deposit formation on heat transfer surfaces is one of the biggest problems for all solid fuel-fired boilers, affecting not only the operational cost but also the emissions [60]. The problems related to ash and ash deposition can be defined as follows [61, 62]:

- Slagging - refers to deposition taking place in the boiler sections where radiative heat transfer is dominant;
- Fouling - takes place in the cooler convective heat transfer sections of the boiler and results from the behaviour of components as the gases cool down;
- Corrosion - takes place when metal from the tube wall reacts with a component from an ash deposit or flue gas;
- Erosion - is due to the impact of hard particles on tube surfaces, tends to occur in the high velocity sections of the convective part of the boiler and is exacerbated by partial blockage due to fouling deposits.

_Fouling and Slagging tendency_

Ash behaviour has been described by its composition, deformation temperature (DT), shrinkage temperature (ST), hemisphere temperature (HT) and flow temperature (FT). These characteristics are combined through several ratios and indexes developed to predict the risk of ash slagging and/or fouling during the combustion of coal and/or biomass. Such risk is substantially influenced by the concentration of potassium, sodium, chlorine and sulphur [63, 64]. In this study, fouling and slagging are determined as follows:

- Fouling index (Fu)

\[
F_u = \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + TiO_2 + Al_2O_3} \times (Na_2O + K_2O) \tag{Eq 3}
\]

According to Pronobis [65], fouling Potential ≤0.6 is low, 0.6<Fu≤1.6 is medium, 1.6<Fu≤40 is high and Fu > 40 severe.
- Slagging index (basic to acid compounds) – B/A+P

\[
B/A = \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O + P_2O_5}{SiO_2 + TiO_2 + Al_2O_3}
\]

(Eq 4)

The slagging potential is low when \( B/A < 0.5 \), is medium \( 0.5 < B/A < 1.0 \), is high \( 1.0 \leq B/A < 1.75 \) and severe when \( B/A \geq 1.75 \) [66].

### 3.2. Wet Torrefaction

Freshly chopped (2-10 mm) umbila (Pterocarpus angolensis) and spruce (Picea abies) samples were separately placed in a 1000 ml autoclave and carbonized using water and H\(_2\)SO\(_4\) (0.1 mol/l). The rotating autoclave, with 800 ml solution and 80 g biomass, was heated to 180±2°C (heating rate at 10°C/min) and kept for 150 and 350 min. After treatment, the autoclave was cooled, the solid and liquid were separated through filtration and moisture content of solid part was reduced at 80°C.

The effects of time and temperature of the treatment process was represented by the Severity Parameter (Ro) as defined by Overend and Chornet [67]. The parameter combines time, \( t \) (min), and temperature, \( T \) (°C), in the form of:

\[
Ro = te^{\left[\frac{(T-100)}{14.75}\right]}
\]

(Eq 5)

The limitations of this model as referred by Brownell et al. [68] are that it does not consider the moisture content and particle size of the feedstock, which have a strong influence on the kinetics of processes such as steam explosion and wet torrefaction. High moisture contents of feedstock have been especially shown to slow down the kinetics because before the water temperature is reached the voids in the biomass are filled with condensate [69].

In this work, four sets of pretreatment conditions are considered (Table 4) and untreated biomass is referred to as U0 (umbila) or S0 (spruce), which were included in this study for comparison purposes.
**Table 4** Treatment conditions considered in this study.

<table>
<thead>
<tr>
<th>Treatment designation</th>
<th>Treatment agent [-]</th>
<th>Residence time (min)</th>
<th>$R_0$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(UW1 or SW1)</td>
<td>Water</td>
<td>150</td>
<td>4.53</td>
</tr>
<tr>
<td>(UW2 or SW2)</td>
<td>Water</td>
<td>350</td>
<td>4.90</td>
</tr>
<tr>
<td>(UA1 or SA1)</td>
<td>$\text{H}_2\text{SO}_4$ [0.1mol/l]</td>
<td>150</td>
<td>4.53</td>
</tr>
<tr>
<td>(UA2 or SA2)</td>
<td>$\text{H}_2\text{SO}_4$ [0.1mol/l]</td>
<td>350</td>
<td>4.90</td>
</tr>
</tbody>
</table>

### 3.3. Crystallinity

The determination of the relative amounts of crystalline and amorphous material in cellulose is of considerable importance in characterizing structure. X-ray diffraction was conducted using an X-ray diffractometer (Siemens D5000), operated at an accelerating voltage and an emission current of 40 kV and 35 mA, respectively. The X-ray diffraction patterns were acquired over the 2θ range from 10 to 70°.

### 3.4. Mass and energy balance

Mass and energy balance calculations are important criteria that are widely used to evaluate the feasibility of the processes from the raw material to the finished product in terms of material and energy.

**3.4.1. Mass balance**

The general mathematical statement can be written as the total mass entering the unit equalling the total mass of products leaving the unit.

\[
\sum m_{\text{in}} = \sum m_{\text{out}} \quad \text{(Eq 6)}
\]
3.4.2. Energy balance

To calculate the energy balance, the method suggested and well described previously by Yan et al. [70] was applied, where:

**Heat of formation for biomass solids** – is determined using the heat of combustion ($\Delta H_c$) of the biomass solids, (Eq 7).

$$\text{CH}_x\text{O}_y(s) + \left(1 + \frac{x}{4} - \frac{y}{2}\right)\text{O}_2(g) \xrightarrow{\text{combustion}} \text{CO}_2(g) + \frac{x}{4}\text{H}_2\text{O}(l)$$  \hspace{1cm} (Eq 7)

where $\text{CH}_x\text{O}_y$ is the chemical formula of the biomass, and the $x$ and $y$ values are determined from the ultimate analysis of the biomass.

$\Delta H_c$ was obtained through combustion in a bomb calorimeter (Parr 6300) and mathematically can be obtained as follow:

$$\Delta H_C = \Delta H_{f_{(products)}} - \Delta H_{f_{(reactants)}}$$  \hspace{1cm} (Eq 8)

Consequently,

$$\Delta H_{f_{(reactants)}} = \Delta H_{f_{(products)}} - \Delta H_C$$  \hspace{1cm} (Eq 9)

**Heat of reaction** - to estimate the heat of reaction of the HTC process, several assumptions were made, such as:

- The gas, which is calculated by balance, consists only of CO$_2$ because it accounts for over 90% in the gas product;
- Glucose represents all precipitates formed at 180°C;
- Acetic acid represents volatile acids;
- The reference condition for the enthalpy calculations is 25°C.

The heat of reaction was determined by the difference of the heats of formation of the products and reactants in all treatment conditions considered in this study.
3.5. TGA and kinetic models

The approach to kinetic parameters of thermal decomposition of biomass depends on its components’ decomposition. The biomass components are assumed to be non-interacting. They undergo a parallel independent reaction \[71\]. The global kinetic parameters are determined by (Eq 10).

\[
\frac{d\alpha}{dt} = k(t)f(\alpha)
\]

(Eq 10)

where \(k(t)\) is determined by using Arrhenius equation shown in (Eq 11).

\[
k = Ae^{(-E/RT)}
\]

(Eq 11)

Because the thermal degradation is performed under the non-isothermal condition, then the temperature is increasing at constant heating rate \(\xi\), as shown in (Eq 12).

\[
dT = \xi dt
\]

(Eq 12)

The kinetic parameters are obtained by solving (Eq 10) with the inclusion of (Eq 11) and (Eq 12) as shown in (Eq 13).

\[
\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\xi} \int_{T_i}^{T_f} e^{\left(\frac{E}{RT}\right)} dT
\]

(Eq 13)

Kissinger's method is one of the common methods to determine kinetic parameters, but the disadvantage of this method is that it assumes the decomposition of the sample material obeys first order kinetics \[72\]. The Coast and Redfern method was used because it is more accurate as reported by Cai \[73\]. This method is represented by (Eq 14) and (Eq 15). (Eq 14) is used for the first order reactions otherwise (Eq 15) is used.

\[
\ln \left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln \left[\frac{AR}{\xi E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}
\]

for \(n=1\)

(Eq 14)

\[
\ln \left[\frac{(1-\alpha)^n - 1}{(n-1)T^2}\right] = \ln \left[\frac{AR}{\xi E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}
\]

for \(n\neq1\)

(Eq 15)
A straight line was obtained. The horizontal axis is $1/T$ and the vertical axis is $y$. $y$ is either $\ln \left( \frac{-\ln(1-\alpha)}{T} \right)$ or $\ln \left( \frac{(1-\alpha)^{1-n}}{(1-n)^{1}} \right)$ depending on the reaction order. The slope of the straight line is $E/R$ and the constant is $\ln \left( \frac{AR}{\xi E} \left( \frac{1-2RT}{E} \right) \right)$.

### 3.6. Py-GC-MS

#### 3.6.1. Teste of umbila

Analytical pyrolysis experiments were conducted using a Pyrola pyrolyser coupled to an Agilent 6890A gas chromatograph and a 5973C mass spectrometer. The gas chromatograph employed a DB-1701ms column (60 m, 0.25 mm ID) and a split/splitless injector (split ratio 30:1). The injector and ion source were kept at 280 and 150°C, respectively. Initially, the oven was held at 313 K for 2 min and then programmed to heat at 4 K/min to 523 K, where it was held for 30 min. Approximately 1 mg of sample was placed on a Pt filament of the pyrolyser. The sample was pyrolysed at a set point temperature of 773 K at a ramp rate of 180 K/ms with the final dwell time of 2 s. Because of the very high heating rate and the small particle size of the sample, the process can be considered as isothermal.

#### 3.6.2. Teste of Spruce

For each feedstock, a sample of approximately 2 mg (1.2 mg when catalyst was added) was pyrolysed using a CDS 5200 pyrolyser coupled to a PerkinElmer Clarus 680 gas chromatograph and 600S mass spectrometer with flame ionization detector (FID). A PerkinElmer Elite-1701 column was used to separate the compounds; the length was 30 m, the inner diameter was 0.25 mm and thickness of the inner coating (14% cyanopropylphenyl and 85% dimethyl polysiloxane) was 0.25 μm. The pyrolyser heated the samples contained in quartz vials at a rate of 20,000 °C/s to a pyrolysis temperature of 600 °C and was held for 15 s. A transfer line, kept at 310 °C, carried the vapours to a Tenax®-TA trap, which was maintained at 285 °C. Then, 1/125th of the vapours were released into the column (via the PTV1070 injection port—maintained at 275 °C); He gas at 30 PSI carried the vapours with a constant flow of 15 mL/min until they reached the end. At the same time, the GC oven was held at 45 °C for 2.5 min and then heated at 2.5 °C/min to 250 °C. The analyses were conducted simultaneously in the MS and FID (using an H2 and Air flame at 45 and 450 mL/min, respectively).
The software NIST 2011 proposed compounds that were assigned to the peaks according to likelihood and experience; the possible range of molar weights was 45–300 g/mol.
CHAPTER 4

4. Energy situation in Mozambique – A review

4.1. Introduction

The analysis of the energy situation and assessment of the potential sources of energy concerns the steps to be taken to increase energy security and promote development. On the other hand, the efficient utilization of any sources of energy is strongly dependent on their properties and qualities as a fuel.

4.2. Results and Discussion

The main available sources of energy are biomass, hydroelectric power (dams), liquid fuels (gasoline and petroleum) and natural gas [74]. The electrification in rural areas is expanding through the use of several sources of energy such as gas, diesel and national and international hydropower sources. Eighty-three district headquarters (of 128) have been electrified. Despite such a considerable achievement, only 13.2% of the population had access to electricity in 2008, and the majority of these consumers are living in the southern part of the country [75]. Almost all gas production (98.7%) is now being exported to South Africa; the rest is used locally for electricity generation (0.1%) and 1.1% is used by the industry [75].
Wood is the major household energy source in Mozambique. The production capacity of firewood and charcoal is estimated at 22 million tons/year. With the present energy demand of approximately 14.8 million tons/year, a positive balance of 7.2 million tons/year is evident [77]. However, the average efficiency of fuelwood used in households is estimated to be less than 10%, which results in a relatively high national average wood fuel consumption per capita in the country, approximately 1.2 m$^3$/year. Despite the reliance of 70% of people on firewood, its use has not been reported as cause of concern for the forest because only dead wood and woodcut for other purposes are collected. Charcoal, on the other hand, is mainly consumed in the urban areas and is mostly produced using the earth-mount kiln method, which has an efficiency of approximately
15% [78]. This activity has been pointed as one of the main causes of deforestation in Mozambique.

The potential biomass from forest logging residue is estimated at approximately 859 TJ or 85,000 tons (50% of logging residue coefficient and using a recoverability of 55%) and 175,000 tons/year, equivalent to 1.9 PJ from timber processing residues, considering that 64% of the log becomes waste and a recoverability of 55% [3]. Therefore, the total residue potential from logging and timber processing residues can reach approximately 2.7 PJ, only a very small fraction of sawmill industries residue used by the communities living around sawmills.

4.2.2. Residues from agricultural sector

The Mozambican agricultural sector is characterized by a large number of dispersed small-scale producers employing manual cultivation techniques, dependent on rain with little or no use of purchased inputs [79, 80]. The biomass potential from agricultural harvesting and processing residues is limited due to the lack of logistics for collecting and processing such scattered resources, which could be costly. However, this is not applicable to crops such as coconut, cashew nut, rice and sugar cane, which are agricultural crops with very high potential for energy and are mainly processed by the entrepreneurial sector, meaning that large quantities of residues of such crops are concentrated at the same place. Coconut fibre and shells are potential sources of energy; its weight can be estimated as one third of the nut weight [81], whereas the cashew nut shell is 50% of nut weight, and the rest is cashew nut shell liquid (CNSL) (25%) and kernel (25%) [82, 83]. Among several usages, shells can be used as a fuel in small-scale industries such as bakeries [82].
### Table 6: Estimated potential of energy of different agricultural crops in Mozambique for 2006.

<table>
<thead>
<tr>
<th>Crop</th>
<th>Production $^1$ (tonne)x10$^3$</th>
<th>Product/Residue ratio</th>
<th>Residue HHV (GJt$^-1$)</th>
<th>Residue energy Potential (TJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar cane</td>
<td>2,060</td>
<td>1:1.6 $^i$</td>
<td>17.9 $^a$</td>
<td>59,007</td>
</tr>
<tr>
<td>Cotton</td>
<td>115</td>
<td>1:2.1 $^{a,b}$</td>
<td>25.0 $^b$</td>
<td>3,834</td>
</tr>
<tr>
<td>Maize</td>
<td>1,395</td>
<td>1:0.3 $^{b,c}$</td>
<td>14.7 $^b$</td>
<td>25,398</td>
</tr>
<tr>
<td>Sweet sorghum</td>
<td>202</td>
<td>1:1.4 $^{b,c}$</td>
<td>14.7 $^b$</td>
<td>3,672</td>
</tr>
<tr>
<td>Groundnuts</td>
<td>85</td>
<td>1:2.3 $^e$</td>
<td>25.0 $^b$</td>
<td>4,443</td>
</tr>
<tr>
<td>Sunflower</td>
<td>7</td>
<td>1:2.1 $^a$</td>
<td>25.0 $^b$</td>
<td>378</td>
</tr>
<tr>
<td>Cashew nut shell</td>
<td>63</td>
<td>1:0.5 $^{e,f}$</td>
<td>18.9 $^d$</td>
<td>594</td>
</tr>
<tr>
<td>Tea</td>
<td>16</td>
<td>1:1.2 $^a$</td>
<td>13.0 $^a$</td>
<td>250</td>
</tr>
<tr>
<td>Coconut</td>
<td>47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• shell</td>
<td></td>
<td>1:0.2 $^a$</td>
<td>18.1 $^a$</td>
<td>255</td>
</tr>
<tr>
<td>• husk</td>
<td></td>
<td>1:0.3 $^{a,f}$</td>
<td>18.6 $^a$</td>
<td>262</td>
</tr>
<tr>
<td>Cassava</td>
<td>3,555</td>
<td>1:0.4 $^b$</td>
<td>5.6 $^b$</td>
<td>7,964</td>
</tr>
<tr>
<td>Rice</td>
<td>93</td>
<td>1:0.3 $^c$</td>
<td>13.4 $^g$</td>
<td>375</td>
</tr>
</tbody>
</table>

$^1$ Source: [84]

As the total energy potentially available from agricultural sector, a calculation of the average crop residues for 2006 was estimated as 106,432 TJ. Sugar cane and maize were the dominant crops, providing 55 and 24%, respectively, of total energy theoretically available (Table 6). This amount of energy represents almost half of the amount of biomass energy produced in the same year, which was 313,611 TJ. However, it should be mentioned that the availability of agricultural residues is limited to certain seasons during the year and that their quantities depend on the time of harvesting, storage-related characteristics, the storage facilities, etc. Because the crop production depends upon the agro-climatic conditions, all residues are not available in all parts of the country. The northern and central parts of Mozambique are more suitable for the expansion of agricultural activities.

$^a$ Source: [148]
$^b$ Source: [101]
$^c$ Source: [102]
$^d$ Source: [82]
$^e$ Source: [83]
$^f$ Source: [81]
$^g$ Source: [103]
The country has been implementing projects to improve the efficiency of charcoal production and consumption of firewood and charcoal through the introduction of improved kilns and stoves (Figure 8).

4.2.3. The Characterization of Wood Species from Mozambique as a Fuel

The contents of lignin and extractives in woody biomass are known to affect the HHV, density and the durability of wood [85]. This was evident in *Pericopsis angolensis*, which showed high amounts of lignin and extractive and consequently the highest HHV (Table 7). Moreover, the percentage of ash was relatively low in this species. On the other hand, the lowest HHV was measured in *Sterculia appendiculata*, which contained the lowest amounts of lignin and extractives compared to the other studied species. This species had, moreover, a very high ash content exceeding 3% on a dry weight basis. The high content of ash in *Pseudolachnostylis maprouneifolia* led to a relatively low heating value despite the very high concentration of lignin (>40%), which was the highest value measured in all of the studied species. This species had also a very high density.
Table 7 Fuel characteristics. Lignin, extractives and ash values are expressed as % free dry weight basis.

<table>
<thead>
<tr>
<th>Species</th>
<th>HHV (MJ/kg)</th>
<th>Ash (kg/m³)</th>
<th>Density (kg/m³)</th>
<th>Extractive</th>
<th>Lignin</th>
<th>FVI</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Afzelia quanzensis</em></td>
<td>20.52</td>
<td>2.06</td>
<td>740</td>
<td>7.17</td>
<td>30.51</td>
<td>6</td>
</tr>
<tr>
<td><em>Pterocephus angolensis</em></td>
<td>21.12</td>
<td>0.77</td>
<td>536</td>
<td>11.58</td>
<td>34.61</td>
<td>4</td>
</tr>
<tr>
<td><em>Millettia stuhlmannii</em></td>
<td>20.68</td>
<td>0.91</td>
<td>887</td>
<td>4.73</td>
<td>36.28</td>
<td>3</td>
</tr>
<tr>
<td>Pseudolachnostyla maprounaefolia</td>
<td>19.99</td>
<td>3.71</td>
<td>1100*</td>
<td>4.00</td>
<td>40.40</td>
<td>7</td>
</tr>
<tr>
<td>Sterculia appendiculata</td>
<td>19.38</td>
<td>3.10</td>
<td>627</td>
<td>2.26</td>
<td>25.06</td>
<td>8</td>
</tr>
<tr>
<td><em>Pterocarpous europensis</em></td>
<td>21.50</td>
<td>1.43</td>
<td>865</td>
<td>8.29</td>
<td>36.10</td>
<td>5</td>
</tr>
<tr>
<td><em>Acacia nigrescens</em></td>
<td>20.13</td>
<td>0.95</td>
<td>1111</td>
<td>4.39</td>
<td>28.70</td>
<td>2</td>
</tr>
<tr>
<td><em>Icuria dunensis</em></td>
<td>19.69</td>
<td>0.76</td>
<td>950*</td>
<td>2.80</td>
<td>25.10</td>
<td>1</td>
</tr>
</tbody>
</table>

* The most common species

The ranking by using the FVI, which assess the suitability of a species as a fuel, showed *Icuria dunensis* as the best ranked tree species and *Sterculia appendiculata* as the worst. The lesser known species showed favourable features as fuel and in some cases even better than the common species. Thus, the species *Icuria*, with its high density and low ash content, was ranked the best, although its HHV was not the highest. It was closely followed by *Acacia nigrescens* and *Millettia stuhlmannii*. The worst ranked species, *Sterculia appendiculata*, had the lowest HHV, highest ash content and relatively low density.

In addition to the FVI ranking, which took into account three measurable quality parameters (HHV, density and ash content), other consumer-related aspects can also affect the choice of the wood fuel. Such aspects include speed of drying, bright flame (as light source), sparkling, odour and smoke released during the burning of wood, etc. Socio-cultural issues such as local habits and taboos should also be considered. These socio-cultural aspects can be evaluated through other ranking methods such as pair-wise comparison.

4.3. Conclusions

The energy situation in Mozambique was reviewed, some woody biomass was characterized and their quality as a fuel was evaluated.

The country is endowed with great potential for biofuels, solar, hydro and wind energy production. However, the production today is still far from fulfilling the energy needs of the country, and the majority of people are still not benefitting from these resources.

Presently, fuelwood and charcoal are the main sources of energy and they will continue to play a very important role in the near future. However, there is a need to invest more in
efficient kilns for charcoal production and improved stoves to reduce the consumption per capita and ultimately the deforestation.

Enormous amounts of energy resources are wasted, especially from logging, timber processing and the agricultural sector. These residues are not visible on national energy statistics.

The evaluated woody species showed considerable variations in their chemical composition and their energy values. However, these values were, in the majority of cases, possible to correlate with the chemical composition of the woody biomass. The concentrations of heavy metals in all species were at low levels and were considered safe to manage.

The FVI showed that by failing to efficiently utilise residues from *Afzelia quanzensis*, *Millettia stuhlmannii* and *Pterocarpus angolensis*, an opportunity to reduce some of the energy-related problems is being missed. On other hand, emerging species such as *Acacia nigrescens* and *Pericopsis angolensis* and especially the lesser-known species *Icuria dunensis* showed that they are good source of energy and can therefore help to reduce the pressure on the known species.
CHAPTER 5

5. The impact of mild sub-critical hydrothermal carbonization pretreatment on Umbila wood - A mass and energy balance perspective

5.1. Introduction

*Pterocarpus angolensis* (Umbila), one of the highly ranked wood species in the previous study, was hydrothermally pretreated. The main objective was to investigate not only the impact of a mild subcritical HTC on the pretreatment of the biomass but also the mass and energy balance of the process by characterizing and quantifying the solid, liquid and gaseous products. For comparison purposes, the results of the effect of HTC treatment on the elemental composition and ash characteristics of spruce are also presented.

5.2. Results and Discussion

5.2.1. Mass balance

At the operating conditions employed, the treatment appears to have a stronger effect than the reaction time the on mass yield. A higher mass yield was recovered on water treatment, 87 and 82%wt for 150 and 350 min, respectively, whereas for acid treatment the mass yield dropped considerably, consequently producing higher yield of CO₂ and other water-soluble compounds (Table 8).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Mass in (g)</th>
<th>Mass out (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wood</td>
<td>water</td>
</tr>
<tr>
<td>UW1</td>
<td>1,00</td>
<td>16,13</td>
</tr>
<tr>
<td>UW2</td>
<td>1,00</td>
<td>16,13</td>
</tr>
<tr>
<td>UA1</td>
<td>1,00</td>
<td>16,94</td>
</tr>
<tr>
<td>UA2</td>
<td>1,00</td>
<td>16,94</td>
</tr>
</tbody>
</table>

Table 8 Mass of reactants and products of umbila in HTC without and with diluted acid
5.2.2. Energy Balance

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Empirical Chemical formula</th>
<th>Heat of combustion (kJg⁻¹)</th>
<th>Heat of formation (kJg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uo</td>
<td>CH₁.353O₀.585</td>
<td>-17.846</td>
<td>-0.183</td>
</tr>
<tr>
<td>UW1</td>
<td>CH₁.296O₀.556</td>
<td>-19.700</td>
<td>-2.055</td>
</tr>
<tr>
<td>UW2</td>
<td>CH₁.243O₀.507</td>
<td>-20.088</td>
<td>-2.797</td>
</tr>
<tr>
<td>UA1</td>
<td>CH₀.971O₀.364</td>
<td>-23.127</td>
<td>-7.659</td>
</tr>
<tr>
<td>UA2</td>
<td>CH₀.940O₀.331</td>
<td>-24.097</td>
<td>-8.839</td>
</tr>
</tbody>
</table>

The addition of acid accelerated the depolymerisation process, leading to a quantitative difference on heat released during the reaction process, which was also clearly affected by the severity of the treatment (Table 9).

Table 10 Enthalpy and heat of reaction of umbila in HTC without and with diluted acid.

<table>
<thead>
<tr>
<th>Enthalpy in (kJg⁻¹)</th>
<th>Enthalpy out (kJg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pretreated wood acetic acid precipitates water acid gas Heat of Reaction</td>
</tr>
<tr>
<td>Treatment</td>
<td>wood</td>
</tr>
<tr>
<td>UW1</td>
<td>-0.183</td>
</tr>
<tr>
<td>UW2</td>
<td>-0.183</td>
</tr>
<tr>
<td>UA1</td>
<td>-0.183</td>
</tr>
<tr>
<td>UA2</td>
<td>-0.183</td>
</tr>
</tbody>
</table>

It is difficult, however, to make direct comparisons between the reaction process behaviour reported in the literature and those observed in the current study, as several factors can influence the process such as the type of biomass, the severity of treatment, temperature, pressure, etc. Although hydrothermal treatment is a slow process, it is important to give time for the treatment to change from endothermic to exothermic reaction process. Yan et al. [70] reported an endothermic reaction process after a 5-min
treatment, despite higher temperatures (200 to 260°C). This process shows that the energy applied in the process is compensated and the system can be energy self-sufficient.

5.2.3. Effect of pretreatment on elemental composition and ash characteristics

Table 11 displays considerable changes in the elemental composition of umbila due to the effect of the treatment and its severity. As a result of carbonization, the volatile content in the solid decreased substantially, especially in the acid treatment, whereas the fixed carbon increased from 19.65 to 41.4%wt and was greatly influenced by process conditions. The ash content varied incoherently with treatments and the severity index. A reduction from 0.77 for untreated biomass to 0.3%wt d.b. for water treatment was observed, as well as an increment on diluted acid treatments.

<table>
<thead>
<tr>
<th>Table 11 Proximate and ultimate analysis of untreated and HTC Umbila</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Proximate analysis [%wt d.b.]</strong></td>
</tr>
<tr>
<td>Fixed Carbon</td>
</tr>
<tr>
<td>Volatile Matter</td>
</tr>
<tr>
<td>Ash</td>
</tr>
<tr>
<td><strong>Ultimate analysis [%wt d.b.]</strong></td>
</tr>
<tr>
<td>Carbon (C)</td>
</tr>
<tr>
<td>Hydrogen (H)</td>
</tr>
<tr>
<td>Nitrogen (N)</td>
</tr>
<tr>
<td>Oxygen (O)*</td>
</tr>
<tr>
<td>Chlorine (Cl)</td>
</tr>
<tr>
<td>Sulphur (S)</td>
</tr>
</tbody>
</table>

* Determined as difference between 100 and the sum of C and H

The concentration of Cl in Umbila (Table 11) and Spruce (Table 12), which during combustion play an important role as alkaline carriers and are also well known to accelerate the corrosion rate through the flue gases, did not change and it was below the detection limits. The concentration of nitrogen (N) showed a very slight change in all treatments. On other hand, a considerable change in the concentration of sulphur (S) was observed, due to the use of H₂SO₄ as catalyst.
However comparing the effect on both species in terms of carbon, hydrogen and oxygen content are slightly higher in spruce, which is reflected in the van Krevelen diagram.

### 5.2.4. Change of biomass structure by pretreatment

It is noticeable that when a sample is hydrothermally treated, the resulting material exhibits a XRD pattern different to that of cellulose, indicating that the microcrystalline structure of the cellulose has been destroyed. Such a tendency is influenced by the treatment and its severity (Figure 9).

**Figure 9** Crystallinity of untreated and pretreated umbila
Ash-related problems such as slagging and fouling in different types of combustion boilers continue to be the most important reason for unscheduled stops of boilers.

### Table 13:
umbila ash composition and evaluation of slagging and fouling tendency based on different indexes

<table>
<thead>
<tr>
<th></th>
<th>Unit</th>
<th>U0</th>
<th>UW1</th>
<th>UW2</th>
<th>UA1</th>
<th>UA2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>%wt d.b.</td>
<td>0.014</td>
<td>0.022</td>
<td>0.010</td>
<td>0.023</td>
<td>0.018</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>%wt d.b.</td>
<td>0.003</td>
<td>0.002</td>
<td>0.002</td>
<td>0.067</td>
<td>0.039</td>
</tr>
<tr>
<td>CaO</td>
<td>%wt d.b.</td>
<td>0.252</td>
<td>0.019</td>
<td>0.011</td>
<td>0.067</td>
<td>0.042</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>%wt d.b.</td>
<td>0.027</td>
<td>0.014</td>
<td>0.012</td>
<td>0.194</td>
<td>0.113</td>
</tr>
<tr>
<td>K₂O</td>
<td>%wt d.b.</td>
<td>0.451</td>
<td>0.010</td>
<td>0.007</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>MgO</td>
<td>%wt d.b.</td>
<td>0.095</td>
<td>0.044</td>
<td>0.014</td>
<td>0.021</td>
<td>0.012</td>
</tr>
<tr>
<td>MnO</td>
<td>%wt d.b.</td>
<td>0.002</td>
<td>0.002</td>
<td>0.000</td>
<td>0.000</td>
<td>0.003</td>
</tr>
<tr>
<td>Na₂O</td>
<td>%wt d.b.</td>
<td>0.003</td>
<td>0.002</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>%wt d.b.</td>
<td>0.020</td>
<td>0.005</td>
<td>0.001</td>
<td>0.004</td>
<td>0.003</td>
</tr>
<tr>
<td>TiO₂</td>
<td>%wt d.b.</td>
<td>0.004</td>
<td>0.000</td>
<td>0.002</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>B/A+P</td>
<td>--</td>
<td>41.525</td>
<td>3.802</td>
<td>3.459</td>
<td>3.287</td>
<td>3.151</td>
</tr>
<tr>
<td>Fu</td>
<td>%wt d.b.</td>
<td>18.430</td>
<td>0.040</td>
<td>0.025</td>
<td>0.031</td>
<td>0.028</td>
</tr>
</tbody>
</table>

In both species all the base compounds (Table 13 and 14) were reduced with exception of Fe₂O₃. The fouling potential of treated umbila was reduced from a high tendency to levels of low risk of fouling potential, below 0.6, whereas the slagging potential, even with a considerable reduction in all treatments, is still at level of severe potential.

### Table 14:
spruce ash composition and evaluation of slagging and fouling tendency based on different indexes

<table>
<thead>
<tr>
<th></th>
<th>Unit</th>
<th>So</th>
<th>SW1</th>
<th>SW2</th>
<th>SA1</th>
<th>SA2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>%wt d.b.</td>
<td>0.035</td>
<td>0.024</td>
<td>0.011</td>
<td>0.032</td>
<td>0.039</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>%wt d.b.</td>
<td>0.021</td>
<td>0.017</td>
<td>0.019</td>
<td>0.026</td>
<td>0.065</td>
</tr>
<tr>
<td>CaO</td>
<td>%wt d.b.</td>
<td>0.096</td>
<td>0.022</td>
<td>0.017</td>
<td>0.021</td>
<td>0.021</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>%wt d.b.</td>
<td>0.011</td>
<td>0.016</td>
<td>0.009</td>
<td>0.061</td>
<td>0.058</td>
</tr>
<tr>
<td>K₂O</td>
<td>%wt d.b.</td>
<td>0.048</td>
<td>0.010</td>
<td>0.001</td>
<td>0.002</td>
<td>0.011</td>
</tr>
<tr>
<td>MgO</td>
<td>%wt d.b.</td>
<td>0.022</td>
<td>0.005</td>
<td>0.014</td>
<td>0.005</td>
<td>0.004</td>
</tr>
<tr>
<td>MnO</td>
<td>%wt d.b.</td>
<td>0.014</td>
<td>0.003</td>
<td>0.000</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>Na₂O</td>
<td>%wt d.b.</td>
<td>0.003</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>%wt d.b.</td>
<td>0.011</td>
<td>0.008</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>TiO₂</td>
<td>%wt d.b.</td>
<td>0.000</td>
<td>0.000</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>B/A+P</td>
<td>--</td>
<td>3.394</td>
<td>1.499</td>
<td>2.399</td>
<td>2.496</td>
<td>0.948</td>
</tr>
<tr>
<td>Fu</td>
<td>%wt d.b.</td>
<td>0.173</td>
<td>0.022</td>
<td>0.075</td>
<td>0.056</td>
<td>0.015</td>
</tr>
</tbody>
</table>

In spruce Na was completely leached out from the feedstock (SW2, SA1, and SA2). Thus, the fouling is in all treatment at low level (below 0.6), on the other hand despite the
slagging index shows reduction it still at severe level. This shows that the HTC process is not highly efficient to remove minerals in the biomass.

5.2.5. Ash fusibility characteristics

One of the key properties of fuel ash materials is the fusion behaviour. The ash fusibility test is one of the most widely used methods of assessing its behaviour.

<table>
<thead>
<tr>
<th>Fusion state (°C)</th>
<th>$U_0$</th>
<th>UW1</th>
<th>UW2</th>
<th>UA1</th>
<th>UA2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shrinkage temperature, ST</td>
<td>830</td>
<td>860</td>
<td>1000</td>
<td>950</td>
<td>950</td>
</tr>
<tr>
<td>Deformation temperature, DF</td>
<td>1400</td>
<td>1170</td>
<td>1385</td>
<td>&gt;1500</td>
<td>&gt;1500</td>
</tr>
<tr>
<td>Hemisphere temperature, HT</td>
<td>1450</td>
<td>1190</td>
<td>1400</td>
<td>&gt;1500</td>
<td>&gt;1500</td>
</tr>
<tr>
<td>Flow temperature, FT</td>
<td>1460</td>
<td>1220</td>
<td>1410</td>
<td>&gt;1500</td>
<td>&gt;1500</td>
</tr>
</tbody>
</table>

In general, increments on ST, DF, HT and FT were observed (Table 15), which shows an improvement of ash quality; however, they were not sufficient to reduce the ash slagging potential, which remains at severe level, index $\frac{B}{A} + P$ higher than 1.75 in all treatments. However, it must be stressed that the fuel composition cannot alone justify the ash behaviour because slagging and fouling also depend on boiler design and operation conditions.

Even though that biomass has a low heavy metal content, even trace amounts of such compounds can be problematic in biomass utilization for thermal energy, causing environmental pollution. Reduction of Pb and other heavy metals were observed in all treatments; however, increments in the Cr, Cu, Ni, Mo and Co concentrations were observed after UA1 and UA2 pretreatments (Figure 10). One of the reasons for such increments is the solid mass decrease combined with the biochar adsorption capacity of heavy metals, especially Zn, Cr, Cd, Cu, Ni and Co. According to Al-Asheh et al. [87], this is due to biomass carbohydrates and phenolic compounds, which have metal-binding functional groups such as carboxyl, hydroxyl, sulfate, phosphate and amino groups, and its pores formed during the HTC process.
The alteration of the biomass composition can be reflected on a Van Krevelen diagram (Figure 11). It shows a decrease of atomic ratio reduction in all treatments, with a major reduction for acid treatment. Such a decrease is mainly due to the significant reduction of carboxyl groups, from extractives, hemicellulose and cellulose.
In general, both the H/C and O/C ratios decreased with time and utilization of acid catalyst. From the van Krevelen diagram, it can also be observed that despite the fact that three processes occur simultaneously (dehydration, decarboxylation and decarbonylation); the prevailing reaction is dehydration, which is in essence, as mentioned before, the removal of the hydroxyl groups. According to Chen et al. [88], carboxyl and carbonyl groups start to degrade rapidly at approximately 150°C, resulting in CO₂ and CO, respectively.
The effect of treatment on spruce follows the same trend, both ratios (H/C and O/C) reduce and the van Krevelen diagram (Figure 12) shows that dehydration plays the main role, but the difference of position between UA1, UA2 and SA1, SA2 the severity of treatment has more impact in hardwood (umbila). However, in terms of reduction of oxygen content and increment of carbon it shows that spruce was more affected by the treatment.

5.2.6. Kinetic of thermal Decomposition of HTC-char

The study of kinetic of biomass pyrolysis is important in the context of energy recovery.

5.2.6.1. Thermogravimetric analysis

To better understand the pyrolysis characteristic of biomass untreated and treated TG are shown in Figure 13 and Figure 14.

It was observed that devolatilization starts below 340°C for the untreated biomass material, whereas the water-treated biomass starts to release volatiles above 340°C. A very slow degradation is observed to untreated and treated biomass. The percentage amount of volatiles released from untreated biomass is lower than that of treated biomass material; this is caused by the hydrolysis process, which is the cleavage of chemical bonds by the addition of water that takes place and plays the main role during water treatment at the studied pretreatment conditions.
Figure 13 TGA and DTG of treated and untreated biomass - effect of severity of treatment
At higher heating rates, the reactions shift to higher temperatures. According to Hatakeyama and Quinn [89], this is due to the conditions of decomposition, which takes place when the vapour pressure of the volatiles is greater than ambient pressure. When the temperature is reached at which this condition is satisfied, decomposition will occur. In the case of high heating rates, diffusion of the volatiles is inhibited and consequently the decomposition temperature is increased.

At same heating rate, it can also be observed that the curve reaction moves to higher temperature with treatment (raw material, water and acid treatments). This shows the removal of cellulose by reduction of the peak sizes (Figure 14– h, j, l). On the other hand, comparing the degree of conversion rate in different heating rates, it can be observed that the water treatment at 150 min presents higher peaks at all heating rates (Figure 13– b, d and f).
Figure 14 TGA and DTG—effect of treatments and heating rate during the pyrolysis
For the spruce raw material, the TGA curve shows a shoulder at 310ºC, which represents the hemicellulose, whereas in hardwood (umbila) and treated spruce, such a curve is not visible.

Table 17 Decomposition characteristics of umbila after different treatment methods and severity

<table>
<thead>
<tr>
<th>Species</th>
<th>Heating rate (ºC/min)</th>
<th>5</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T&lt;sub&gt;i&lt;/sub&gt;</td>
<td>T&lt;sub&gt;sh&lt;/sub&gt;</td>
<td>T&lt;sub&gt;max&lt;/sub&gt;</td>
<td>dm/dT(%)/ºC</td>
</tr>
<tr>
<td>U&lt;sub&gt;0&lt;/sub&gt;</td>
<td>194</td>
<td>--</td>
<td>330</td>
<td>-0.98</td>
</tr>
<tr>
<td>UW1</td>
<td>163</td>
<td>--</td>
<td>356</td>
<td>-1.4</td>
</tr>
<tr>
<td>UW2</td>
<td>173</td>
<td>--</td>
<td>353</td>
<td>-0.95</td>
</tr>
<tr>
<td>UA1</td>
<td>109</td>
<td>--</td>
<td>458</td>
<td>-0.195</td>
</tr>
<tr>
<td>UA2</td>
<td>109</td>
<td>--</td>
<td>420</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

In all heating rates (5, 10 and 20ºC/min) and treatments, the temperature of maximum decomposition (T<sub>max</sub>) increased, although with a slight reduction on higher severity in both treatments.

5.2.6.2. Kinetic parameters

The kinetic parameters seem to vary with treatment method. The untreated material has highest activation energy and pre-exponential factor, whereas the sample that is treated by acid has lowest kinetic parameters (activation energy and pre-exponential factor). This can be described as the untreated biomass and is very difficult to decompose because its chemical bonds did not destruct, but when biomass is treated by water or acid the chemical bonds become weak and decompose. The values of kinetic parameters are presented in Table 18. The kinetic determination was estimated as shown in Figure 15.
The activation energy of biomass when treated using water was 110.474 kJ/mol. whereas biomass that was treated using acid was 22.124 kJ/mol. These values were observed when the treatment time was 150 min. When the time was increased, the activation energy of biomass was decreasing. This is revealed when time was increased to 350 min, and the activation energy of biomass was decreased to 85.772 kJ/mol and 14.493 kJ/mol for treatment by using water and acid, respectively. The same differences were observed for the pre-exponential factor.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time, min</th>
<th>Activation Energy(E), kJ/mol</th>
<th>Pre-exponential factor(A), s⁻¹</th>
<th>Reaction order (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uo</td>
<td></td>
<td>112.885</td>
<td>1.545x10⁹</td>
<td>0.7</td>
</tr>
<tr>
<td>UW1</td>
<td>150</td>
<td>110.474</td>
<td>2.167x10⁸</td>
<td>1</td>
</tr>
<tr>
<td>UW2</td>
<td>350</td>
<td>85.772</td>
<td>1.274x10⁴</td>
<td>1</td>
</tr>
<tr>
<td>UA1</td>
<td>150</td>
<td>22.124</td>
<td>1.441</td>
<td>1.5</td>
</tr>
<tr>
<td>UA2</td>
<td>350</td>
<td>14.493</td>
<td>1.213x10⁻³</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The biomass treated by acid has the same activation energy as that of lignin. Several pieces of literature reported kinetic parameters of lignin from lignin biomass treated by using sulfuric acids to be in the range of 12.1 – 38.3 kJ/mol [90, 91]. In this study,
the biomass treated by acid had an activation energy of 22.124 kJ/mol treated for 150 min and 14.493 kJ/mol when treated for 350 min.

The reaction order is also affected by the treatment method used, although the relationship is not linear. The untreated biomass has a 0.7\textsuperscript{th} reaction order, whereas the biomass treated by water is first order. The treatment by acid has a 1.5\textsuperscript{th} reaction order at 150 min and a 1.1\textsuperscript{th} reaction order at 350 min.

### 5.3. Conclusions

The effects of different HTC conditions/severity of treatments were studied. Experimental results indicate that for the process conditions employed, the mass and energy balance of the HTC is considerably more affected by the treatment than the severity of the treatment.

The chemical composition of the biochar produced is substantially different than the feedstock. The use of diluted acid as the catalyst improves the biochar quality, namely in terms of the energy density and ash characteristics; however, the increment of the S content in the final product should be considered for market acceptance (because the fuels have a maximum allowance for S concentration). Moreover, wastewater treatment of this process is also more demanding.

The thermal behaviour of the untreated and treated umbila was also investigated. The thermogravimetric analysis showed clearly that the thermal behaviour of each biomass was affected by the treatment and its severity. Experimental results indicate that for the process conditions employed modified the structure and chemistry of the wood components and reduced the reactivity of the feedstock.
CHAPTER 6

6. Fast Pyrolysis of pretreated biomass

6.1. Introduction

In pyrolysis processes, the characteristic of the feedstock affects the composition and consequently the quality of the bio-oil. Alkali metal cations lead to catalytic cracking of pyrolysis liquids in the vapour phase, reducing organic liquids and increasing the water yield, char and gas, resulting in low calorific value bio-oil.

6.2. Results and Discussion

6.2.1. Fast pyrolysis of umbila (hardwood) and Spruce (softwood)

Several groups of the main decomposition products such as acids, alcohols, ketones and aldehydes, aromatic, methoxy phenols, phenols furans are presented (Figure 16 and Figure 18).

The majority of derivatives of carboxylic acids were produced by the pyrolysis of untreated biomass, which can be indicators of the decomposition of levoglucosan, anhydrosugars and cellulose due to the presence of potassium in the biomass and consequently can be expected to produce bio-oil with high corrosiveness. On the other hand, it is noticeable that the pretreated biomass produced more compounds mainly derived by lignin such as methoxy phenols, phenols and aromatic hydrocarbons.
The removal of cellulose and hemicellulose led to a reduction in ketones, aldehydes, furans, alcohols and acids. However, UA2 showed an unexpected reduction of phenols, which could possibly be due to the recombination of phenols in an acid environment, producing more aromatic hydrocarbo (Figure 17).

**Figure 16** Peak area% of untreated, water and acid treated Umbila

**Figure 17** Aromatics production via (a) Diels-Alder cyclization; (b) lignin derived compounds transformations [92]
According to Bridgwater [93] the removal of the hemicellulose is desirable because the products from its pyrolysis are responsible for the instability and smell of bio-oil. However, part of cellulose, which means carbon, was also removed, which would consequently affect the quality of the oil.

Comparing the results for the hardwood (Figure 16) and softwood (Figure 18), the spruce peak area% shows a disagreement with what would be expected, especially the amount of acid, aromatics, furans and sugars. However, in both species there are reductions of phenols at an acid treatment time of 350 min.
6.2.2. Effect of zeolite on product yield and composition during pyrolysis of hydrothermally pretreated Spruce

The detected compounds were classified in groups that consist of acids, alcohols, alkenes, amines, aromatics, furans, ketones and aldehydes, phenols and sugars in both cases (Figure 19 and Figure 20).

6.2.2.1. Effect of biomass pretreatment on the products of fast pyrolysis

It was observed that with an increment of severity of the treatment, the yield of some compound groups supposedly from holocellulose such as acids and furans increased, even with a reduction of cellulose and hemicellulose with treatment. According to Lu et al. [94], the increment of acids might be due to the substantial presence of Fe₂O₃ and sulphur, which are five and six times of the fresh biomass, respectively (Table 13 and 14), and which promote catalytic cracking and consequent production of acids.

Lignin products, such as methoxy phenols, seem to remain non-decomposed in the sample and as cellulose and hemicellulose break down, methoxy phenols are concentrated (reaching a maximum percentage of 33%). The concentration of aromatics and phenols were also inconsistent. Instead of a reduction, an increment from 7.5% for untreated biomass to 17% for acid-treated for 350 min was observed, whereas furans increased from 6.2 to 15.6% for untreated biomass to acid treated for 350 min, respectively (Figure 19). Pentanoic acid, 4-oxo (C₅H₈O₃) was the major organic with a yield of acid that increased from zero for S0 to 15.55% for SA2, whereas the acetic acid was reduced from 6.12 to 1.44% (Table 4). Another possible reason for this trend is due to higher sulfur content in the biomass by the acid pretreatment. It is also found that aromatic productions have been increased by acid pretreatment. A similar result can be seen when a more acidic catalyst ZSM-5 has been used; the organic phases revealed a more aromatic and polyaromatic compounds [95].

On other hand, the reduction of cellulose and increment of lignin content promoted the reduction ketones and aldehydes and the rise of methoxy phenols and phenols. Unexpectedly, the yield of aromatics increased while the yield of furans decreased. According to Adam et al. [96], the quality of oil is characterized by the aldehyde yield because it is responsible for many reactions in the aging procedure and by the organic acid yield because low pH values make combustion in engines difficult due to corrosion. The phenol yield is also interesting because of its price: a high phenol yield makes the process relatively cheaper.
It was also observed that when treated biomass alcohols and pyrans were produced in small amounts (below 0.5% by area). The yield of levoglucosenone was the same for raw biomass and acid-treated SA1 approximately 2.5%, and for SA2, a substantial yield reduction was observed (0.6%) (see paper VI, Table 4). In terms of total yield (FID area) by sample mass, a decrease with treatment severity was found. This decrease corresponded fairly well with the volatile content of the sample. The total yield, by sample mass, of methoxy phenols remained fairly constant, which indicates that the percentage of lignin is largely the same in biomass and acid-washed biomass. However, because the cellulose carbonized, the resulting vapours will contain a higher percentage of methoxy-phenols.
Once again, the acid 150 min treatment presented a higher yield, which shows that probably there is no need to go to a much higher residence time in the treatment, considering not only the yield but also the composition of pyrolytic vapours. Nonetheless, with treatment no sugar, pyrans were produced, varying, respectively, from 3.6% and 1.0% (S0+HZSM-5) to zero (SA1+HZSM-5 and SA2+HZSM-5). In general, no substantial differences in yield were observed in either case.

The yield of furan in pyrolysis of raw and HTC spruce has an increasing trend, and due to the catalysis, it has the opposite trend; moreover, benzofuran appeared only in small amounts in the catalytic pyrolysis of raw biomass. Hydroxymethyl l-furfural is only produced in pyrolysis of S0, thus can be concluded that the treatment avoids the production of this compound.
Figure 21 shows a set of compounds with different trends in FID area/sample weight and percentage of peak due to treatment and catalyst (HZSM5). Creosol (Figure 3a) generally increases in absolute value in both treatments SA1 and SA2, however in terms of percentage area of the peak, only SA2 presents a higher value compared with the catalytic case.

The methoxy-phenols Cresol and Eugenol, both derived from lignin, show a deviation in the trend. The absolute yield of Cresol remains constant, whereas for Eugenol it decreases both with and without catalyst. Comparing the acid-washed samples with differences in treatment severity, SA1 and SA2, the highest severity (SA2) yields the lowest of absolute yield of methoxy-phenols and most other compounds, even though the effect is small.
6.3. Conclusions

The results from fast pyrolysis of mild wet torrefied umbila has shown that the pretreatment process reduced the acetic acid levels, as well as increased significantly the compounds derived by lignin, which can consequently affect the quality of the bio-oil. In spruce the effect of treatment on fast pyrolysis was inconsistent with the reduction of cellulose and hemicellulos, especially the yield of acids and furans. Due to the catalytic activity, there are several changes in the pyrolysis product composition. The most important catalytic effect on the products of pyrolysis of spruce was the reduction of acid, aldehydes and ketones and the production of levoglucosan in catalytic pyrolysis of raw spruce (S0). The catalytic and non-catalysed pyrolysis affects the total yield of vapours, the composition and the groups of compounds.
CHAPTER 7

7.1. General Conclusions

The hydrothermal carbonisation of Mozambican woody biomass residue (with/without acid as catalyst) was performed and solid biochar that resembles low-grade coal was produced.

Other major conclusions are summarized below:

Review the current energy situation in Mozambique and assess the available and potential renewable sources, including residues from agricultural crops and forest industry as energy.

✓ The energy situation in Mozambique was reviewed, some woody biomass was characterized, and their quality as a fuel was evaluated.
✓ The country is endowed with great potential for biofuels, solar, hydro and wind energy production. However, the production today is still far from fulfilling the energy needs of the country, and the majority of people are still not benefiting from these resources.
✓ Enormous amounts of energy resources are wasted, especially from logging, timber processing and agricultural sector.

Determine the main physical and chemical characteristics of common and less-used hardwood species growing in Mozambique and evaluate their quality as a fuel.

✓ The evaluated woody species showed considerable variations in their chemical composition and their energy values. However, these values were, in the majority of cases, possible to correlate with the chemical composition of the woody biomass. The concentrations of heavy metals in all species were at low levels and were considered safe.
✓ The FVI showed that by failing to efficiently utilise residues from Afzelia quanzensis, Millettia stuhlmannii and Pterocarpus angolensis, an opportunity to reduce some of the energy-related problems has been missed. On other hand, emerging species such as Acacia nigrescens and Pericopsis angolensis and especially the lesser-known species Icuria dunensis showed that they are good source of energy and can therefore help to reduce the pressure on the known species.
Investigate the impact of the mild wet torrefaction process using water and diluted H$_2$SO$_4$ as catalyst, on physical and chemical biomass characteristics.

- Hydrothermal carbonization (HTC), also known as the wet torrefaction or wet pyrolysis process, was conducted with the addition of diluted sulphuric acid to pretreat umbila and spruce. A solid HTC biomass that resembles low-grade coal was produced.
- Experimental results indicate that for the process conditions employed, the use of diluted acid as catalysts improves the HTC-biomass quality, namely in terms of energy density and ash characteristics; however, the increment of the S content in the final product should be considered for market acceptance (because the fuels have a maximum allowance for S concentration). Moreover, waste water treatment of this process is also more demanding.
- The mass and energy balance of the HTC is considerably more affected by the treatment than the severity of the treatment.
- The process conditions employed modified the structure and chemistry of the wood components and reduced the oxygen content. These modifications may not favour the formation of certain important bio-oil compounds.
- The effects of different HTC conditions/severity of treatments were studied. Experimental results indicate that for the process conditions employed the mass and energy balance of the HTC is considerably more affected by the treatment than the severity of the treatment.
- The chemical composition of the HTC biomass produced is substantially different than the feedstock. The use of diluted acid as catalysts improves the HTC-biomass quality, namely in terms of the energy density and ash characteristics; however, the increment of S content in the final product should be considered for market acceptance (because the fuels have a maximum allowance for S concentration). Moreover, the wastewater treatment from this process is also more demanding.
- The thermal behaviour of the untreated and treated umbila was also investigated. The thermogravimetric analysis showed clearly that thermal behaviour of each biomass was affected by the treatment and its severity. Experimental results indicate that for the process conditions employed it modified the structure and chemistry of the wood components and reduced the reactivity of the feedstock.

Investigate the effect of the mild wet torrefaction process on fast pyrolysis.

- The results from fast pyrolysis of mild wet torrefied umbila has shown that the pretreatment process reduced the acetic acid levels and considerably increased the compounds derived by lignin, which can consequently affect the quality of the bio-oil. However, in spruce, the effect of treatment on fast pyrolysis was inconsistent with the reduction of cellulose and hemicellulose, especially the yield of acids and
furans. Due to the catalytic activity, there are several changes in the pyrolysis product composition.

- The most important catalytic effect on the products of pyrolysis of spruce was the reduction of acid, aldehydes and ketones and the production of levoglucosan in the catalytic pyrolysis of raw spruce (S0). The catalytic and non-catalysed pyrolysis does affect the total yield of vapours, and the composition and the groups of compounds.

- In general the HTC reduces the oxygen content in the feedstock, however this modifications may not favour the formation of certain important bio-oil compounds.

### 7.2. Recommendations for Future Work

**Process**

- Optimization and simulation of HTC process conditions, followed by experimental investigation could be a great option for better understanding of process;
- Investigation/understanding the chemistry of the process for converting biomass into HTC-biomass;
- Investigate the effect of leaching before and after HTC process; and
- Investigate the utilization in HTC process of acid waters from production of bio-oil (fast pyrolysis).

**Application**

- HTC-biomass considering co-firing with coal, gasification, pyrolysis followed by experimental investigation could be a great option for better understanding of process and HTC-biomass potential; and
- Pellet production using HTC-biomass as feedstock or/and as binder.
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